Smart textile coatings and laminates
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Smart textile coatings and laminates

Edited by
William C. Smith
Industrial Textile Associates
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Abstract: Coating and laminating (C/L) of fabrics and textiles in all forms are techniques and finishes used in virtually every segment of industry and our lives. Most C/L fabrics are passive, providing a specific function or aesthetic value. By applying some of the latest technology, materials have become ‘smart’ or ‘intelligent’, with finishes that also allow materials to react to outside stimuli to do such things as conduct electricity, change color, warm/cool, give off chemicals or medicines, or perform some other special function. Such materials promise a bright future for the global C/L industry.

Key words: coated fabrics, smart/intelligent textiles, C/L applications, C/L growth issues, C/L techniques, C/L definitions.

1.1 Introduction

This is a book of potential, a book of ‘what is to come’, a book to stimulate your thinking. The chapters in this book present some basics of what is involved in smart/intelligent coatings and laminates, but more often you will find technical information on developments and research in coating/laminating and fabric technology, provided to stimulate ideas of what can be done. New ideas and new products are being developed rapidly; research is ongoing, many products are being developed with special properties allowing them to ‘do something’ rather than just look good or have good physical properties.

When people first found out they could smear animal grease onto a skin or grass-cloth and make it more waterproof, the coated fabrics industry was born. Later, we find other materials such as natural latex were used, beginning a never-ending search for better products and performance. We have been putting something on fabrics ever since to look nice, repel water or other liquids, protect from chemicals and heat/fire, to hold gases, and a huge variety of other applications and reasons. Coating and laminating have evolved substantially into a multi-billion dollar industry (actually industries), using coatings and laminates to improve the performance of fabrics, to make new forms of materials possible/practical, to provide aesthetics and/or decorate materials, providing working surfaces, or to replace other
types of materials (i.e. leather). Some products are luxurious, some as ‘working’ materials or of a highly technical nature, many components of other products, machines, equipment, or systems. Coated and laminated fabrics touch virtually every segment of our lives, quite frequently not seen, are taken for granted and not given much thought.

When that early man first used the animal grease for waterproofing, it was, in that context, a ‘smart’ or ‘intelligent’ product – it ‘did something’, it improved a material, giving it new properties and greater utility. It was ‘high tech’ in that day, it was a major development. The ‘high tech’ item of yesterday, that miracle product that made new things possible, are now normal, everyday parts of our lives. Think of the beginning of the synthetic fibers era in the early twentieth century – nylon was truly a high performance, miracle fiber – today it is ‘just another fiber’. Likewise for polyester – scorned for so many reasons, but the most widely used of all synthetic fibers. Many coated or laminated fabrics were, likewise, considered high tech when they were introduced, even smart/intelligent in what they permitted. Like the miracle fibers, they are now routine.

As the industry evolved, people discovered new fibers, elastomers and other materials, and techniques, and developed new applications not previously dreamed of (think computers and space travel) – and effectively applied coated and laminated fabrics to help solve problems and make some applications possible and others cost effective. Coatings have continued to evolve. While they may have been ‘smart’ in the context in which they were developed – fabrics with fluoropolymer coatings/laminates that breathe, allow passage of water vapor from the body, while keeping out larger water molecules, for instance – most coated and laminated fabrics seem relatively passive.

The definition of ‘smart’ or ‘intelligent’ keeps shifting; we expect even more special (‘smart/intelligent’) properties, properties that allow the material to ‘do something’ unique in order to qualify as smart/intelligent. From keeping out water or chemicals, or providing a working surface/material, or imitating leather, we now have materials that provide outstanding and extreme temperature ranges, important in space projects and fire service. We have body-friendly, biocompatible coatings useful in medical applications, including implants and patches that emit medicines in measured doses. Coated fabrics provide protection from a wide variety of heat and/or chemical hazards and exposures, many life-threatening. We use coated fabrics in solar panels to generate electricity, and in filters to make fresh water from brackish or seawater. We have coated fabrics that react to heat/cold to regulate temperature to keep one warm or cooler; fabrics may emit controlled amounts of substances such as medicines, aromas, insecticides, pesticides, products that provide antibacterial/antimicrobial functions; fabrics that change colors as possible indicators of something.
needing attention, they may become electrically conductive, selectively or continuously, or ‘do something’ in response to outside stimuli. In that context, coated/laminated fabrics have indeed become smart and/or intelligent. With evolving technologies, such as nanotechnology and electrospinning (those and many others are covered in the book), we can build new and even more extreme properties into more effective products, often with superior cost and performance benefits. The list increases year after year.

1.2 Industry basics

While many of the chapters will go into greater detail about various finishes, polymers, and coating and laminating techniques, it may be good to begin by providing a few of the basics as we start our look into potential for smart/intelligent coating and laminates.

To be sure, coating and laminating of textiles are textile finishing processes designed to add or improve function, to add value to a material, and/or to create a material with specific properties. In essence, anytime you add something to a fabric to aid performance, such as a nanotechnology-based finish that impregnates the fibers of the fabric, you are creating a coated fabric. The coating or laminate may work in different ways. The coated fabric may rely on the fabric simply to provide reinforcement and physical properties while the coating ‘does the work’ providing aesthetics or chemical, breathable, or other important properties. The coating may also improve the fabric properties to provide needed physical properties such as abrasion resistance and/or smoother surface. The reasons we use coating and laminating vary greatly with the desired end use.

We can define coating as applying a polymer or elastomer, usually in viscous form, directly to the fabric and curing it, if necessary. A variety of techniques are used. A bond-coat may or may not be used to improve adhesion of the coating to the fabric. Many types of machines and techniques will be discussed further in the book.

Laminating is using a pre-made or extruded film (or other fabric), bonding it to the primary substrate, generally with thermal or adhesive bonding. Curing is generally not required. Various properties, such as tear, can be affected by the material and technique used in the bonding.

It is important to realize that textile coating and laminating can involve virtually every textile form, not just fabric. These may include fibers, yarns, fabrics (woven, knit, or nonwoven); and the use of many polymers/elastomers, including rubbers of all types (natural and synthetic), acrylic, vinyl, urethane, silicone, polytetrafluoroethylene (PTFE), or combinations. The list is large and more are being developed for specific applications. Combinations of polymer and substrate are virtually endless.
In theory, combinations are chosen to suit the needs of the end use, with specific properties necessary to ‘do the job.’ In practice, combinations are chosen most often because they are available, inexpensive, or simply convenient, important considerations in meeting cost constraints of the finished product. There are applications where very specific materials may be developed and cost may be secondary. An example may be multiple passes of different elastomers/polymers for use in chemical haz-mat garments to hold-out/hold-in specific gases or chemicals or other contaminants. In this case, performance in a life-threatening situation is more important than cost, though cost does enter into the picture.

Many techniques are used, and many of these are discussed in subsequent chapters. These may include, but not limited to:

- yarn coating (think screens and yarns for outdoor furniture fabrics);
- spread coating – many variants are used;
- dipping/impregnating, a common practice;
- calendering, often with rubber;
- extrusion coating/laminating;
- film-to-substrate bonding (or film-to-film bonding through an open-mesh fabric – a scrim);
- fabric-to-fabric or to other substrates;
- combinations of polymers and substrates and coating/lamination techniques.

Coating and laminating may be done for aesthetics or for function. The end product may be disposable (limited use) or durable (reusable and long lasting). Coated and laminated textiles may be seen or unseen, with routine, enhanced, or critical properties, simple or sophisticated, high volume or specialized, inexpensive or costly. Coating and laminating systems and materials are versatile, allowing their development and use virtually everywhere.

It is impossible to put a finite number on the size of the market as it is vast and fragmented making accurate counting of production or usage extremely difficult. Many areas are not reported and not counted. Some estimates put usage at about 750 million square yards \((630 \times 10^6 \text{ m}^2)\) in North America in 2008 with a 3–4% annual growth rate, though declines in the global economy 2009 will have a profound effect. It is likely that much more exists, at least, in the rest of the world.

Make no mistake, the industry is global – and becoming more so. This is affecting the location of coating/laminating plants as it has in the general textile industry, with many going to lower wage, less developed countries, especially where hand labor is required. We see less and less of roll goods being shipped with fabricating and shipping of finished products becoming the norm.
The following issues will impact the growth in the industry:

- The increasing globalization mentioned above is perhaps the greatest factor shaping the industry: where are the plants, who is making the fabric, doing the coating or laminating, and who is doing the fabricating.
- Environmental issues will have more impact. Recycling is rapidly becoming a major environmental issue. Many countries are trying to ban one of the most common polymers used, polyvinylchloride (PVC), as being environmentally detrimental.
- New techniques and materials will evolve to help resolve problems and create better products. Better control of solvents and off gases will help, but solventless techniques are being commercialized as performance improves and costs are lowered. Expect improved material properties requiring less material to do the same job.
- Verticalization will increase. Major and forward-thinking companies will reach down and up, acquiring companies in the supply chain to gain greater control over the end product. This will likely reduce the number of companies, creating larger companies with economies of scale. Alliances and partnerships will be more common.
- Increased usage of nonwoven fabrics as substrates is occurring and will continue to grow as improvements in nonwoven fabric properties improve and costs are reduced.

1.3 Applications

While the following list is certainly only partial, it is beneficial to review just some of the areas where coated and laminated fabrics are used; many of these present opportunities for smart/intelligent applications. The headings or areas listed (first developed by Messe-Frankfurt, producer of the Techtextil trade shows) are just some of several ways the industrial/technical textile industry may be segmented. There are others but this is a good start to try and understand the industry and potential for coatings and laminates.

- **Agriculture**
  - Bulk containers
  - Fencing
  - Seed/crop covers
  - Bags
  - Shade materials
  - Irrigation systems
  - Pond liners
  - Irrigation
  - Hoses

- **Construction**
  - Safety fencing
  - Wind covers
  - Concrete curing
  - Safety vests
  - Hoses
  - Conveyor belting

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○ Truck covers
○ Drainage ditches

• **Clothing – technical components**
  ○ Shoe uppers and linings
  ○ Artificial leather/bags/belts
  ○ Rainwear
  ○ Garment linings
  ○ Backing/liners/stiffeners

• **Geotextiles**
  ○ Settling pond liners
  ○ Irrigation liners
  ○ Landfill liners and covers

• **Home furnishings – technical**
  ○ Upholstery
  ○ Trim
  ○ Carpet backing

• **Industrial**
  ○ Conveyor belts
  ○ Filtration
  ○ Barrier materials
  ○ Field covers
  ○ Abrasive backing

• **Medical**
  ○ Barrier materials
  ○ Implants
  ○ Bandages
  ○ Prosthetic devices
  ○ Gloves

• **Transportation**
  ○ Seating/trim for automotive, trucks, aircraft, buses
  ○ Hoses/belts
  ○ Tires
  ○ Headlining

• **Sport/leisure**
  ○ Athletic shoes
  ○ Artificial leather/bags/belts
  ○ Rainwear
  ○ Backpacks
  ○ Tents
  ○ Exercise mats
  ○ Exercise equipment

○ Substrate preparation
○ Architectural structures

○ Water/stain repellants
○ Combining different materials
○ Gloves
○ Hats

○ Soil stabilizers
○ Erosion barriers

○ Drapery backing
○ Bedding
○ Artificial leather

○ Mechanical rubber goods – drive belts, hoses
○ Tarps and covers
○ Signs, billboards, and banners
○ Marine covers

○ Incontinence materials
○ Upholstery
○ Body bags
○ Hygiene products
○ Surgical aids

○ Seating
○ Carpeting
○ Airbags
○ Truck covers

○ Balls
○ Seating
○ Field covers
○ Inflatable boats
○ Movie screens
○ Artificial turf and tracks
○ Sails
1.4 Conclusions

The versatility of the coating and laminating processes allows creative problem solving. We have just scratched the surface as to applications and the potential for improvement with smart/intelligent coated and laminated fabrics. It is in that context we look to the future. Look at what has been done, what is being done, and to the future of what can be done. Think outside the box and dare to dream of new concepts, products, and applications, many not yet even thought of or invented. This book can help stimulate some thought.
Abstract: Coating and laminating are an essential part of highly functional and technical textile development. This chapter discusses general features of coating and laminating process and materials preparations. It also introduces the basic concept of adhesion in the multilayer structure production. Then, the chapter reviews different techniques used to produce coated and laminated fabrics.

Key words: coating, laminating, adhesion.

2.1 Introduction: basic principles of coating and laminating processes

2.1.1 General features of coating and laminating

Coating is a process in which one or several layers of material are deposited on the surface of a substrate. Many different coating techniques have been developed to address the characteristics of a wide range of coating materials and substrates, to deliver the required performance in the final product, and to achieve the required productivity levels. Most coating materials are liquid, but solids and gases are also used, and each requires different processing methods to form layers on the substrate. This chapter focuses on textile substrates, but even here the coating process still varies, depending on substrate characteristics. For instance, a highly delicate, stretchable fabric requires completely different coating techniques and conditions to one with a dense structure and high strength.

While coating techniques vary depending on materials and final product characteristics, all coating techniques eventually pursue the same objective – producing a uniform and stable coating with the desired thickness, and with good or desired adhesion to the substrate surface. To achieve this goal, most coating techniques require three processes, ‘metering, transferring, and fixing’ of the coating materials to the substrate (Greer & Stelling, 1994; Scott, 1995). Understanding and controlling these processes are essential for all coating techniques, regardless of the great differences among them.

Metering controls the amount of coating material to be applied to the substrate. Coating processes can be categorized by whether and when the
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metering occurs, in free meniscus coating, pre-metering coating, or post-metering coating. The simplest and most basic type of coating application is the free meniscus coating process, which is done by withdrawing the substrate from the liquid (dip coating) or withdrawing the liquid from the substrate (coating-by-drainage). The coating thickness is determined solely by the rheological properties of the liquid, the applicator geometry, and the substrate speed. In pre-metered coating methods, such as slot coating and curtain coating, the coating liquid is fed into the coating die by a metering device, e.g. a displacement pump. In post-metering coating, an excess of coating material is applied to the substrate, followed by removal of the excess material. Examples of post-metering coatings are knife coating and air-knife coating.

Transferring is the process where the coating material is deposited on the substrate and forms a coating layer. It can be done with a series of rollers or calendars, spray, direct extrusion to the substrate, or immersion of the substrate in a coating bath. Wettability and rheology of the coating liquid, as well as applicator geometry, are important for achieving a uniform coating layer and controlled penetration. Fixing is usually the final step of the coating process, where transferred and metered coating layers are fixed to the substrate through drying, curing, pressing, or solidifying processes.

Controlling processing parameters in these three aspects of coating affect the amount of coating material applied to the substrate, uniformity of the coating layer, adhesion between the coating layer and the substrate, and penetration of the coating material into the substrate. It eventually determines performance, properties and durability of the coated textiles (Scott, 1995). A multi-disciplinary approach is needed to understand and control the coating process, including wetting, spreading, adhesion, fluid mechanics, rheology of fluids, and phase transition. Cost, production rates, reproducibility, environmental impacts, versatility, and fast adjustment are other important features of the coating process.

Laminating is a process that combines multiple substrates together. The goal of lamination is to produce a stable, multilayer structure with properties that cannot be achieved by a single substrate (Woodruff, 2002b). Substrates used in textile laminating processes are textile fabrics, pre-prepared polymer films, membranes, foam, and fibers (Scott, 1995; Swedberg, 1998).

While laminating is different from coating, laminating and coating processes share many of the same principles, requirements, and machineries (Swedberg, 1998). Like coating processes, strong adhesions between layers are the essential requirement of lamination. In lamination, adhesion can be obtained by adhesive, heat, pressure, or mechanical bonding (Scott, 1995; Nair & Pandian, 2006). In adhesive-based lamination, a substrate coated
with adhesive by a coating process is bonded with another substrate (Schindler & Hauser, 2004). In this case, the coating process is the heart of the laminating process.

2.1.2 Adhesion in coating and laminating

As discussed above, coating and laminating processes both involve bonding of different material layers, though they aim at distinctive and different processing goals. Achieving strong interlayer bonding is one of the key objectives of these processes and adhesion is highly related to interfacial strength between different layers. Direct interactions between adhesion and other properties, such as tear strength, resistance to flex, and peel strength, have been found in multilayer structures (Dartman & Shishoo, 1993). There are notable exceptions, where less adhesion between the laminated film and the fabric is desired. Widely used lightweight vinyl film laminates that utilize a three-layer film-to-open-mesh-fabric-to-film laminate, require less adhesion to the fabric scrim in order to allow the fabric to slip and move in the tearing process. This causes yarns to bunch up and provide greater resistance to tear, a hallmark of this type of laminate. In this case, it is desirable to have film-to-film adhesion through the fabric interstices, achieved by heat and pressure in the laminating process. The fabric is often treated with an adhesion inhibitor.

Adhesion is the attraction between two materials in contact. The level of adhesion is determined by cohesion forces of bulk materials and interactions between the layers (Yosomiya, 1990; Wicks et al., 1999). In the simplest case of a flat and smooth interface, the work of adhesion, \( W_a \), i.e. the energy required to separate two layers in contact, is defined as:

\[
W_a = \gamma_1 - \gamma_2 - \gamma_{12}
\]

where \( \gamma_1 \) and \( \gamma_2 \) are the surface tensions of components 1 and 2, respectively, and \( \gamma_{12} \) is the interfacial tension between components 1 and 2 (Yosomiya, 1990; Dartman & Shishoo, 1993; Dahlquist, 2001).

Equation 2.1 summarizes the physical-chemical aspects of adhesion on the interface in terms of surface energy. It indicates adhesion is a function of the surface/interfacial energies of materials, which are highly related to the nature of intermolecular interactions (Dartman & Shishoo, 1993). The positive work of adhesion indicates the tendency of two surfaces to adhere, while the negative work of adhesion indicates a tendency towards delamination (Schonhorn, 1985). Generally speaking, the larger the work of adhesion, the better the adhesion is. Two materials with high molecular affinity will generate the low energy interface and high work of adhesion, which will yield high adhesiveness. The work of adhesion is determined by the chemical natures of materials and therefore types of polymer in the
substrates, coating, or adhesives and their chemical affinities are the fundamentals in achieving good adhesion in coated and laminated fabrics. When materials comprising different layers do not have enough affinity, interfacial adhesion is poor. Adding a third material with affinity to both layers will improve adhesion, and this is called a tie-layer (Cole & Macosko, 2000).

Another factor contributing to adhesion is the interfacial diffusion of polymer chains. When there is sufficient interaction and affinity between two phases, it is possible for polymer molecules to diffuse beyond the interface to form entangled structures with the other phase (Schonhorn, 1985). This can be particularly true when polymer molecules possess high mobility. When material is heated above its glass transition temperature, the polymer chains have greater mobility and can penetrate deeper by diffusion, and adhesion strength increases if time permits (Wicks et al., 1999). Therefore, time and temperature in coating and lamination processes play an important role in adhesion strength.

Another consideration regarding how an adhesive interface forms between two layers during the coating and laminating process is wetting and spreading. Wetting can be defined as the displacement of a fluid from a solid surface by a second, immiscible fluid (Padday, 1978). The first fluid is usually air and the second is a fluid used in the coating process. Wetting phenomena involve interactions between liquid–substrate, liquid–liquid and liquid–air, and are represented by the appropriate interfacial tensions. When a liquid is in contact with a flat solid surface, two possibilities exist. The liquid may spread over the solid, displacing the original fluid (air in most cases), and finally come to a halt when the angle between the liquid–air and solid–liquid interfaces reaches a certain value, the contact angle, $\theta$ (Fig. 2.1). When there is no relative movement of the contact line with the substrate surface, this angle is referred to as a static contact angle. The static contact angle is determined by the balance of interfacial tensions in the three-phase contact line. Young’s equation relates the static contact angle and the surface tension of the liquid to the surface tension of the solid/liquid interface and the solid/air interface for conditions of thermodynamic

![Figure 2.1 Interfacial tensions and the static contact angle.](image)

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equilibrium and a perfectly flat homogeneous solid surface. It can be derived from interfacial force balances, see Fig. 2.1, and is given by (Young, 1805):

\[ \cos \theta = \frac{\gamma_s - \gamma_{SL}}{\gamma_L} \]  \[2.2\]

where \( \theta \) is the equilibrium contact angle, \( \gamma \) the interfacial tension between solid and vapor, \( \gamma_{SL} \) the interfacial tension between solid and liquid, and \( \gamma_L \) is the interfacial tension between liquid and vapor.

Wetting phenomena can be characterized by the value of the contact angle. The contact angle, \( \theta \), is a measure of wettability that refers to the response when a liquid is brought into contact with a solid surface, initially in contact with a gas or another liquid. A low contact angle means high wettability and a high contact angle means poor wettability (Berg, 1993). When the contact angle between the coating liquid and the substrate is zero, the coating liquid spreads spontaneously without a limit and forms a film. Thus, wetting and spreading are the basic criteria for obtaining good adhesion (Dartman & Shishoo, 1993). However, the static contact angle is an incomplete measure because it does not indicate the length of time needed for the liquid to spread over the solid surface (Dussan, 1979). In addition, in many coating and laminating processes, the contact line is in motion due to external forces, sometimes referred to as forced wetting. In this case, the kinetics of wetting becomes relevant and other rheological properties, such as viscosity of the fluid, also influence interface formation and adhesion.

From a practical point of view, the interface between two layers in coated and laminated fabrics is never smooth, and frequently one component penetrates through the surface of the other component. The effect of wetting on adhesion strength is intensified when the surface is rough. As illustrated in Fig. 2.2, a coating liquid with good wettability spreads on the rough
substrate surface while filling grooves and pores. As a result, the coating material and the substrate surface form an intimate contact and the actual area of contact is larger than the geometrical area. Surface roughness thus enhances adhesion strength between the coating layer and the substrate. When the fluid does not wet the surface, then it cannot penetrate through the surface pores, the area of the contact is smaller than the geometrical area, and adhesion strength becomes weak (Dartman & Shishoo, 1993; Wicks et al., 1999).

Textile substrates are not just rough but porous, so penetration through the structure can occur, governed by the kinetics of wetting. If the coating liquid penetrates into fibrous structures, this results in a larger interface area and also produces mechanical locking. Consequently, interlayer adhesion in coated and laminated fabrics is a combination of mechanical anchoring and interfacial interactions (Yosomiya, 1990; Dartman & Shishoo, 1993), and adhesion is therefore a function of coating material penetrations (Wake, 1973; Yosomiya, 1990; Dartman & Shishoo, 1993). However, there is an optimum penetration depth beyond which the material mechanical properties are degraded. When a coating liquid penetrates deep into the fibrous structures, adhesion increases owing to the high interface area and mechanical anchoring effects, while the substrate structures lose its freedom of movement and becomes rigid. Since a rigid structure cannot redistribute applied stress, the coated fabric becomes weak (Farboodmanesh et al., 2005). Thus penetration in the coating and laminating process should be controlled to balance good interface adhesion and preserve the flexibility of the structure.

Here, it is worth pointing out that wettability is not the only factor to govern penetration. Other factors, including viscosity of the coating liquid, temperature, substrate structures, pressure applied during the process and coating method, all affect the degree of penetration. Fabric adhesion is highly dependent on its structure, including openness, yarn and fiber sizes, and surface finishes, which affect wettability and the penetration of coating materials (Bluestein et al., 1975; Mewes, 1989).

Bulk properties also affect adhesion strength, even their effects are smaller than interfacial properties. Weak mechanical strength and big differences in thermal shrinkages between the layers reduce interlayer adhesion strength.

**2.2 Preparation for coating and lamination**

**2.2.1 Substrate preparation**

As discussed, the nature of the surface has a great impact on the outcome of the coating process, so substrate surfaces need to be prepared to ensure
optimum conditions. The substrate surface needs to be clean because any surface contamination alters surface characteristics, produces surface inhomogeneity and negatively affects interlayer adhesion. In addition, the chemical nature and amount of surface soil can vary, making coating results unpredictable and the coating process lack reproducibility (Bragole, 1974). To remove unwanted surface contamination, it is necessary to have preparation steps that include washing or scouring. Scouring/washing involves cleaning the textiles with water media, with the aid of surface active agents or scouring agents. Surface active agents or scouring agents ensure wetting of the substrate by aqueous media, loosen the soil–substrate interactions, and generate emulsification, suspension, or solubilization of the impurities removed from the surface (Ellis, 1995). After scouring, the substrate should be thoroughly rinsed, otherwise any remaining scouring agent may interfere with adhesion.

Theoretically, a perfectly clean surface is best for interlayer adhesion. However, in reality, a perfectly pure polymer surface may result in processing difficulties, due to static and friction between the processing equipment and the substrate (Fung, 2002). Textile substrates inevitably have a surface finish, which improves ease of processing but may reduce the adhesion capability. Choice of finish should take into account its potential impact on adhesion and be balanced against improvements in processing (Schindler & Hauser, 2004).

Other than surface preparation, a substrate also needs to be stabilized before coating and lamination, since it needs the strength and stability to withstand mechanical stress, heat, moisture, and pressure during the process. Heat-induced shrinkage is one of the most commonly encountered problems during coating/laminating, and results in substrate distortion, reduced adhesion strength, delamination, and processing problems. To prevent shrinkage-related problems, the substrate is stabilized by heatset under a temperature higher than that required by the coating/lamination process (Fung, 2002).

2.2.2 Preparation for coating/adhesive materials

Materials used as coatings and lamination adhesives should deliver the desirable properties in the final product and be compatible with the coating/laminating process used, as well as providing good adhesion properties. To satisfy these requirements, most coating materials and adhesives are complex mixtures formulated with multiple components. Most coating formulations contain binders, medium, and additives (Wicks et al., 1999). Binders adhere to the surface of the substrate, providing bonding among other components and the substrates, and so determine the adhesion properties between the coating and the substrate. They form a continuous
film on the substrate surface and govern the mechanical properties of the coating layer. In textile coating and lamination, binders are mostly organic polymers, or polymer precursors to be polymerized during the coating/laminating process. Medium is the carrier of the coating components. It provides adequate flow properties during the process and evaporates afterwards. Depending on the medium used, coating materials are classified as solvent-borne, water-borne, and 100% solid. Solvent-borne coating materials were the most popular until 1945, since it is easy to evaporate them after application. However, their use has diminished because of environmental concerns and government regulations regarding high VOC (volatile organic compound) emission and environmental toxicity. Water-based coatings are more environmentally friendly but harder to dry after coating, and thus require longer drying time at elevated temperatures and more energy use. Solid coating materials, such as powder and hot melt, use no medium and have advantages from an environmental point of view. Additives and pigment components impart the properties required from the coating – such as color, opacity, antistatic properties, and processability. Catalysts, flow modifiers, emulsifiers, and wetting agents are common additives used in coating formulations (Wicks et al., 1999). In many cases, one component can play multiple roles.

Coating materials can be liquid, melt, powder, or a continuous solid layer, such as a film, web, or foam. Preparation of coating/adhesive materials varies depending on the physical form of the coating formulations. Liquid coating formulations, including solutions, emulsions, and dispersions, are prepared through mixing, de-aeration, and filtering. One-part coating materials can be fully mixed and supplied as ready to apply by coating formulation suppliers, but two-part coating systems, where mixing the components initiates reactions such as polymerization and cross-linking, need to be mixed just before application. In this case, the necessary components are mixed first, any air entrapped during the mixing process is removed under moderate vacuum (de-aeration), and contamination is removed through filtering just before application (Licari, 2003). Coating applicators should be aware of the ‘shelf-life’ and ‘pot-life’ of coating materials. The shelf-life is the length of time one can store a coating formulation in an unopened container without significant loss of its properties. Pot-life is the length of time that coating materials can be used after the container has been opened (one-part system) or a two-part system coating formulation has been mixed (Licari, 2003). For materials with a very short pot-life, i.e. most two-part coating systems, mixing and dispensing immediately before the application process are necessary. Improper preparation and storage of coating liquid may cause changes in liquid rheology, adhesion properties, and reduction in process reproducibility, resulting in degradation of coating quality and uniformity.
Materials for hot melt coating are supplied in the form of pellets or power. Melting and filtering units directly connected to the applicator unit deliver hot melt at the right temperature and rheology. In both hot melt and liquid coating, it is very important to control the rheology of the coating materials. Viscosity is the most important rheological characteristic of coating materials, and affects transfer and deposition of the coating material, kinetics of wetting, and penetration. For most coating liquids, viscosity is the function of shear rate and temperatures, so the viscosity under application conditions, which varies greatly depending on the mode of application, is what mostly matters. More interestingly, most coating formulations change from liquid to solid, which results in dynamic changes in viscosity during application. Hence the viscosity profile during the coating process is important, and the coating should be formulated appropriately, depending on application method (Rohn, 1989).

Powder coating consists of binders and additives without a liquid medium, so does not require de-aeration or filtration. The coating is prepared by mixing the components needed, extruding the premix, grinding and sifting, and then supplying it to the application step (Waelde, 2001).

2.2.3 Laboratory- and pilot-scale coating trial

Coating and laminating processes can be highly unpredictable owing to the complexity of the system. Therefore, a series of laboratory-scale and pilot-scale evaluations is highly desirable before testing in the full production line, where the process is expensive and less flexible.

Simple laboratory tests to evaluate the properties of coating materials and substrates help to screen materials, and optimize coating formulations and the application process. Evaluating the liquid/melt rheology of the coating material is one of the most fundamental tests, and provides insight into how the material will behave in the coating process. Testing conditions closely resembling the expected application method are most desirable, but not always practical because of limitations in lab testing equipment and lack of knowledge about the conditions imparted by the application equipment. Evaluating substrate properties ensures the substrate has enough strength and stability to withstand the coating process without significant damage or distortion due to pressure, stress, and heat. Substrate-coating material interactions, such as adhesion and wettability, also can be evaluated. From the results of the lab tests, a range of optimum coating formulations and processing parameters can be selected for pilot production (Benedek, 2004).

Even though the results of such material evaluations are valuable, they are insufficient for predicting ease of processing and quality of coating in the production line. In most cases, producing small coated or laminated
samples with a lab coater or pilot line is necessary. Flexible but still realistic lab-scale coaters, such as the Werner Mathis Lab Coater, laboratory coating rags, and small-scale multipurpose coaters can be used.

It is worth noting that whatever system is used for the sample coating, understanding the processing and its conditions and limitations is important when scaling the pilot production up to full-scale production. Ideally, the conditions used in the lab/pilot line process should resemble the actual production process – tension, air flow, shear, pressure, temperatures, time, but this is not always achievable. However, processing conditions can be further optimized through the pilot coating trial, which will increase the potential for successful full-scale production, reduce the cost, and improve product quality. Lab and pilot testing are more critical when developing a new product and using new materials, where processing conditions and possible outcomes are unknown (Fung, 2005; McIntyre, 2006).

2.3 Coating methods

2.3.1 Immersion/dip coating

The simplest and most fundamental coating application is free-meniscus coating, which is done by withdrawing the substrate after immersing it in a bath of coating liquid. This is called ‘dip coating’ or ‘immersion coating’. Even though dip coating is one of the oldest coating techniques, it is still used widely to form thin films, mostly using low viscosity coating liquids. The principles of dip coating can apply to many applications, especially when these principles can be used to predict the thickness and the stability of the coating (Kistler & Schweizer, 1997). The thickness of the coating layer in this process is the result of a balance of various forces acting on the dynamic meniscus where the substrate exits the coating liquid bath. The shape of the dynamic meniscus and the thickness of the film, which are essential in industrial applications, are determined by those forces, which depend on the properties of the liquid and the substrate, and process variables that include substrate geometry, liquid viscosity, liquid surface tension, coating velocity, and applicator geometry. Non-ideality of liquid, wettability of the fiber, and surface roughness affect the thickness of the final film.

The major forces involved in the coating process are intermolecular (disjoining pressure), capillary, viscous, inertial, and gravitational. Figure 2.3 schematically illustrates the role of various forces in film formation during the dip coating process. Typically, hydrodynamic drag and inertial forces pull liquid up to make the film thicker, while capillary pressure attempts to maintain the shape of the static meniscus. Generally speaking, a coating liquid with higher viscosity yields a thicker film through higher hydrodynamic drag. A higher withdrawing velocity, \( V \), increases inertia and
hydrodynamic forces and yields higher liquid pickup. The disjoining pressure, which acts only over small distances, has a dual role depending on substrate–liquid interactions and film stability. The direction of the gravitational field is determined by the applicator geometry. Most of the studies on gravitational effects have been performed with the fiber withdrawn vertically, so that the fluid drains, making it thinner. If desired, a porous substrate impregnated with coating liquid can be passed through a squeeze roll (dip-squeeze coating) or doctor blade (dip and scrap coating) to remove excess coating materials (Whiteman, 1993).

2.3.2 Knife or blade coating

In knife coating, an excess of coating material is applied to the substrate and the final amount or thickness of the coating layer is controlled by a metering blade. One type of knife coating is a blade-over-air, or floating knife, process. In this process, the knife is fixed above the substrate and actually touches the substrate (Fig. 2.4a). The doctor blade presses the upper surface of the substrate and forces the coating layer to penetrate into the substrate. The amount of coating applied is controlled by fabric tension and the depression of the knife. The sharpness of the blade, alignment angle, and the degree of depression into the substrate influence the amount of coating applied (Woodruff, 1992). This method is usually used for applying relative small amounts of coating material to the fabric (Scott, 1995; Fung & Hardcastle, 2000).
Another type of knife coating process is knife-over-roll coating, and this is a more common technique. In this process, as shown in Fig. 2.4(b), the knife blade is suspended above a roller. The roller can be steel or rubber coated. The knife does not touch the substrate directly and there is a gap between substrate and knife, which controls the thickness of the coating. The gap between the roller and the blade can be set very accurately to enable precise thickness control, but variations in substrate thickness can make the thickness of the coating non-uniform (Woodruff, 1992; Scott, 1995; Fung & Hardcastle, 2000). Other possible knife configurations are knife-over-fixed-table and knife-over-conveyor (Herrera, 1991).

In knife coatings, blade geometry (the shape and angle of the blade), blade flexibility, and the rheology of the coating fluid affect the amount of coating applied and the extent of penetration into the substrate (Schindler & Hauser, 2004).

### 2.3.3 Air knife coating

The air knife coating process is illustrated in Fig. 2.5. Instead of a knife blade, excess coating material is applied to the substrate and blown off by an air jet coming from the so-called air knife.

### 2.3.4 Metering rod coating

When the amount of coating material applied is controlled by a wire wound metering rod, the process is called metering rod coating. As shown in
2.5 Air knife coating.

Fig. 2.6, excess coating material is removed by a metering rod, where only the desired amount of coating liquid is allowed to pass between the wires. A metering rod is also called an applicator rod, a Mayer bar, an equalizer bar, a coating rod, or a doctor rod. The typical metering rod is constructed with a stainless steel core tightly wound with polished stainless steel wires. The construction of wire rods affects the amount of coating deposited on the substrate, and wet thickness of the coating is directly governed by the cross-sectional area of the grooves between the wire coils of the rod. As illustrated in Fig. 2.6(b), increasing the wire diameter will result in higher
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Cross-sectional area of the grooves and increasing coating thickness. Thick coatings can be achieved with a rod having a second, smaller wire wound around the primary wire, also shown in Fig. 2.6(b) (MacLeod, 2001). Replacing the wire bar is fast and easy, and this method is used to provide precise coating thickness control at relatively low cost.

Metering using a wire-wound bar leaves striations on the coating layer. These striations are eventually leveled and smoothened by liquid surface tension, but this is not immediate and depends on the liquid’s rheology. High viscosity liquid takes longer to level, so more time is needed between metering and drying. Leveling after metering is the limiting factor for coating speed and liquid viscosity. Coating with a metering rod works best with low viscosity liquid, since it flows easily between the wire windings and levels quickly. Other factors, such as liquid viscosity under shearing action, substrate speed, substrate tension, metering rode rotation, and penetration into the substrate, also affect coating thickness and quality. Substrate tension should be adjusted to ensure intimate contact between the metering rod and the substrate, but not too high that the wires cause substrate deformations.

2.3.5 Transfer coating

Transfer coating is a sequential coating process where the coating material is first applied to a silicone release paper and then dried. This coated silicone release paper passes through the laminating rollers with the substrate, with the coating layer facing the substrate surface. Heat and pressure applied by rollers and ovens cause coating layer bonding with the substrate. The release paper is then peeled away, leaving a smooth or embossed, as desired, coated surface (Fig. 2.7) (Scott, 1995; Fung, 2002).

Despite the fact that transfer coating is more expensive than direct coating, it can be used for very delicate substrates, since little or no tension is applied during the process. Another advantage is the low degree of penetration, which reduces stiffness and generates flexible coated fabrics (Keeley, 1991; Fung, 2002).

2.3.6 Roll coating

Applying a coating with rotating rollers is one of the most well-known coating methods, and refers to kiss roll coating or roll coating. A variety of roller configurations are used in roll coatings, and they can be categorized by the number of rollers used (one to four, or more), the direction of rotation in relation to the substrate surface (reverse roll coating vs forward roll coating), and surface textures of the rollers (flat roll coating vs engraved roll coating).
2.7 Transfer coating.

The simplest roll coating set-up using a single roller is shown in Fig. 2.8. In this set-up, a single rotating roller acts as both a metering device and an application device. The bottom half of the roller is immersed in coating fluid bath and as it rotates, the coating material forms a film on the roller surface, with its thickness determined by hydrodynamics. Some of the film transfers to the substrate that is in contact with the upper part of the roller. The rotating speed of the kiss roller, the substrate speed, and rheological properties of the coating fluid (surface tension, viscosity, and density) determine the amount of coating deposited on the substrate (Wright, 1981).

The amount of coating applied to the substrate can be further controlled by the addition of a separate metering roller, which meters the thickness of
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Coating material on the applicator roller. This is a precise process controlled by the metering gap, relative speed and coating fluid rheology (Abbott et al., 1972; Greer, 1995). Both forward metering and reverse metering configurations are used (Fig. 2.9) (Hannachi & Mitsoulis, 1990). In reverse metering, applicator and metering rollers rotate in the opposite direction, while they rotate in the same direction in forward metering. Reverse metering and reverse application produces a smoother film with better stability. Forward roll metering is prone to generating unstable, non-uniform films due to split pattern and ribbing. Reverse roll coating is widely used, with basic types of reverse roll coating configurations including nip feed coating, L-head coating, and 4-roll pan feed coating (Fig. 2.10) (Grant, 1978; Greer, 1995).

Figure 2.10(a) shows 3-roll nip feed coating. This consists of three rollers, a metering roller, an applicator roller, and a back-up roller. The nip is flooded with coating fluid and functions as a reservoir (Grant, 1978; Greer, 1995). A liquid film is formed on the applicator roller by the metering roller rotating in the reverse direction. A doctor blade cleans the metering roller surface before it enters the metering zone. Failure to clean the metering roller surface will result in coating defects, such as streaks or film roughness. The metered film formed on the applicator roller is then deposited on to the substrate surface located on the backup roller, rotating the opposite direction to the applicator roller. Nip feed configuration has an advantage because it uses minimal amounts of coating fluid, but there can be problems with the coating fluid leaking, particular with low viscosity liquids.

In 3-roll pan feed or L-head coating (Fig. 2.10b), an applicator roller rotates through the liquid bath to pick up the coating liquid; a liquid film is formed on the applicator roller and metered by metering roller rotation. This configuration is limited to low viscosity and low speed applications (Grant, 1981; Greer, 1995). To overcome these limitations, a fourth pick-up roller running at a reduced speed is added, making a 4-roll pan fed coating system (Fig. 2.10c) (Grant, 1978).
Reverse roll coating methods are widely used for water-based solutions, solvent-based solutions and hot melts (Grant, 1981). A hot melt roll coating uses heated melt rollers. Solid pellet feed is melted between the rollers, forming a melt film on the roller, and the film is delivered to the substrate, which is usually preheated in a heating zone (Zickler, 1978).
Roll coating is a pre-metered coating process, where a metered film is first formed on the roller surface before it is applied to the substrate. To control the coating process, it is important to understand the flow hydrodynamics in the system, which will eventually affect the quality of coated substrates (Alonso, 2003). Many studies discuss the effects of various parameters, but detailed discussion of coating nip flow is beyond the scope of this chapter. However, it should be pointed out that nip geometry, rheology of the fluid and the relative speed of the two surfaces are key parameters in roll coating processes, and other factors, such as roller deformability, diameters of metering rollers, and drying, also affect coating outcomes (Alonso, 2003). It is worth noting that the amount of coating material delivered to the substrate is pre-metered and nearly independent of the structure of the substrate to be coated. Therefore varying substrate thickness does not result in uneven coating thickness (Scott, 1995; Anon, 2002a; Glawe et al., 2003).

2.3.7 Gravure or engraved roll coating

Gravure roll coating is the process where engraving on the roller acts as a metering device. The engraved roller is partly submerged in the coating bath and as it rotates, coating liquid fills the engraved pattern and excess coating liquid forms a film on the roller’s surface (Fig. 2.11). A doctor blade removes the excess surface film from the gravure roller surface and it then presses against the substrate to transfer the coating material in the engraved pattern.
to the substrate. This method can operate in either forward or reverse mode, but, as discussed before, the reverse mode generally provides greater stability (Grant, 1981; Hewson et al., 2006).

The amount of coating material delivered to the substrate is mainly controlled by the engraved patterns. Various patterns are used, examples being regular dot, irregular, quad, net structured, and rhomboid patterns (Hewson et al., 2006). The most important characteristics of engraved patterns that affect the amount of coating material delivered are the land area, cell openings, cell depths, cell volumes, cell angles, and cell spaces (Robinson & Marrick, 2006). Other parameters include viscosity of the coating material, application pressure on the substrate and type and structure of the substrate. Gravure roll coating can be used for different fluids, including hot melt adhesives (Anon, 2002a). It can also produce patterned coating (Stukenbrock, 2003).

2.3.8 Screen coating

Screen coating is the deposition of a coating material on a substrate through a mesh screen by squeezing (Licari, 2003). The amount of coating is determined by the screen mesh number, squeeze pressure, the angle between the squeeze blade and the screen, and the viscosity of the coating fluid (Goossens, 2001). It induces little or no friction or tension between the screen and the substrate, so lightweight and delicate substrates can be processed (Goossens, 2001). Screen printing is also ideal for applying even coatings to substrates with uneven surfaces (Scott, 1995).

One application of screen coating is paste dot coating. In paste dot coating, a dispersion paste consisting of a mixture of thermo-fusible powder, a binder and water, is directly applied onto the substrate through a rotating screen (Fig. 2.12). It is frequently used in interlining production for

2.12 Paste dot coating.
adhesive coatings on delicate fabrics (Goossens, 1994; Anon, 2002b). A hot melt dot coating can be done using screen coating. It is sometimes referred to as hot melt printing. Pre-melted hot melt resin is transferred to the substrate through the screen. This method has advantages over engraved roll coating due to the screen being cheaper, shorter exchange times, ease of controlling the amount of coating applied, and lower friction (Goossens, 2001; Anon, 2002a). Screen coating is also used for electrical applications, such as circuit board printing, because it provides good pattern definition with a properly masked screen and precise coating thickness control (Matthews, 1993; Licari, 2003).

2.3.9 Slot die or extrusion coating

In slot die or extrusion coating, a plasticized coating compound is pressed through a sheeting die and transferred directly onto the substrate to be coated (Zickler, 1978; Whiteman, 1993), as illustrated in Fig. 2.13. In the traditional slot die coating system, the die lip is in contact with the substrate and backed by the roller, which imparts pressure on the substrate. This is called a ‘closed system’, where there is no contact between the coating materials and the air (Glawe et al., 2003). The substrate needs to have some stability since it is often under high shear pressure and tension. Some modern slot die systems allow a gap between die lip and the substrate (Lippert, 2001; Anon, 2002a).

The quality of coating is influenced by the die, the lip shape, the die position, the angle of contact, lip opening, and the die-to-roller gap. A
balance between die pressure and substrate tension, flow rate, and flow distribution is needed for good quality coating. Coating weight is principally controlled by pump delivery rate and substrate line speed (Lippert, 2001; Anon, 2002a; Glawe et al., 2003). Adhesion between melt and the substrate is determined by the compatibility of the coating material and substrate, but is also affected by other processing factors, such as extrusion melt temperature, air gap, film thickness, coating nip pressure, substrate construction, resin melt flow index, coating line speed, and coating roll temperatures (Mamish, 1990).

One major application of slot die coating is coating with hot melt. In the hot melt coating system, thermoplastic resin or reactive adhesives are fed and extruded to the substrate surfaces (Anon, 2002b). Despite the high viscosity of the hot melt, slot die coating is able to produce a wide range of coating thickness, from very low to very high (Woodruff, 1992). High line speed is another advantage of slot die coating. However, dies are expensive and require frequent maintenance to achieve accurate coating control.

2.3.10 Curtain coating

In curtain coating, the coating fluid forms a freely falling liquid sheet and is deposited onto a moving substrate, as shown in Fig. 2.14. No friction is involved, so the coating fluid is not forced to penetrate the substrate structures but follows its surface to form a film. This method is capable of producing a thin film, with a range of a few microns, and the film thickness is not affected by substrate roughness. Preventing air entrapment and establishing stable fluid curtains are the keys to achieving quality curtain coatings (Chazey & Kaneko, 2000; Weinstein & Ruschak, 2004).

![Curtain coating](image)

2.14 Curtain coating.
2.3.11 Powder coating

Powder coating is one of the methods that used 100% solid coating material. In powder coating, pre-prepared coating powder in the solid form is deposited directly onto the substrate. This is an environmentally friendly process compared with fluid-based coating methods since it does not use solvent, releases very low amounts of VOC, and generates few waste materials or hazardous chemicals. No drying is necessary since no water is used, which may result in energy savings (Waelde, 2001). Beyond its environmental attractiveness, powder coating also has unique characteristics because the particles have a high surface area. It is also possible to create rich coatings with minimal penetration.

One of the oldest powder coating methods is fluidized bed coating. Air passes through a container filled with coating particles, and raises the particles gently. As a result, fluid-like particle motions are generated. When a heated substrate is dipped into the fluidized bed, the particles touching the substrate melt and adhere to it (Waelde, 2001). This has the advantage of creating a uniform coating thickness, but requires the substrate to be preheated above the fusion temperature of the coating powder, which may not be appropriate for most textile substrates (Licari, 2003). Hence it is mostly used for metal coating processes (Waelde, 2001). An electrostatic fluidized bed coating process overcomes preheating problems (Bellemare, 1997). Instead of air, it uses electrostatic charges to separate the powder particles and generate the necessary fluid-like motion before deposition.

Scatter coating is a powder coating method where the coating powder is spread evenly on the substrate surface with a rotating scatter roller. The amount of powder applied is determined by the dosing roller, its rotation speed and the substrate line speed (Jarrell, 1992; Glawe et al., 2003). In powder dot coating, the coating powder is delivered directly onto the substrate surface by means of an engraved roller, as illustrated in Fig. 2.15 (Jarrell, 1992; Anon, 2002b).

2.3.12 Spray coating

A coating material can be sprayed directly onto the substrate surface. Spray coating methods include pressed air vaporization, airless pressure spray, hot flame spray, hot vapor impelled spray, electrostatic spray, and dry powder resin spray (Waelde, 2001; Licari, 2003). The most common method is compressed air vaporization, where air and coating materials are pressed out through a nozzle (Glawe et al., 2003). Even though spray coating is a widely used and effective way to apply coatings to electronic parts with irregular shapes, it is hard to achieve a uniform coating on a wide width of textile substrate, and it is expensive (Woodruff, 1997). However, spray coating can
be used for specialized narrow web bonding applications, where the substrates are irregular in size and fast adaptation to different shapes is required.

2.3.13 Non-conventional and novel coating methods

Apart from the coating processes commercially available and widely used in the textile industry, there are various methods in development or being used in other industries, and it is worth mentioning some of these techniques (Anon, 2005).

An interesting development is electrospun coating. In electrospinning, nano-size fibers are formed by electrostatic forces pulling a polymer solution jet. Direct electrospinning on the substrata forms a coating layer of nanofibers on the surface of the substrate (Heikkila et al., 2007).

Metal coatings and conductive coatings are an area of intense study for applying non-conventional coating materials to textile substrates (Liepins, 2001). Examples of methods used for conductive coating and other thin film coating applications include electroless plating, where surface layers of metals are formed on the substrate via chemical reactions in a coating bath (Vaskelis, 2001), sputter coating, where a thin layer of metal is formed by incident particles or ions accelerated by an applied electrical potential colliding with the surface (Aufderheide, 2001), PVD (physical vapor deposition), where vaporized material is transferred to the substrate surface and deposits a thin film on it (Mattox, 1998), and CVD (chemical vapor
deposition), in which the surface is modified by depositing layers through chemical reactions in a gaseous medium (Bhat, 2001). Other methods, such as coating with supercritical fluid (Baumert, 1998) and sol–gel processes, may be valuable for producing advanced textiles with high functionality.

2.4 Lamination methods

Laminating processes are categorized according to several criteria: substrate type combinations, the number of layers, and the method used combining. Here, laminating processes are classified by bonding methods into adhesive lamination, flame lamination, and ultrasonic lamination. Adhesive lamination is further classified into three groups according to the nature of the adhesive; wet adhesive lamination, hot melt lamination, and dry heat lamination.

2.4.1 Flame lamination

Flame lamination is the process in which a pre-prepared thin, thermoplastic foam sheet is passed over an open flame to generate a thin layer of molten polymer. Polyurethane foam is most frequently used. Molten polymer layers act as an adhesive to bond two substrates by nip pressure between calenders and produce a laminated fabric as they cool (Scott, 1995; Mansfield, 2003). Triple-ply lamination can be achieved by using a dual burner or two-pass lamination (Gillessen, 2000), and does not require drying or a curing oven. Processing variables are gas type, flame height and spread, foam burn-off, line speed, and nip pressure (Mansfield, 2003). The line speed should be held constant, and flame intensity should be optimally adjusted to ensure sufficient melting while preventing burning and preserving the thickness of the adhesive layer (Gillessen, 2000).

It is a simple and easy to use laminating method, production rates are high and costs are low. However, it is environmentally unfriendly because flame laminating produces harmful emissions. Another disadvantage is that the process produces solid bond layers with little porosity, making the laminates stiff (Gillessen, 2000).

2.4.2 Wet adhesive lamination

Wet adhesives used in the laminating process are either water-based or solvent-based (Walker, 1994). They are applied to one substrate surface in liquid form by conventional coating methods, such as gravure roll coating, spraying, roll coating, and knife coating. Then, the adhesive coated web is bonded with other substrates under pressure, and dried or cured in an oven (Grant, 1981; Swedberg, 1998; Stukenbrock, 2003).
Adhesive performance, such as bond strength, durability, and resistance to heat, depends on the chemistry of the adhesive as well as the laminating process. Crystallinity, viscosity, flow characteristics, chemical resistance, and set times of adhesive used all affect performance (Crabtree, 1999). Penetration of the adhesive into the substrate structure should be controlled. While some penetration is necessary to achieve good adhesion, deep penetration may generate stiff structures and loss of drapability, hand, tear strength, and breathability (Crabtree, 1999; Stukenbrock, 2003).

A solvent-based adhesive has the advantage of being fast-drying, but poses environmental risks, such as high VOC emission and hazardous waste generation. Owing to the environmental concerns and government regulations, conventional solvent adhesives are only used when coupled with expensive incineration or recovery equipment (Halbmaier, 1992; Gillessen, 2000). Water-based adhesives do not use toxic solvents, but water is difficult to evaporate, so a drying unit is required, which has high energy requirements and occupies a large amount of floor space (Gillessen, 2000).

2.4.3 Hot melt lamination

Hot melt lamination uses hot melt adhesive as the bonding agent (Anon, 2002a). Hot melt adhesives are 100% solid and melt to the liquid phase in temperature ranges of 80 to 200 °C, solidifying to form bonding when they cool (Glawe et al., 2003).

Hot melt adhesives are mostly polymers and their compounds, specially formulated to satisfy lamination requirements (Nussli, 2001). They should have the appropriate melt viscosity, melting temperature, curing time, hardness, and good adhesion with the substrate to provide good peel, shear, and tensile strength. Depending on applications, breathability, lightness, porosity, and washing durability may also be required (Mansfield, 2003). The appropriate adhesive is selected to achieve the desired quality, coating flexibility, and cost (Nussli, 2001; Anon, 2002a).

There are two different hot melt adhesives classes; thermoplastic polymer-based systems and reactive hot melt adhesive systems (Glawe et al., 2003). Thermoplastics soften and solidify solely according to temperate changes, and include ethylene vinyl acetate (EVA), polyamide (PA), polyethylene (PE), polyvinylchloride (PVC), and polyester-based compounds (Crabtree, 1999; Glawe et al., 2003). These are sensitive against steam and water and, due to low softening points, the application ranges are limited.

Reactive hot melt adhesives are fully crosslinked by the reaction with moisture, after being applied to the substrate. After crosslinking, heat does not soften the adhesive. They are highly durable and have good boiling and climate resistance, but are rather expensive. This group includes moisture-crosslinking polyurethanes (PUR) (Mansfield, 2003; Woodruff, 2002c).
Hot melt adhesive is normally melted in an off-line melting unit and delivered to a hot melt coating unit (Gillessen, 2000). Many conventional coating processes are used to apply hot melt adhesives, including roll coating, gravure coating, slot die coating, screen coating, knife-over-roll coating, and spray coating. The coated substrate is subsequently bonded with another substrate to form a multilayer laminate.

Hot melt adhesives are replacing water- and solvent-based adhesives due to their environmentally friendly operating conditions (Glawe et al., 2003). They also have advantages over dry lamination for heat-sensitive substrate coating, since the substrate is not exposed to direct heat during the laminating process (Woodruff, 2002a). Nor is a drying step required, where the energy requirement can be high (Anon, 2002a; Glawe et al., 2003). Laminating can be achieved at low coating levels, so it can produce soft handling and flexibility (Anon, 2002a). Bonds are formed almost instantly without drying, so operating speeds are not limited by the rate of drying and high productivity can be achieved (Halbmaier, 1992). The shelf-life of hot melt adhesive is longer than that of wet adhesives. However, the hot melt adhesive system has some drawbacks. Changing the adhesive type means that the entire pre-melt and application system must be cleaned, and these adhesives are relatively expensive (Glawe et al., 2003).

### 2.4.4 Dry heat lamination

Dry adhesive is another type of 100% solid adhesive. Unlike hot melt adhesive, this type is applied to the substrate in solid form and later activated by heat and pressure to form a laminated product. Dry adhesives are powders, webs or films made from polyester, polyamide, EVA, polyethylene and thermoplastic polyurethane (Anon, 2002c; Gillessen, 2000). High solid content without harmful emissions is advantageous from an environmental point of view; however, the energy requirement for melting dry adhesives and the high heat exposure of the sample are drawbacks (Gillessen, 2000).

Powder adhesives are cryogenically ground to a fine texture, with sizes from 1 to 500 μm. They can be applied by scatter coating, powder dot coating, or paste dot coating. When melted, they form a discontinuous bond between two layers, imparting bonding while provide high softness, drape, and permeability. Even though they do not produce any harmful emissions, fine particles may generate airborne dust (Crabtree, 1999; Gillessen, 2000).

Other dry adhesives come in the form of films and webs. The adhesive rolls are simply inserted between or over the substrate to be laminated (Jarrell, 1992). These can be used to laminate textiles with open structures, where powder adhesives tend to fill the voids instead of staying on
the surface (Crabtree, 1999; Gillessen, 2000). Lower add-on can also be achieved. However, they tend to be more expensive than powder adhesives, and it is difficult to adjust add-on level and application width. They also require the use of different rolls of adhesive to change add-on or application width (Gillessen, 2000).

One way to produce dry adhesive lamination is flat bed dry heat lamination. Dry adhesives are sandwiched with two substrates and transported through the heating tunnel by an upper and lower conveyer, where the adhesive melts and forms a bond between the two layers. Further pressure can be added by nip rollers at the end of the heating section as the materials cool (Field, 2001). This is a high-volume production and can take place in a continuous operation. It also enables the use of dry adhesive at relatively low temperatures, so reduces the problem of substrate heat exposure (Field, 2000).

2.4.5 Ultrasonic laminating

Ultrasonic laminating uses sound energy instead of adhesives to combine multiple layers of substrate (McIntyre, 2006). Ultrasonic is high frequency sound waves, with frequencies of 20 kHz to 1 GHz. This range is beyond what humans can hear, but ultrasonic waves carry energy, which can generates bonding in different materials. Ultrasonic bonding or welding has been used for embossing, perforating, slitting, cutting, and slicing, as well as laminating (Brieger, 2006).

In the ultrasonic welding process, high frequency electric signals produced by a generator are converted to mechanical oscillations in a weld horn or a sonotrode. This causes repeated compression and friction of the fibers in the substrate, resulting in melting and bonding (Knorre, 2001; Brieger, 2006). The most frequently used frequencies are 20, 30, 35, and 40 kHz. The amplitude of vibrations and the welding force, the forces that the sonotrode applies to the material, affect bond strength. Optimum amplitude depends on type of the material to be bonded and the welding force, and needs to be adjusted according to desired bond strength, materials, welding time, substrate feeding speed, and coverage area of the bonding pattern (Brieger, 2006). Using an engraved anvil drum can produce patterned bonding points. The percentage pressing area of the engraved roll, the gap between the ultrasonic head and the anvil roller, and the speed of substrate are important processing parameters (Knorre, 2001).

No use of adhesive (mostly made from petroleum-based materials) and no heat application make this an environmentally friendly and safe process. Ultrasonic lamination is also very versatile, since multiple layers, up to 6 to 12, can be laminated simultaneously and pattern variety can be used to improve appearance and tailored properties. Ultrasonic bonds provide
textile-like hand, open characteristics, high loft, softness, breathability, and high absorption, without causing stiffness since the substrate is only melted at the point of pattern (Gil, 1999; Knorre, 2001; McIntyre, 2006). This method is used for multilayer wipes, sorbents, and medical products (Brieger, 2006).

2.5 Conclusions

Coating and lamination are key technologies in broadening the possibilities for textiles, because they can be used to add valuable functions and properties, and create highly engineered composite systems (Woodruff, 2002a). These methods have been widely used in traditional textile applications, such as apparel and upholstery, providing resistance to liquids, gases, and soiling, conferring fire retardation properties and leather-like appearance. Coating and lamination are also indispensible tools for technical textiles, such as filtration, automotive applications, geo-textiles, and hygiene articles (Scott, 1995).

Important demands on current coating and lamination technology come from concerns over the environment and sustainability. Development of coating and lamination processes that use less energy, produce less pollution and hazardous wastes, and use materials from renewable resources or with high recyclability are becoming critical issues. Increasing the use of high solid content coating, such as powder coating and hot melt adhesive, is an example of the trend towards environmentally friendly coating and laminating processes (Woodruff, 2002c).

Another demand comes from advances in functional and technical textiles. Textiles are transforming from commodity into highly engineered products with tailored properties, and coating and lamination are key technologies in this ongoing transfer. More flexible, precise and diverse coating and laminating processes with the capability of handling a variety of coating materials – substrates, polymers, and films – are needed. Versatile coating equipment that can conduct multiple coating processes has been introduced to the market, representing the importance of a quick response to demand and process flexibility.

With advances in fluid dynamics and engineering, more precise control of the coating process is becoming possible. Innovations in materials science, nanotechnology and biotechnology are bringing new materials to coating and laminating processes, broadening the possibility of high functional textiles. This trend is highlighted in the development of smart and intelligent textiles. There are great opportunities in developing coating and laminating technology that can combine textile structures with materials with functionality – conductivity, shape memory, drug delivery, for example – and make it possible to produce integrated systems that respond to environmental stimuli and perform engineered functions (Yonenaga, 2001).
2.6 References


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GILLESSEN G (2000), ‘Flame, dry or hot-melt’, International Dryer, 185 (11), 34.


WAKE W C (1973), ‘The adhesion of polymers to fibrous masses’, *Journal of Coated Fabrics*, 3, 84.

woodruff f a (2002c), ‘Exciting prospect for PUR compounds’, International Dyer, 187 (11), 34.
yosomiya r (1990), Adhesion and Bonding in Composites, New York, Marcel Dekker, Inc.
Base fabrics and their interaction in coated fabrics

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Abstract: This chapter discusses the complex interaction between fabric architecture, coating, and mechanical response. A brief introduction to fabrics and test methods is provided. Picture frame experimental studies and modeling studies are used to explore the effect of yarn mobility (i.e., fabric weave pattern, yarn size and spacing, and coating penetration) on shear behavior. Similarly, trouser tear experiments demonstrate the effect of del zone yarn mobility on tear strength. Finally, more representative coated fabric finite element models are addressed through discussion of distinctive factors such as crimp effect, locking angle, and coating adhesion.

Key words: fabric and coating interaction, textile architecture, coating thickness and penetration, shear and tear deformation, finite element analysis (FEA).

3.1 Introduction

3.1.1 Importance of base fabrics and the interaction between fabric structure and coating

Coated fabrics have wide applications in fields such as medical substrates, protective clothing, flexible membranes for civil structures, airbags, geotextiles, and industrial fabrics (Chou, 1989; Gillette, 1992; Bridgens et al., 2004a). Early coated fabrics were coated with different natural treatments, such as resins, tars, waxes, and natural oils; one of the most successful of these products was waterproof oil-cloth. The main disadvantage of these earlier coated fabrics was the stiffness and brittleness imparted to the fabrics (Gillette, 1992). With the introduction of rubber as a coating, a soft, flexible (at least at normal ambient temperatures), and waterproof material became readily available (Gillette, 1992). However, the capability of the base fabric and coating to withstand different conditions (e.g. over a wide range of temperatures and prolonged storage in folded form) can still vary with the type of elastomer and fiber (Chou, 1989).
Since the introduction of rubber (elastomers) and other flexible polymer coating materials, many applications have been developed to take advantage of combined properties of both the textile and the coating. There are many different coating methods for textiles, such as knife coating, porous roll coating, dip coating, calendaring, ink jet coating and vapor deposition coating (Sen, 2001; Tracton, 2006). Many of these processes are described in greater detail in Chapter 2. Since most coating or laminating processes require pulling the fabric through a knife-roll gap or roll-roll gap at relatively high speeds, textile structures that distort under very low tensions are more difficult to process. Manufacturers must understand how a material will behave in converting and end-use operations to optimize material and process selection.

Experimentally, researchers have shown that the fiber substrate governs the strength, elongation, and dimensional stability, while the coating influences permeability, bonding, and abrasion properties (Chen et al., 1995; Wilkinson, 1996). Nevertheless, design of a fabric to meet such end-use requirements can be a complex engineering problem since there are often many interrelated and sometimes conflicting factors involved in fabric performance (Argyris et al., 1992). Selection of the optimal combination of textile materials, textile structures, and coating compounds for the anticipated loading condition is often based on the strength of the textile substrate alone. Yet, it has been shown that the in situ (coated) properties can differ significantly from that predicted based on the properties of the constituents prior to coating. This is true especially for more complicated conditions that are heavily dependent on the interaction between fiber structure and coating, such as stability during the coating process, tear and seam strength, and formability without loss of barrier and strength properties (Chen et al., 2002). The discrepancies and the consequences are likely to be further exacerbated by the desire to utilize new textile substrates (woven and nonwoven) to obtain technically superior properties with less material. The aim of this chapter is to provide some insight into the design or selection of substrates (e.g., weave pattern, yarn size, and yarn spacing) and coating parameters (e.g., desired thickness and penetration) to optimize the response to complex loading conditions.

The specific objectives of this chapter are to provide insight on:

- advanced test and measurement techniques for characterizing coated fabrics;
- effect of textile structure on coated fabric shear and tear deformation behavior;
- effect of textile structure on coating penetration and thickness, and ensuing end-use properties;
- current approaches to modeling coated fabric response.
3.1.2 Background on base fabrics

While there are many different textile structures, e.g., woven, nonwoven, braided, knitted, the most common base fabrics are woven or nonwovens. In this chapter, we will focus primarily on woven fabrics, which can be described by defining weave pattern, fiber material, yarn size, and yarn spacing. A woven fabric is a system of orthogonal, interlaced yarns, with the longitudinal ones referred to as warp yarns and the yarns crossing them referred to as weft or fill yarns. Different weave patterns can be formed by having fill yarns undulate over and under different numbers of warp yarns. Many variations on the undulation patterns exist, with plain (1 × 1), twill (2 × 2), and satin (e.g., 3 × 1, 7 × 1) weaves being among the most common. Figure 3.1 shows schematics of the unit cell for a plain weave (PW), represented by yarns that travel over and under each alternating crossing yarn, and for two different satin weaves, a 4-harness satin weave (4HS) with fill yarns that undulate over three and under one warp yarn, and an 8-harness satin weave (8HS) with fill yarns that cross over seven and under one fill yarn. Each of these patterns is repeated throughout the fabric.

![3.1 Woven fabrics weave patterns top view (left images) and crossovers (right images): (a) plain weave (PW), (b) 4-harness satin weave (4HS) and (c) 8-harness satin weave (8HS).](image-url)
For woven fabrics, there are often trade-offs between shear stiffness and tensile stiffness or between weave handling stability and formability. The plain and twill weaves tend to have lower tensile stiffness in the yarn directions than the satin weaves, owing to the higher undulation, resulting in an initial yarn straightening or decrimping response. The high undulation also tends to improve handling stability but can reduce formability. The satin weaves tend to be more formable, looser structures in terms of shear but may be susceptible to undesired distortion while handling. One benefit, however, is that the satin weaves exhibit stiffer behavior in tension in the yarn directions due to the longer sections of straight yarns. The greater number of undulations in the plain weaves also presents a more convoluted path for the coating to infiltrate.

In addition to their weave pattern, fabrics are typically defined by their areal weight (e.g., g/cm², oz/yd²) rather than density because of the difficulty of measuring thickness, and by their yarn count or spacing. Yarn count is given as \( A \times B \) where \( A \) is the number of warp ends and \( B \) is the weft picks, per inch or per centimeter. As with the thickness, yarn size can be difficult to measure because the yarns can easily deform and the edges are not clearly defined. Thus, yarn size is typically reported in terms of linear density in units such as denier (grams per 9000 meters) or tex (grams per 1000 meters). These yarns can vary in construction from the twisted filaments, twisted staple fibers, and plied strands more commonly seen with polyester, nylon, and natural fiber yarns, to the parallel fiber tows that are seen in carbon and glass fabrics.

### 3.2 Methods of characterization of base fabric and coated fabric properties

In contrast to bulk metal or polymer materials, coated fabric behavior can be significantly affected by the mesoscale or yarn–yarn and yarn–coating interaction. As a result, many distinct standard testing methods for fabrics and coated fabrics have been developed by the American Society for Testing and Material (ASTM) and the British Standards (BS). These tests include adhesion (peel bond), abrasion resistance, fabric handle, drape and stiffness, tensile strength, tear strength, and burst (Sen, 2001; Fung, 2002). One unique aspect of woven fabrics is their nonlinear shear response. While not yet a standard test method, the picture frame or the trellis frame experiment has been used extensively for the characterization of fabric shear deformation (Clifford et al., 2001; Lussier et al., 2001; Liu et al., 2005; Farhoodmanesh et al., 2005, 2006; Cao et al., 2008). The shear behavior is an important factor in formability, tear, permeability, and several other coated fabric properties. This section will briefly describe several common methods for mechanical and materials characterization of coated fabrics.
3.2.1 Uniaxial tensile testing

Several different test methods exist for determining woven fabric uniaxial response, including the tensile strip test D278-09, ravel strip test D4964-98 (2008), and grab test D5034-09. These test methods vary in terms of how they address the edge effects, the Poisson or crimp interchange effects, and related interlaced yarn interaction. A standard rectangular strip can be used to determine uniaxial tensile behavior, but if the yarns are loose or large relative to the specimen width, the tensile values can be too low to be representative. In the ravel strip test, the yarns in the loading direction outside the grip width are removed, leaving the transverse yarns free to contract but not as loose free ends. Typically, the grab test is the simplest test to run, with the specimen a simple rectangle larger than the grip width and the test section is typically a 2:1 ratio (length : width), as shown in Fig. 3.2. The test is conducted at a quasi-static strain rate and the fabric is pulled uniaxially in the warp or weft direction. In a modified grab test, slits or side cuts at the edge of the specimen are used to generate a controlled and consistent failure and to prevent failure at the grips. A typical tensile curve is shown in Fig. 3.2(b). Note that even in tension, the load–strain curve is nonlinear, with an initial low stiffness region resulting from straightening of the crimp in the undulated yarns. In coated fabrics, the ravel strip test is impractical, since individual yarns cannot be removed, but the coating provides sufficient structural stability for the tensile strip and grab tests to be suitable.

![Uniaxial tensile test setup: (a) modified grab test setup and (b) typical tensile behavior of fabrics.](image)
3.2.2 Biaxial testing

Many coated fabric applications such as inflatables, airbags, and geotextiles involve pressurization or other biaxial loading conditions. The hemispherical punch loading case, such as that shown in Fig. 3.3, can be used to generate uniform loading in the warp and fill directions. The fabric is deformed by a hemispherical punch attached to the Instron crosshead, and punch load versus crosshead displacement data is recorded. Biaxial tests can also be conducted by sealing the edges of a cylinder and applying air or liquid pressure (Fig. 3.4). Pressure alone generates a 2:1 ratio of circumferential to axial loading, but this ratio can be varied somewhat by application of an axial displacement (Fig. 3.4c). To test other loading ratios, a
true biaxial test frame must be used (Fig. 3.5). For loading ratios not close to 1:1 or for unbalanced weaves, the clamping on each side is preferably separated into segments rather than one solid clamp to allow the fabric to contract laterally in response to Poisson or crimp interchange effects (Boisse et al., 2001a).

3.2.3 Shear testing

Bias extension tests (i.e., uniaxial tensile tests at 45° to the warp) are often used to characterize fabric shear behavior due to the simplicity of the test setup. A disadvantage of this method is that the shearing is not uniform. For example, in Fig. 3.6, the central diamond region is in pure shear, but the two triangles at the top and bottom contain yarns that are directly clamped and exhibit no shear. The four remaining triangles exhibit an intermediate response. In addition, at higher extensions, yarn slippage can occur, especially for loose fabrics. Thus, interpretation of the test data can be more complicated.

In contrast, the trellis frame or picture frame test (Fig. 3.7) generates a more consistent pure shear but requires a non-standard test fixture and careful attention to the experimental procedure. Lussier and Chen (2002) presented a detailed discussion of the testing procedures and data analysis techniques for a picture frame test. The fabric is clamped onto the frame by means of toggle clamps and a grooved surface to prevent the material from slipping (Fig. 3.7). This results in a small level of tension in the material, along the fiber direction, during testing. The yarns are aligned parallel to the sides of the frame such that rotation does not cause any additional tension in the yarns. A milled slot located in the middle of the vertical link guides the upright displacement of shear fixture. The smaller linkage below the main fabric area generates a loading rate multiplier effect for higher shear rate testing. A detailed design of this modified trellis frame can be
3.6 Bias extension test setup (Peng and Cao, 2005).

3.7 Shear frame fixture (Trellis frame) with toggle clamps and grooved surface.
found in Lussier et al. (2001). Variations of the picture frame design can also be seen in Cao et al. (2008).

The locations at which the yarns overlap are called the crossovers. Figure 3.8 shows a typical shear behavior obtained for woven fabric (Lussier et al., 2001; Farboodmanesh et al., 2006). The concave shape of the curve can be divided into three distinct regions: (1) the friction-dominated region at low shear loads; (2) the yarn compaction region, where the slope increases with shear angle; and finally (3) the post-locking angle with a sharp, relatively linear increase in shear load. The magnitude of this mechanical response depends significantly on fabric structural parameters – e.g., weave pattern, yarn size, and yarn spacing.

When using a picture frame fixture for obtaining the shear response of uncoated and coated fabrics, several points should be addressed including frame weight, mechanical conditioning, fabric pretensioning, and yarn alignment parallel to the frame sides. Initial testing without any fabric in the frame results in a relatively constant frame load that is subtracted from the results in all tests. Lussier et al. (2001) recommended the use of mechanical conditioning to improve the repeatability for uncoated fabrics. Mechanical conditioning involves mounting the fabric in the frame and opening and closing the picture frame close to the complete extension five times. As a result, the yarns become more aligned and parallel to the sides of the frame. For the example results presented in this chapter, all uncoated fabrics were mechanically conditioned. Coated fabrics do not benefit from such

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mechanical conditioning because the coating resists any alignment created by the repeated shearing. If mechanical conditioning is not conducted or significant yarn misalignment remains, the misalignment can result in large increases in the shear load, owing to yarns being loaded in tension instead of pure shear (Chen et al., 2001). This tends to cause poor repeatability at higher shear angles. The mechanical conditioning also tends to reduce the amount of pre-tensioning in the fabric by balancing the in-plane tension along sections of the frame. Such pre-tensioning is only desirable when purposely defined as part of the test condition, and must be taken into account in the analysis of the shear results. In-plane tension has been shown to increase shear loads and reduce the onset of wrinkling. The tension increases the friction at the crossovers, thus increasing the slope of the initial part of the curve.

Analysis of the shear frame geometry (Fig. 3.9) is used to determine the shear load and shear angle. The fabric shear angle ($\theta$), which is defined as the angle through which the fabric has been sheared, is defined in Equation [3.1]. Thus, $\theta$ starts at $0^\circ$ and increases as the trellis frame deforms (Liu, 2005).

$$
\theta = \frac{\pi}{2} - 2 \cos^{-1} \left( \frac{\delta_a + \sqrt{2}}{2L_f} \right)
$$

[3.1]

where: $\delta_a =$ cross-head displacement, $L_f =$ length of one side of the frame, and $\theta =$ Shear angle.
The shear load can be calculated from the cross-head load as shown in Equation [3.2] and Fig. 3.10 (Liu, 2005).

\[ F_s = \frac{F_{\text{cross-head}}}{2L_a / L_a \cos \theta} \]  

[3.2]

where: \( F_s \) = shear force, \( F_{\text{cross-head}} \) = cross-head force, and \( L_a \) = length of one side of multiplier linkage. Note that in trellis frames with different loading rate multiplier linkages, the equations for displacement and force need to be adjusted accordingly.

### 3.2.4 Tear testing

As with tensile tests, there are several different ASTM methods for tear testing, including the trapezoidal (ASTM D5587), Elmendorf (ASTM 1424), and trouser tear (ASTM 2261) tests. Figure 3.11 shows a trouser tear setup according to ASTM method D2261-07a. The middle of the sample width is precut for a controlled tear path that causes the tear to propagate across the desired yarn direction. Each ‘leg’ of the specimen is then clamped in either the top or bottom grips and a load versus displacement response is obtained. As a modification to test loose uncoated fabrics under a constrained condition, both longitudinal sides of the test strips (away from
the tear-affected del zone) can be coated to prevent the yarns from moving and breaking at the edges of the grips, shown in Fig. 3.11(b).

Figure 3.12 illustrates a typical trouser tear curve measured using a 1000 N load cell, and a cross-head speed of 50 mm/min. From this curve several parameters may be obtained. The initiation load is taken as the mean of the maxima of the load peaks, representing the load required for
propagation of the tear. The arrest load is taken as the mean of minima in the curve, revealing the load where the crack stops propagating. The stiffness is taken as the average of the slopes from each minimum to maximum in the tear curve. The number of yarns per peak, which shows the average number of yarns ruptured at once, can be calculated for steady-state tear propagation, from the number of peaks for a given cross-head displacement divided into the warp yarn count for the fabric.

3.2.5 Fabric deformation measurements using 3D image correlation

An additional measurement capability that can enhance a broad range of mechanical testing is a full-field optical technique or three-dimensional (3D) image correlation technology (Schmidt and Tyson, 2003; Schmidt et al., 2005), such as the ARAMIS 3D image correlation system (Trilion Optical Test Systems, Plymouth Meeting, PA). In this non-contacting method, the fabric is viewed by a pair of high resolution digital charge-coupled device (CCD) cameras that are a known distance from each other. A random pattern with good contrast is applied to the fabric surface, e.g., black spray paint on a light fabric. After a calibration procedure, consecutive images are divided into facets and analyzed. Using principles of photogrammetry, the center of each facet is defined as a measurement point and is tracked through each digital image with sub-pixel accuracy. Depending on the resolution of the cameras and the field of view, the image correlation system is capable of in-plane and out-of-plane resolutions in the single microns. The results are the 3D shape of the fabric and the 3D displacements that can be used to define strain, velocity, and acceleration.

Figure 3.13 shows an example of the contrast pattern and the subsequently measured complex deformation of a coated fabric used for parachutes (Carney, 2006). Note that in this case, data is lost in regions where the camera cannot ‘see’ the contrast pattern, but more complex deformations can be obtained by stitching together images from several sets of cameras.

3.2.6 Microscopy methods

Different microscopy methods may be used to characterize fabric cross-sections to determine coating adhesion, thickness and penetration. Optical microscopes or electron microscopes may be used for characterization. With an optical microscope, an overall image of the sample may be obtained, but a scanning electron microscope (SEM) can provide high resolution, depth of field and chemical composition (Fig. 3.14). For electron microscopy characterization, the fabric is typically cut to about 2 cm × 1 cm (width ×
length), depending on the microscope stubs or sample holders, and non-conductive fabrics can be sputter-coated for 2–3 minutes with palladium/gold (Pd/Au) or carbon to reduce charging of and subsequent damage to the fibers. An example of a sputter coater is the Denton Vacuum DV-502 (Mooresstown, NJ).

Cutting of most coated fabrics can be done easily with a sharp knife or high quality scissors; if cutting creates undesired damage or roughness, microtoming or fracture after subjecting to liquid nitrogen can be used to generate a cleaner surface. One of the challenges of using microscopy to
quantify the yarn cross-sectional shape or undulation is the need to ensure that the specimen has been sectioned precisely orthogonal to the yarn cross-section. Images with distorted fiber cross-sections or fibers that disappear further along their length are indications of an angled cut, which can be misleading for obtaining geometric values.

Coating penetration can be determined qualitatively from the SEM images, and if necessary, energy dispersive X-ray spectroscopy (EDS) can be conducted to determine the chemical composition within a particular region to confirm the presence of coating versus fabric (assuming the coating has at least one chemical component unique from the fabric). Such methods can also be used to identify the presence of contaminants or additives within the coated fabric. While still time-consuming, new methods such as X-ray tomography are being used to obtain 3D images or a series of image slices of the interior of a fabric.

3.3 Materials and experimental setup for parametric studies

Sections 3.4 through 3.6 of this chapter discuss the effect of several key coated fabric parameters – weave pattern, fill yarn size (or warp yarn/fill yarn size ratio), and coating thickness – on the response under two distinct and complex loading conditions – shear and tear. While tensile response along the yarn directions has been well characterized (Chen et al., 1995), shear and tear are two loading conditions that depend heavily on the interaction between the coating and the fabric.

The discussions of shear and tear are informed by the results of extensive experimental studies on three distinct types of coated fabrics: (a) low areal weight polyethylene terephthalate (PET or polyester) airbag fabrics with thin coatings; (b) medium areal weight PET fabrics with thin and thick coatings; and (c) high areal weight glass fabrics with thick coatings. These three coated fabric types are not meant to be comprehensive, but are distinct enough to provide general insight. Details on the test fabrics and the test conditions are provided here for reference (Table 3.1). For example, the fabric label 2CM-4HS-5P stands for double-coated, medium areal weight, 4-harness satin weave with 500 denier fill yarns and polyester fibers.

3.3.1 Materials

*Low areal weight, coated polyethylene terephthalate airbag fabrics*

Because airbag fabrics were originally designed as pillow-type geometries for front-impact, the fabrics are typically balanced weaves (i.e., same yarn size and spacing for warp and weft directions). The coating is also designed
Table 3.1 Fabric IDs used in Chapter 3

<table>
<thead>
<tr>
<th>Fabric type</th>
<th>Areal weight</th>
<th>Coating</th>
<th>Fabric ID&lt;sup&gt;1,2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate (PET) airbag fabrics</td>
<td>Low</td>
<td>Thin</td>
<td>CL-PW-fill yarn size&lt;sup&gt;3&lt;/sup&gt; P</td>
</tr>
<tr>
<td>PET fabrics</td>
<td>Medium</td>
<td>Thin to thick</td>
<td>(U or C)M-PW-fill yarn size P &lt;br&gt;(U or C)M-4HS-fill yarn size P &lt;br&gt;(U or C)M-8HS-fill yarn size P</td>
</tr>
<tr>
<td>Glass fabrics</td>
<td>High</td>
<td>Thick</td>
<td>CH-PW-fill yarn size G</td>
</tr>
</tbody>
</table>

<sup>1</sup> Uncoated or coated and areal weight-weave pattern-fill yarn size and fabric material.<br>
<sup>2</sup> C represents the coated fabric. The coated fabrics might be single, double, triple, or coagulant coated fabrics; therefore, there will be a corresponding 1, 2, 3, or X before the C.<br>
<sup>3</sup> The fill yarn size (denier) is divided by 100 for all of the fabric labels.

Table 3.2 PET airbag fabric properties

<table>
<thead>
<tr>
<th>Fabric ID</th>
<th>Fill yarn size (denier)</th>
<th>Areal weight (g/cm&lt;sup&gt;2&lt;/sup&gt; × 1000)</th>
<th>Yarn spacing* (yarns/cm)</th>
<th>Number of crossovers/cm&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-PW-3P</td>
<td>315</td>
<td>22</td>
<td>23 × 23</td>
<td>460</td>
</tr>
</tbody>
</table>

* Warp × Fill.

to allow rapid unfolding, followed by controlled leakage of the internal gas upon passenger impact to decelerate the forward motion at a rate meant to minimize injury. While several airbag fabrics were studied, results from only one representative fabric will be presented to compare and contrast with the other classes of coated fabrics discussed in this chapter. Table 3.2 lists the properties of this representative airbag fabric.

Medium areal weight, uncoated and neoprene-latex-coated polyethylene terephthalate fabric

Nine different uncoated PET fabrics were fabricated (Prodesco, Inc., Perkasie, PA), with three different weave patterns (Plain Weave (PW), 4-Harness Satin weave (4HS), and 8-Harness Satin weave (8HS)) and three different fill yarn sizes (220, 500, and 1000 denier). The warp yarn size is constant throughout all of the samples (2-ply, 150 denier/ply). Table 3.3 provides the fabric construction and corresponding sample labels for each fabric type. PET fabric and a neoprene latex coating were chosen in this
study due to the ease of obtaining and using these materials and for their general broad use in many coated fabric applications.

The purpose of having these fabrics made was to obtain an improved fundamental understanding of the mechanical response of coated fabrics, by having controlled variations in individual parameters (e.g., fill yarn size) while keeping the other parameters constant (e.g., warp yarn size). Obtaining controlled fabric variations for testing is not always possible, as many parameters are dependent upon one another. For example, it was not practical to keep the fill yarn spacing the same for all three yarns, because either the 220 denier fill yarn fabric would be too loose, or the 1000 denier fill yarn fabric would be too tight. It was decided to keep the 220 and 500 denier fill yarn fabrics at the same yarn count, and have the 1000 denier fill yarn fabrics similar in areal weight to the 500 denier fill yarn fabrics (Table 3.4). Table 3.4 lists all other relevant fabric properties, including the number of crossovers per area. A crossover is defined as the region where the fill yarn crosses over the warp yarn, shown in Fig. 3.1(b).
Neoprene latex or polychloroprene (Heveatex Corporation, Fall River, MA) was chosen as the coating material. Neoprene latex has a wide variety of applications, e.g., coatings and adhesives. Neoprene latex is well suited for coating fabrics due to the high initial strength of the deposited film and its final properties, including heat and ozone resistance, weatherability, oil and chemical resistance, and good tear strength (Franta, 1989). Table 3.5 shows the properties of the water-based neoprene latex used in this parametric study.

The dip-coating process was used for these PET fabrics. Because of the interest in determining the effect of coating on yarn mobility and subsequent shear response, different amounts of coating could easily be obtained by controlling the number of times that the fabric was coated or dipped, and by the use of a coagulant agent. The fabrics were dipped in the latex multiple times: once, twice, or three times without the coagulant agent, or once with the coagulant agent. The coagulant agent enables rapid build up of a thick coating layer, but often results in poor bonding or penetration of the fabric itself. Figure 3.15 shows a single-coat PET fabric being dipped and after the dipping, drying, and curing process was complete.

To determine the properties of the rubber alone, the latex was slowly poured on a glass sheet, where the sides of the glass sheet were supported by raised tape. Then a guide blade was run along the tape border to

<table>
<thead>
<tr>
<th>Table 3.5 Neoprene latex properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content, % 47.8</td>
</tr>
<tr>
<td>pH 11.6</td>
</tr>
<tr>
<td>Viscosity (Brookfield #1 @ 60)(cps)</td>
</tr>
<tr>
<td>As received liquid density (g/cm³) 0.95</td>
</tr>
</tbody>
</table>
obtain uniform and controlled thickness. The sheets were dried at room temperature (RT) for a day, followed by 30 minutes of slow cure in the oven at 60°C. Afterwards the sheets were left at RT for about an hour to cool, and then put back in the oven for complete cure at 120°C for 5 to 15 minutes, with thicker sheets left in the oven for longer times. Figure 3.16 shows a rubber sheet with a thickness of 0.985 cm.

**High areal weight, vinyl ester-coated glass fabrics**

Another type of coated fabric is a much heavier weight fabric used for architectural applications and as pre-impregnated (prepreg) materials for forming of composite structures. Table 3.6 shows the material description for fiberglass fabrics with a thermoset (vinyl ester) coating.

While not comprehensive, the range of coated fabrics and the parametric test results presented in the following sections provides insight into the effect of coating-substrate interaction and provides guidance in selection of base fabrics for coated fabric applications.

![Rubber sheet with thickness of 0.985 cm.](image)

**Table 3.6** Fiber glass fabrics with vinyl ester coating description

<table>
<thead>
<tr>
<th>Fabric ID</th>
<th>Fill yarn size (denier)</th>
<th>Areal weight (g/cm² × 1000)</th>
<th>Yarn spacing (yarns/cm)</th>
<th>Number of crossovers/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH-PW-150G</td>
<td>15</td>
<td>58.3</td>
<td>1.4 × 2</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*Warp × Fill.*
3.4 Effect of weave pattern

3.4.1 Effect of weave pattern on shear behavior of uncoated fabrics

As described in Section 3.1.2, there are many different weave patterns (e.g., plain weave (PW), twill weave (TW), and satin weave (4HS, 8HS)) with different degrees of tightness and with balanced versus unbalanced warp and fill yarns. Both plots in Fig. 3.17 compare the shear behavior of fabrics with the same fill yarn size (220 and 500 denier), but different weave pattern. The warp yarn is 2-ply 150 denier/ply in both cases. The weave pattern affects the rotation of the yarns, with a tighter weave pattern leading to a stiffer fabric and higher shear loads. Because the yarn sizes and spacing are the same, the fabric tightness increases from 8HS to 4HS to PW, with a corresponding increase in shear load. The PW fabrics exhibit the highest shear loads, increasing rapidly beyond 15°. In PW fabrics, the warp and fill yarns have the most undulation, as well as restriction; therefore, there is a very small gap in between the yarns. At an early loading stage, the gap in between the yarns closes quickly and the yarns must undergo compaction or compression for any further rotation. Since compaction loads increase rapidly once the gap closes, the locking angle (i.e., the angle at which the
yarns are no longer able to rotate) is reached at relatively low shear angles for the tight PW. For the 4HS and 8HS with their looser weave patterns, the rapid rise from the locking angle effect does not occur until about 30° and 40°, respectively. The 4HS exhibited a slightly higher shear load because of its tighter weave pattern in comparison with 8HS, but because both fabrics have a very loose structure, there is much less difference between the two satin weaves compared with the PW. Also, as will be discussed in more detail in Section 3.5, the greater fill yarn size leads to higher shear loads.

To better understand the quantitative relationships amongst the weave patterns, the number of crossovers (Table 3.4) within the tested area (182.3 cm²) is examined. The assumption is that the number of crossovers is directly related to the shear load for the fabric. That is, the total shear load is related to the summation of the compaction and the friction at each crossover. To test this assumption, the loads in Fig. 3.17 were normalized with respect to the number of crossovers for each fabric type. If each crossover contributes the same shear resistance, then it would be expected that the curves would collapse onto a single line. Figure 3.18 shows the normalized behavior of the fabrics. All three curves did not collapse completely on one another, although they did get closer, especially at low shear angles (region I). This suggests that in the friction-dominated portion of the shear deformation, the resistance does correlate with the number of cross-

![Graph of normalized behavior of fabrics](image)

**Figure 3.18** Effect of number of crossovers in shear deformation of uncoated fabrics with different weave patterns and the same fill yarn size: (a) 220 denier and (b) 500 denier.
overs. Clearly though, in region II, the normalized curves rise quickly. The higher load was most likely caused by the effect of density of crossovers on the yarn compaction. For the PW fabric, the frequent undulation, shown in Fig. 3.1, forces the yarn to be compacted along almost its entire length. In contrast, for the satin weaves, the crossovers are isolated, with neighboring sections that allow ease of expansion and movement of the fibers when compaction occurs at the local crossover (Liu, 2005). Thus, the satin weaves start to show a sharp increase in load at around 50°, but this is significantly delayed compared with the PW.

3.4.2 Effect of weave pattern on shear behavior of thin-coat fabrics

The rubber sheet shear behavior was studied to get an understanding of the contribution of the rubber in the coated fabric. The rubber sheets were tested with the same procedure as for the PET fabrics. Figure 3.19 shows the curve for the rubber sheet shear deformation had a convex shape towards the load axis, in contrast to the concave shape of the uncoated PET fabrics. The loads were normalized by the thickness. This curve could then be used to generate curves for a rubber sheet of specified thickness, within the range tested, to compare with the shear behavior of the uncoated and coated fabrics of the same specimen size. Figure 3.19 suggests that when

![Shear deformation of six rubber sheets with load normalized by thickness, from 0.20 to 1.45 mm.](image)
the load is normalized by the thickness of the sheet, the curves collapse to a reasonable degree, resulting in an approximate mean curve for normalized rubber shear behavior.

Figure 3.20 shows a comparison of the typical shear responses from an uncoated and a thin-coat 4HS fabric. While the uncoated fabric shear curve is concave, the coated fabric curve starts out convex and then transitions to concave after about 30° (Fig. 3.20). The coating fills the gaps between the yarns and the loads required to deform the coating and fabric far exceed the initial low load needed for shear of the fabric only. The variation in uncoated fabrics was due to the fabric tension and misalignment that play a larger role as the shear deformation increases. For the coated fabrics most of the variation was probably due to slight differences in coating penetration and coating thickness that affect the early shear behavior.

Figure 3.21 shows the behavior of the coated fabric with the same fill yarn size, but different weave pattern. There appear to be two distinct regions in the plot. Region I is dominated by the expected convex rubber sheet behavior within the coated fabric, where the loads are independent of the weave pattern. Beyond roughly 20° (region II), the curves start to diverge and a transition from convex to concave occurs. The concave shape is more typical of uncoated fabric shear behavior. Therefore, after a certain angle the fabric shear loads (i.e., yarn compaction loads near the locking angle) start to play
a more significant role in the overall shear behavior of the coated fabric. For the satin weaves, this involvement of the yarns is observed at much higher shear angles than for the PW.

In addition to the demonstrated effect of weave tightness on shear loads, a second contributing factor in the different inflection points for the PW, 4HS, and 8HS is the amount of coating penetration. Figure 3.22 shows the masses of the uncoated fabric and the rubber coating for each sample type. Note that despite differences in fill yarn denier and fill yarn count that led to differences in uncoated fabric mass, the rubber gained by each fabric

3.21 Comparison of different weave patterns with the same fill yarn size on the PET fabric coated with neoprene latex: (a) 220 denier, (b) 500 denier, and (c) 1000 denier.

3.22 Mass of coating gained by each fabric type.
type is consistent with weave pattern. For example, the PW samples gained the least amount of rubber, while the 8HS samples picked up the most amount of rubber. This appears to be due to the amount of exposed warp yarn surface area.

Scanning electron microscopy (SEM) images of the rubber penetration for the fill yarn (1CM-PW-10P) and the warp yarn (2 ply/150 denier) can been seen in Fig. 3.23. The images indicate that the rubber penetrates and adheres much better to the 2-ply warp yarns. The greater penetration of the rubber in these warp yarns was also supported by yarn pullout and tear test studies (Tao et al., 2005). Long sections of warp yarns are more exposed in the satin weaves than in the plain weaves, leading to the greater coating masses seen in Fig. 3.22. Greater coating penetration in the 8HS and 4HS led to coated fabric behavior in shear that was dominated by the more convex rubber coating behavior. In contrast, the coated PW fabric exhibited an inflection to a concave, more yarn rotation-dominated behavior at a lower shear angle.

In summary, the choice of weave pattern directly affects the degree of undulation and fabric tightness (given the same fill yarn size). The higher undulation and tightness in plain weaves led to yarn-compaction-dominated behavior at lower shear angles and thus a more rapid increase in shear loads than in satin weaves for both uncoated and coated fabrics. A thin coating penetrated the warp yarns more than the fill yarns in these medium areal weight fabrics, and greater coating penetration was seen in the looser satin weaves versus the tighter plain weaves. As a result, the satin weaves exhibited more convex coating-dominated behavior for a greater portion of the shear curve. Thus, if greater formability, shearing, or coating
penetration is desired, looser satin weaves would be a better selection than a tight plain weave.

3.5 Effect of fill yarn size

3.5.1 Effect of fill yarn size on shear behavior of uncoated fabrics

Three specified fill yarn size were considered here, 220, 500, and 1000 denier (Table 3.4). The uncoated fabrics with the same weave pattern but different fill yarn size were compared (Fig. 3.24). If the yarn spacing is held constant, the larger fill yarn size is expected to have higher shear loads and an earlier locking angle. Since the larger yarns have smaller gaps between them, contact at the crossovers would occur sooner, and the compaction and friction would increase more rapidly. For example, in Fig. 3.24, the 500 denier fill yarn fabric (diamond symbols) exhibited a much higher shear load than the 220 denier fill yarn fabric (cross symbols) for both the PW and 4HS fabrics. The 1000 denier fill yarn fabric (triangle symbols), while having much larger yarn sizes, were fabricated with lower yarn spacing. At 16 fill yarns/cm versus 10 fill yarns/cm, the total number of crossovers for the 500 denier fill yarn fabric was a little less than double that for the 1000 denier fill yarn fabric. This plus the larger gaps between the yarns for the ‘10P’

![Graphs showing shear load vs. shear angle for different fill yarn sizes and weave patterns.](image.png)

3.24 Effect of different fill yarn size with the same weave pattern: (a) PW and (b) 4HS. Insert shows an expanded view of 4HS.
fabrics offset the effect of the larger yarn size and resulted in the same or lower loads for the 1000 denier fill yarn fabrics.

In many cases (Chen et al., 2001; Farboodmanesh et al., 2006), wrinkling is observed close to the end of the test, once the yarns ‘lock’ and are no longer able to rotate in response to the loading. For fabrics with small yarn sizes, the resistance to buckling or localized bending is low and wrinkling can occur early in the test.

### 3.5.2 Effect of fill yarn size on shear behavior of thin-coat fabrics

The shear behavior of coated fabrics with the same weave pattern, but different fill yarn denier is shown in Fig. 3.25. In Section 3.5.1, the effect of the weave pattern could be seen in the difference in the shape of the curve and to some extent the shear loads. Here, for the 4HS and 8HS weaves, there is very little effect of fill yarn size on the shape or magnitudes of the shear curves. For the PW fabric, less coating penetration led to greater effect of the fill yarn size.

Since the larger yarns exposed more surface area to the latex during the dip coating, it was expected that the amount of coating on the fabric would increase with larger denier fill yarns. This theory did in fact correlate with the 4HS and 8HS results seen in Fig. 3.26, albeit the mass differences did not appear to be proportional to the increase in fill yarn surface area. In contrast, the PW fabrics show a decrease in coating gain with increasing fill yarn size. These results again support the dominance of the warp yarn in

![Graphs](image_url)
terms of the coating penetration. The PW structure (Fig. 3.1) has each warp yarn being wrapped by the fill yarn, which restricts the exposure of warp yarn to the rubber. Therefore, the amount of coating would decrease with the increase in fill yarn size, since the exposure of warp yarns becomes less. Because the warp yarns are much more exposed in the satin weaves, the total increase in yarn surface area from larger fill yarns is enough to result in a net increase in coating mass.

Therefore, for a given weave pattern, smaller gaps as a result of larger yarns and/or smaller yarn spacing (higher yarn count) lead to higher shear stiffness and less formability. If, however, the fabric has a combination of large yarns and large spacing, these two factors can offset each other.

3.5.3 Effect of fill yarn size on tear behavior of uncoated fabrics

The tear behavior of fabrics is demonstrated using this same series of PW fabrics with three different fill yarn sizes, 220, 500, and 1000 denier corresponding to samples UM-PW-2P, UM-PW-5P, and UM-PW-10P, respectively (Tables 3.3 and 3.4). The warp yarn is a 2-ply, 150 denier yarn. Tear orientation was chosen such that the propagation of the tear was always perpendicular to the weaker warp yarns. The difference in tear behaviors of these three fabrics should be a function of the fill yarn effect on mobility of the warp yarns.

On the application of force to a tear specimen, a fabric structure responds in several ways. First, the longitudinal yarns (fill) held in the grips stretch
and lose their crimp, then the transverse yarns (warp) begin slipping and rotating along the longitudinal yarns at the tear tip to form a triangular opening or the ‘del’ zone, in which there are no longitudinal yarns (Fig. 3.11). As the load increases, the transverse yarns continue to be drawn into the del zone, increasing the size of the del. Adjacent to the del zone there are many crossovers between the fill and warp yarns in a small area. With the increase of the number of crossovers per area, slippage is prevented and the load is progressively transferred to the transverse yarns, which are under tensile loading in what are referred to as ‘pseudo-jaws’. With further increase in the load, eventually some of the transverse (warp) yarns fail, as evidenced by a dramatic drop in the load as the del is broken. The process repeats itself to form a new del, continuing the cycle until the specimen is torn completely.

This analysis of the tear behavior of a fabric structure can be used to first explain how tear path width relates to yarn mobility. Here, as described in Section 3.2.4, tear path width refers to the unconstrained (uncoated) specimen width. Figure 3.27 presents the number of yarns per peak as a function of tear path width for PW specimens with different fill yarn size (220 and 500 denier). As was described in Section 3.2.4, the number of yarns per peak represents the number of yarns ruptured in the del zone for each cycle. Figure 3.27 shows that the number of yarns per peak increases with tear path width until the path width reaches 30 mm, after which the number of yarns per peak remains relatively constant. Therefore, beyond 30 mm, the crossover friction holds the transverse yarns in place such that they are not drawn into the del zone and do not contribute to the tear strength.
Examining the average tear stiffness (average slope of the curves from the minimum to maximum peaks) as a function of various path widths for UM-PW-2P and 5P (Fig. 3.28), a similar plateau occurs at the 30 mm path width. At smaller path widths, the stiffness goes up linearly with increasing path width; this is a result of the increasing number of warp yarns that can be pulled into the del zone, increasing the number of yarns over which the load is distributed. After the path width exceeds 40 mm, the behavior changes. The size of the del zone remained the same, but the longitudinal fill yarns began bunching together against the edge of the coated section. The wider the path width, the more the fill yarns bunched together. The result is also consistent with the yarn compaction in the fabric shear tests (Farboodmanesh et al., 2006). Note that the stiffness for UM-PW-2P does not increase sharply until the number of fill yarns is greater than 100 yarns (>70 mm tear path width). UM-PW-5P has larger gaps between fill yarns, such that the compression of the fill yarns occurs later and at higher fill yarn numbers than for UM-PW-5P.

To understand the effect of fill yarn size on tear response, the initiation and arrest loads are shown in Fig. 3.29. In each plot, the dependent values are plotted against the number of fill yarns in the tear path. Note that 48 fill yarns represent the 30 mm tear path width plateau seen in Figs 3.27 and 3.28 for the 500 denier fill yarn fabric. The initiation loads increase with increasing number of fill yarns in the tear path for each fabric, but the arrest loads remain relatively constant for the 220 and 500 denier fill yarn fabric.

For the 220 and 500 denier fill yarn fabrics, the yarn spacing is the same, so at the same number of fill yarns, the geometry of the del is the same. Thus, the number of warp yarns involved and the tear loads are the same. In contrast, the 1000 denier fill yarn has a spacing of only 10 yarns/
cm versus 16 yarns/cm for the smaller denier fill yarn fabrics. Even if one accounts for this difference in spacing (e.g., by comparing tear loads at 30 vs 48 or 60 vs 96 yarns on the x-axis), the initiation and arrest tear loads are much higher for the looser ‘10P’ weave.

In the tests, it was found that the warp yarns of UM-PW-10P slipped easily because of the lower number of restricting yarn crossovers and lower curvature of the yarns due to their greater width. This slippage resulted in crowding of the warp yarns at the tear tip. Also, it was noted that a wrinkle formed in the fabric ahead of the tear tip, and the degree of wrinkling increased as the tear path width increased. This wrinkle remained at the tear tip, even after rupture of the del zone, allowing for the storage of additional strain energy in the wrinkle. This is one possible reason for the higher arrest load for UM-PW-10P.

### 3.5.4 Effect of fill yarn size on tear behavior of thin-coat fabrics

Table 3.7 reveals the effect of rubber coating on the tear response. Note that the coated fabric result is expected to correspond to the results from...
the uncoated fabrics as the number of fill yarns in the tear path approaches zero. In fact, the initiation loads did correspond well, but the arrest loads for the 200 and 500 denier fill yarn fabrics were much lower than in the controlled tear path width specimens and the number of yarns per peak are much higher (Table 3.7). This suggests that a thin coating on the fabric causes the angle of the del to be small, such that multiple adjacent yarns are at similar strains and fail at once. In contrast, if the angle of the del is large, yarn failure tends to occur one at a time. Note that a thin coating on the largest fill yarn (‘10P’) fabric does not have much effect on the del zone geometry nor on the tear loads.

The results from the tear behavior of uncoated and coated fabrics highlight the critical role of fabric construction. Constrained tear path width tests show the influence of yarn mobility. As the tear path width increases, yarn mobility increases, resulting in a greater value for the initiation loads. By examining fabrics of similar and dissimilar fill yarn count and yarn size, the results support the theory that the tear behavior is dominated by the fill yarn count, i.e., the number of crossovers per area. It has been shown that the fabric tear behavior and del zone reach a steady state condition at a constant number of crossing fill yarns, relatively independent of yarn denier and yarn spacing. Fabric construction and yarn mobility also affects the shape of the del zone and the subsequent number of yarns per peak. With larger yarns and fewer crossovers, a larger angle del zone is created, resulting in individual yarn failure, while for a small angle del zone, multiple yarns fail at once. Stiffness increases with an increase in the tear path width. In the first stage, the increase in the stiffness results from the development of the del zone. In the second stage, when the del zone is fully formed, the stiffness increases exponentially, indicative of bunching and compacting of the fill yarns against the rubber-coated edges. As the coating thickness increases, yarn mobility and compression are constrained, resulting in a lack of del zone development. The tear behavior thus exhibits none of the unique characteristics of uncoated fabric tear.

### Table 3.7 Trouser tear properties of coated fabric

<table>
<thead>
<tr>
<th>Coated fabric</th>
<th>Areal weight ((\times 10^4 \text{ g/mm}^2))</th>
<th>Initiation load (N)</th>
<th>Arrest load (N)</th>
<th>Stiffness (N/mm)</th>
<th>Number of yarns per peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1CM-PW-2P</td>
<td>2.43</td>
<td>49.46</td>
<td>10.35</td>
<td>6.95</td>
<td>4.5</td>
</tr>
<tr>
<td>1CM-PW-5P</td>
<td>2.95</td>
<td>47.07</td>
<td>10.26</td>
<td>6.14</td>
<td>3.9</td>
</tr>
<tr>
<td>1CM-PW-10P</td>
<td>3.20</td>
<td>55.42</td>
<td>43.79</td>
<td>7.57</td>
<td>1.5</td>
</tr>
</tbody>
</table>
3.6 Effect of coating thickness and penetration on shear behavior

The coating penetration and thickness can affect shear behavior of coated fabrics, primarily through restriction of yarn rotation and mobility in shear and tear, as well as through contribution to load-carrying capability. In this section, the effect of coating, i.e., multi-coat and coagulant-coat PET, on fabric shear result is presented (Farboodmanesh et al., 2005).

3.6.1 Double- and triple-coat polyethylene terephthalate fabric shear behavior

Figure 3.30 shows the shear behavior of the medium areal weight PET fabrics, with one, two, or three coating layers and a coagulant-aided coating. Uncoated PET fabric results are also plotted for reference purposes.

Figure 3.30 suggests that the increase in the coating thickness leads to higher shear loads and a delayed transition from convex to concave shape for the double- and triple-coat PET fabrics. The double-coat specimen shows almost a linear shear behavior, but the inflection point can still be
identified at around 30°. The rubber penetration was not quite complete. Therefore, the yarns could rotate somewhat freely at a moderate shear angle and exhibit a fabric-dominated response. It was explained previously that free rotation is the rotation of the yarns, resulting in extension of the fabric without significant tensile loading of the yarns. This behavior causes a low shear stiffness response followed by an increase in the shear stiffness as the yarn rotation becomes more restricted, thus generating a concave shape. As was seen in Section 3.4.2, this transition occurs for single-coat PET fabrics at shear angles of 20°–30°, while for double-coat samples it is delayed to greater than 30°. For the third coat, the rubber had completely penetrated and adhered the yarns together, preventing free rotation of the yarns. As a result, the fabric with three coats shows precisely the same linear behavior as embedded cord networks in rubber; the transition from rubber-dominated to yarn rotation-dominated has been eliminated (Clark, 1964; DeEskinazi and Cembrola, 1984).

Figure 3.31 shows the mass of the coating added to the fabric specimen (196 cm² area) for the single-, double-, and triple-coat sample with 4HS weave pattern. Note the total mass of the coating increases in a fairly linear manner from the first dip to the third dip.

Figure 3.32 shows SEM images of the warp yarn cross-section (2 ply/150 denier) for multi-coat PET fabrics, where the penetration and thickness differences with increasing number of coatings can be seen for sample 4HS-5P. In Fig. 3.32, it is seen that the overall thickness from the first coat to the second coat does not increase as much as the coating mass has
increased. Therefore, it was assumed and confirmed by SEM images that the latex continued to penetrate into the yarns, rather than simply adding to the outer layer. In contrast, by the third dip, a significant layer of rubber has begun to build up on the outer surface of the coated fabric, as well as more coating penetration in between the yarns, where the gaps are completely eliminated, shown in Fig. 3.32(c).

3.6.2 Coagulant-coat polyethylene terephthalate fabrics shear behavior

Figure 3.33 shows the thick layer of rubber sheet that was formed on both sides of the coated specimens with coagulant agent. In addition, Fig. 3.33 clearly shows the lack of rubber penetration in between the yarns. The mass and thickness of these coagulant-induced coatings varied, even though the procedure was kept consistent, but in all cases the mass of the rubber was in the order of three times greater than the regular dip-coated specimens.

It was expected that the coated fabrics with the coagulant agent would have higher shear loads because of the greater rubber thickness on these specimens. Figure 3.34, however, shows that the shear load of the coagulant-coat fabrics was lower than that of the triple-coat fabric. Note that the shapes
of the curves are the same, indicating that the shear behavior is rubber dominated in both cases. The lack of penetration of the coating into the fabric reduces the contribution of the fabric to the load, resulting in a lower load for the fabric coated with the coagulant, despite its greater thickness.

This dependence on mobility of the yarns rather than overall coating thickness is also seen in Fig. 3.35 in the higher areal weight glass fabrics (diamond symbols). The coatings in these materials are heavy, but allow yarn rotation. Hence, the shear resistance is low and the shape of the curve is concave throughout. In contrast, the lightweight airbag fabric (triangle symbols), which had a coating that was well penetrated, exhibited higher shear stiffness and a less concave response.

3.6.3 Effect of coating penetration and thickness on multi-coat polyethylene terephthalate fabrics with different weave pattern but the same fill yarn size

Figure 3.36 shows the mass of the coating for multi-coat specimens for each weave pattern with the same fill yarn size. The rank order amount of coating gained by each fabric type is consistent with weave pattern, i.e., tighter PW samples (PW-5P) gained the least amount of coating, while the looser 8HS samples (8HS-5P) picked up the greatest coating amount.
Shear behavior of coated fabric with different coating thickness.

3.35 Shear behavior of coated fabric with different coating thickness.

Amount of coating gained by multi-coat PET fabrics with different weave pattern (PW, 4HS and 8HS), but the same fill yarn size (500 denier).

3.36 Amount of coating gained by multi-coat PET fabrics with different weave pattern (PW, 4HS and 8HS), but the same fill yarn size (500 denier).

Figure 3.36 also demonstrates the amount of coating gained by the coagulant-coated samples, where regardless of their weave pattern, the amount of coating for all three samples is almost the same (i.e., percentage difference is small) in comparison with the samples coated without the coagulant agent.
3.37 Effect of coating thickness and penetration on shear behavior of coated PET fabrics with the same fill yarn size, but different weave pattern: (a) double-coat, (b) triple-coat, and (c) coagulant-coat.

Figure 3.37 (double- and triple-coat) shows the behavior of the multi-coat PET fabrics with the same fill yarn size but different weave patterns. For single-coat PET fabrics (Fig. 3.24), the transition region from the rubber-dominated to fabric-dominated section occurred at different angles for each weave pattern. For example, the transition angle for PW was less than 20°, whereas for 4HS and 8HS the transition was almost 35°. This difference in behavior is due to the combined effect of the tightness of the PW fabric and the smaller amount of coating gained by the PW, which allowed the fabric to continue to dominate the shear response. In contrast, the transition to the concave fabric-dominated region disappears from the plots in Fig. 3.37 as the coating thickness increases. The rotation of the yarns is more restricted with higher amounts of coating, resulting in a higher shear angle for the transition from region I (rubber-dominated region) to region II (fabric-dominated region). Figure 3.37 shows the transition occurring at nearly the end of the test (~40°) for the double-coat and essentially disappearing for the triple-coat fabrics and coagulant-coat fabrics. Note that between two and three coats, the weave pattern no longer has a significant effect on the shear deformation at lower shear angles. However, at higher shear angles the PW shows higher shear loads.

3.6.4 Effect of coating penetration and thickness on multi-coat polyethylene terephthalate fabrics with different fill yarn size but the same weave pattern

The amount of coating gained by the fabrics was not proportional to the fill yarn size, shown in Fig. 3.38. For these 4HS fabrics, the coating penetration was moderate, and the mass of the coating gained for a given number
of coats was very similar, despite different fill yarn sizes. These results supported the dominance of the warp yarn in terms of the coating penetration. Even though the fill yarn size increased from 220 to 1000 denier, the length of warp yarns exposed to the latex was roughly the same for the same weave pattern. While the larger fill yarns might cover more of the warp yarn surface, the larger gaps left when they undulated over and under the warp yarns offset any difference. Note that the yarn count for samples 4HS-2P and 4HS-5P were the same, but the yarn count was reduced for the sample 4HS-10P.

The shear behavior of 4HS coated fabrics with the same weave pattern, but different fill yarn denier, is shown in Fig. 3.39. Previously in Fig. 3.25(b), the shear load for 4HS-10P with a single coat was slightly higher than the others because of the greater amount of coating. As the coating penetration and the thickness increased with the addition of two and three coats, the shear angle transition occurred at higher shear angles and the convex-to-concave shape of the coated fabric shear behavior was gradually converted to linear behavior.

In general, sample 4HS-10P showed slightly higher shear results, because of the higher amount of rubber penetrated and adhered to the sample compared with samples 4HS-2P and 4HS-5P. The amount of coating gained was almost the same in the specimen with 220 denier and 500 denier fill yarn fabrics, and just slightly higher in the 1000 denier fill yarn fabrics. Also, the effect of coagulant (as explained previously) resulted in coated fabrics with thick coatings that masked the effect of fabric construction, shown in Fig. 3.39(c).
To summarize the results from this section, the coated fabric exhibited a much higher load value than either the rubber or fabric alone. The rubber-reinforced fabric shear response was a combination of that of the two components, where the coating compound first dominated the behavior and then was overtaken by the fabric at higher shear deformation levels. This transition was affected by various fabric and rubber parameters, i.e., the fabric architecture, the amount of coating penetration, and the coating thickness. Therefore, the desired function of these flexible composites can be obtained by considering the effect of each parameter. The uncoated fabric behavior is wholly concave. With the increase in coating thickness and penetration, the shear responses become convex–concave and approach linear behavior similar to that of more rigid fabric-reinforced rubber, shown in Fig. 3.40.

3.39 Effect of coating thickness and penetration on shear behavior of coated PET fabrics with the same weave pattern, but different fill yarn size: (a) double-coat, (b) triple-coat, and (c) coagulant-coat.

3.40 Change in shear responses with increase in coating thickness and penetration of PET fabrics.

To summarize the results from this section, the coated fabric exhibited a much higher load value than either the rubber or fabric alone. The rubber-reinforced fabric shear response was a combination of that of the two components, where the coating compound first dominated the behavior and then was overtaken by the fabric at higher shear deformation levels. This transition was affected by various fabric and rubber parameters, i.e., the fabric architecture, the amount of coating penetration, and the coating thickness. Therefore, the desired function of these flexible composites can be obtained by considering the effect of each parameter. The uncoated fabric behavior is wholly concave. With the increase in coating thickness and penetration, the shear responses become convex–concave and approach linear behavior similar to that of more rigid fabric-reinforced rubber, shown in Fig. 3.40.
3.7 Modeling of coated fabric behavior

3.7.1 Analytical models

Models of coated fabrics typically represent the material as a non-linear elastic or inelastic material or as a visco-elastic material (Minami and Nakahara, 1981; Thomas and Stubbs, 1984; Chou, 1989; Kennedy, 1994). Some models predict the response of a fabric based simply on a rule-of-mixtures type approach. More extensive models have been developed which use classical lamination theory (Chou, 1989) or represent the combination of crimp interchange and elastic behavior based on results from uniaxial tests of the coated fabrics in the principal directions (Testa and Yu, 1987). Some complex geometries have been investigated with finite element models (Argyris et al., 1992; Bridgens et al., 2004a, b).

These existing models of mechanical behavior have primarily focused on predicting response to axial and biaxial loadings of coated woven fabrics. For axial and biaxial loading, the behavior is dominated by the fiber and yarn tensile response. Even with membranes used for inflated structures, where the loading is primarily biaxial, the existence of seams results in a very different local stress distribution. These stresses, combined with the potential weakness of the bond, lead to the common occurrence of seam failures.

Loading off-axis to the fiber direction results in shearing, which involves a more complex interaction of fiber rotation, yarn compression at intersecting points, and flow or straining of the coating. Because of the increased complexity, little research has been conducted on the response under arbitrary loading paths and histories (Chou, 1989). Figure 3.41 compares the behavior of the coated fabric with that of the uncoated fabric (4HS-2P), as well as to the estimated behavior of rubber sheets with the thickness equal to the measured thickness of the coated 4HS-2P. Note the correlation between the shape of the coated fabric and the rubber curves at the lower shear angles, and the correlation between the shape of the coated and uncoated fabric curves at the higher shear angles. A simple rule-of-mixtures additive relationship would make prediction of coated fabric shear behavior simple. In fact, as seen from the curve with triangle markers in Fig. 3.41, the superposition of the shear behaviors of the uncoated fabric and the upper limit rubber sheet was lower than the shear behavior of the coated fabric. Therefore, a more complicated model that considers the interaction of the coating and the yarns is required.

3.7.2 Finite element modeling

The finite element (FE) modeling of coated fabrics remains a challenge. Owing to the high complexity of fabric material behaviors, it is unlikely a
single material model can simulate the material behaviors under various loading conditions. Depending on the purpose of the simulations, the FE models tend to focus on some aspects of the fabric properties more than others. For example, in cloth draping simulations commonly performed for visualization and engineering purposes in the textile industry, the cloth element’s position, velocity and internal strain energy are of most interest (Wu et al., 2003), while in airbag deployment simulations in the automotive safety industry, more attention is paid to fabric deformation and failure.

Two methodologies are available in fabric modeling. The first one is the micro-mechanical approach. The micro-mechanical structures of a fabric are modeled. Coating is modeled as a separate layer of materials. Materials properties of the coating layer, the yarns and their geometrical construction are replicated in the model. Such a micro-mechanical model can precisely describe the elongation and rotation of the fiber yarns, and the fabric’s macro-behaviors, such as the extension and shear deformation, can be output from the model. This type of model is suitable for detailed fabric material property study. But in many engineering applications, it is not practical to simulate millions of yarns and their elongations and relative movements (Jauffres et al., 2009a, b, c).
A homogenization procedure is then established to ‘map’ the micro-mechanical model to a macro-FE model. The macro-mechanical properties of the fabric, such as the effective stiffness matrix, are derived from the micro-mechanical model. The fabric is then modeled as a continuum material in a macro-FE model.

While providing thorough understanding to the fabric behaviors, this approach’s complexity limits its applications in engineering problems. The second approach treats fabrics as engineering composite materials and constructs simplified equations to model the material behaviors. The inputs for such models are often directly from experimental tests. Many commercial FE analysis software packages, such as LS-DYNA, have special material models for fabrics. This approach is discussed in more detail in this section (Peng and Cao, 2005; Jauffres et al., 2009a, b, c).

A fabric FE model has to address the following characteristic behaviors of fabric materials (Boisse et al., 2001a, b; Stein et al., 2004).

The ‘crimp’ effect

During a fabric weaving process warp yarns are typically stretched out in straight lines, then weft yarns are woven across (above and below) the warp yarns. The ‘tightening’ of both warp and weft yarns results in the crimping effects on both directions.

The material properties of a tightly woven fabric are a combination of the axial properties of individual yarns and their interactions. The crimping effects change the fabric stiffness in both tension and shear directions. Under tension loading, the fabric responds to the load by first straightening out the yarns at relatively low loads. The straightening out of yarns will conversely introduce crimping into the cross-yarns, thus shrinking the fabric in the transverse direction.

The crimp interchange phenomenon can generate a Poisson’s ratio much larger than typical continuum materials. The structural behaviors of the yarns, rather than the continuum behaviors of the yarn material, dominate the Poisson’s ratio. Some uniaxial tensile tests report a Poisson’s ratio above 0.8 that have been correlated by optical microscopy. Figure 3.42 illustrates the micro-level calculation of Poisson’s ratio. Figures 3.43 to 3.46 show the measurements of the variables.

At the micro-level, Poisson’s ratio is shown in Equation [3.3]:

\[
Poisson's \ ratio = \frac{\Delta X}{\Delta Y} = \frac{X_1 - X_2}{Y_2 - Y_1} \tag{3.3}
\]

For this fabric, Poisson’s ratio is 0.92 (using Equation 3.3). Such a Poisson’s ratio imposes challenges to the fabric material models in many commercial FE analysis software packages. For example, it is observed that in LS-DYNA...
3.42 Micro-level calculation of Poisson’s ratio.

3.43 Initial state at X direction.

fabric material model *MAT_FABRIC, such a Poisson’s ratio is simply ignored and the default value calculated based on Young’s modulus and orthotropic composite model is used instead (LS-DYNA, 2003).

The ‘lock-up’ angle

Under shear loads, the warp and weft yarns of a fabric typically display a trellis-like movement with little resistance, until the yarn compaction or
3.44 Initial state at Y direction.

3.45 X direction length under loading.

‘lock-up’ angle is reached. The ‘lock-up’ angle is a function of yarn spacing and the geometrical construction of the fabric.

The ‘lock-up’ angle is reflected by a sharp increase in the slope of the shear stress vs shear angle curve. For loosely woven fabrics that undergo small shear deformation, the ‘lock-up’ angle has direct impact on the level of correlation of an FE model. In tightly woven fabrics or coated fabrics, the ‘lock-up’ angles are relatively small and are not conspicuous on the
shear stress vs shear angle curves. Notice that the ‘lock-up’ effects can be more significant in one direction than the other.

The ‘glue’ effects of coating layer

Coating layer is often intended to prevent gas or liquid leakage. But it can effectively enhance the Young’s modulus of the fabric and provide resistance to shear deformation within the small strain range. The coating layer is often not simulated explicitly in FE models. Instead, the macro-material properties of the fabric, with the ‘glue’ effects counted, are input to the standard fabric material models. Because some coating layers can peel off or fail under high stress or high temperature loading conditions, the study of coating layer material properties and behaviors can deepen understanding of coated fabric behaviors, especially their failure criteria.

It is often not practical to perform material property tests on the coating layer alone, but it is safe to treat the coating layer as a thin layer of continuum material with properties derived from its chemical composition.

Strain rate dependency

Some strain rate dependency is observed in fabric behaviors, but not much data is available in the literature. One example of high strain rate loading condition for fabrics is airbag deployment. A tightly folded airbag can fully deploy within 20 ms, reaching a fabric stretch of about 15% or more. This leads to a strain rate in the order of 10/s. Experimental measurements of
Fabric stress vs strain curves under such strain rate are not commonly conducted. The uniaxial tensile tests under various strain rates for some coated airbag fabrics show that the strain rate dependency of these fabrics is not significant. As a result, fabric stress vs strain curves under a quasi-static loading condition is often used for airbag deployment simulations.

Many fabric FE models have the capability to incorporate strain rate effects. They can be specified for the warp and weft axial stiffness using Cowper-Symonds, Johnson Cook or other user-defined functions.

‘Tension-only’ behavior

Fabrics can take only tension load, not compression load. But a pure tension-only material model can lead to numerical instability. Some level of ‘artificial’ compression stiffness is generally added to the material model for numerical purpose. In LS-DYNA, a so-called elastic liner is defined when the ‘no-compression’ option of the material model is invoked. This liner is not used to simulate the coating layer, even though conceptually they seem to share some similarity. The coating layer does not take compression load, and it has the ‘glue’ effects that limit the relative movement of fiber yarns.

Failure criteria and prediction

Fabric failure mechanisms have been studied extensively, but the prediction of fabric failure by FE models remains a challenging task. The failure criteria depend on fabrics and their specific applications. Take the fabric ballistic test as an example. This test simulates fragments impacting fabric barriers in the fuselage wall of a commercial aircraft. It is often used to test the fabric’s energy absorbing and failure behaviors in lightweight barrier systems design. At first, yarns around the fragment rupture in what is called a ‘local failure’ mode. When one yarn fails, the yarns next to the failed one take the load and redistribute themselves. These result in a load drop, but not complete failure of the fabric. Next, yarns distant from the loading site begin to separate. This is called a ‘remote failure’ mode. The load curves actually show a steady increase for this phase. Finally, yarns on the boundaries begin to pull out, resulting in a nearly linear load drop to zero (Simons et al., 2001). Most FE models for engineering applications avoid modeling failure mechanisms explicitly. Instead, the overall response of load vs fabric stretch is prescribed by a function measured from experimental tests. This methodology lacks the ability to predict fabric failure under certain loading conditions that are different from experimental tests. More efforts are undertaken to simulate the fabric failure mechanisms using FE models and predict the failure mode and load.
When a fabric material model is constructed, a few simple validation models are made to verify the performance of the material model. The following three-step material model verification process is recommended.

1. **Verify the uniaxial tensile test results in warp, weft and 45° (bias) directions.** An FE model is set up to simulate the uniaxial tensile tests, with Instron machine loads as inputs and the displacements as outputs or vice versa. The stress and strain can also be output from the FE model. However, since stress and strain are not directly measured in the tests, they are not the primary variables for model correlation. The fabric yarn orientation should be properly defined in the FE model.

   The FE model should give very close results compared with test data in warp and weft directions. The difference between FE modeling results and test data should be within 5%. As easy as it may seem, many fabric models in commercial FE analysis software packages are not able to pass this verification, due to the complex nature of fabric behavior.

   The 45° tensile test or bias extension test is actually a complicated loading case, as discussed in Section 3.2.3. A more relaxed correlation criterion can be used for this loading condition. A 10% to 20% difference is considered acceptable.

2. **Verify the biaxial test results.** Biaxial tests discussed in Section 3.2.2 provide a simple axial-symmetric loading condition. Unlike in uniaxial tensile tests, the boundary of the fabric sample is completely fixed with no free edge in a biaxial test. The fabric sample is loaded in all directions, putting both tensile and shear properties of the fabric material model in play. The load of the biaxial test machine is used as input to the FE model, and the displacement of the test head is the primary output for correlation, or vice versa.

   Figure 3.47 shows the FE model for the cross-shape specimen used for biaxial tests such as that shown in Fig. 3.3. One drawback is that, as a result of the cross-shape of the sample, stress concentration occurs at the four corners. To reduce the effects of stress concentration, only the deformation of the small central area is measured and used for FE model correlation. Variations on the sample shape have been proposed to further mitigate the influence of stress concentration.

   The FE model results of biaxial tests should be fairly close to the test data. A difference around 10% is within acceptable limits for most engineering applications.

3. **Verify the seam or stitch strength if applicable.** In many applications the seams or stitches are designed to be stronger than the fabrics. Failure is not likely to occur on the seams or stitches. Therefore, often not much attention is paid to the modeling of the seams or stitches. They are either
not modeled explicitly, or are modeled as linear or nonlinear connections between two nodes, similar to welds. The strengths of the seams or stitches (load vs deformation curves) can be input into the FE models as characteristic functions. When applicable, the modeling of the seam or stitch strength also needs to be verified. A simple uniaxial tensile test on a sample with a seam or stitches can be modeled and the results compared with test data. A correlation with less than 5–10% difference is adequate for most engineering applications.

The simulation and prediction of coated fabric behaviors are far from a routine task. New fabric models are continuously introduced to clear the hurdles of simulating the ‘crimp’ effects, the ‘glue’ effects of coating layers, the failure criteria and prediction, etc. When used properly and with discretion, FE models are an efficient tool for fabric researches and their engineering applications.

3.8 Summary and sources of further information and advice

Coated fabrics with different fabric architecture, coating penetration and coating thickness have been characterized under shear loading and tear conditions. It was shown that the behavior of coated fabrics is not simply an additive combination of its two components (uncoated fabric and rubber sheet). Rather, the response is sensitive to the yarn mobility, as affected by factors such as the weave pattern, yarn size and spacing, and coating pen-
etration. In general, greater mobility leads to increased formability due to lower initial shear stiffness and greater tear strength due to increased number of yarns in the del zone.

Providing a comprehensive discussion of fabric and coated fabric behavior could easily be the subject of an entire book. The purpose of this chapter is to provide some basic background and a brief presentation of current understanding of more complex mechanical deformation response of uncoated versus coated woven fabrics. For more information on related fabric properties, some current references and sources of information include the following:


### 3.9 References


ASTM 1424-09, ‘Standard test method for tearing strength of fabrics by falling pendulum (Elemendorf-type) apparatus’.

ASTM 2261-07a, ‘Standard test method for tearing strength of fabrics by the tongue (single rip) procedure (constant-rate-of-extension by tensile testing machinery)’.

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ASTM D2261-07a, ‘Standard test method for tear strength of fabrics by the tongue (single tip) procedure (constant-rate-of-extension tensile testing machine)’.
ASTM D5587, ‘Standard test method for tearing strength of fabrics by trapezoid procedure’.


BURESH F M (1962), Nonwoven Fabrics, Reinhold Publication Corporation, NY.


NIEZRECKI C (2009), Personal communication, Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, MA.


cameras’, Proceeding of 2005 SEM Annual Conference and Exposition, Portland, OR.


Testing heat and mass transfer through membranes and coatings for textiles

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Abstract: Smart coatings and membranes are currently flourishing on the market. There is hence an important need to characterize their properties, especially their behaviour in term of heat and mass transfer at different climate conditions. This chapter describes the basic equations used to quantify the heat and mass transfer, the different methods that are used to characterize these transfers. The latter methods are divided in methods to determine the heat transfer, the mass transfer, and combined methods that can be used to simultaneously or separately measure both transfers. This chapter reports on standard methods but also on new promising methods, which are suitable to test the new class of smart coatings and membranes.

Key words: adaptive membranes, characterization of heat and mass transfer, thermal manikin, water tightness, water vapour transmission rate.

4.1 Introduction: basic equations of heat and mass transfer

The thermodynamic processes of heat and mass transfer occurring in porous layers are very complex. Physical quantities such as heat conductivity or heat capacity can be determined, or a defined state of the material can be analysed at a precise time, and the thermal or the water vapour transport can be assessed in steady-state conditions. However, the analysis of coupled heat and moisture transfer remains very difficult and there exist only a few methods to assess these coupled processes. An exact description of all the processes would imply that all interactions and all physical quantities in the material would be known at any time.

The transient heat and mass transport in a material are both described with continuity equations. For the heat:

\[ \frac{\partial \rho \dot{q}}{\partial t} + \text{div} \vec{q} = 0 \] [4.1]
with \( \rho_0 = \lim_{\Delta V \to 0} \frac{\Delta Q}{\Delta V} \) (heat quantity \( \Delta Q \) contained in a volume \( \Delta V \))

\[ \dot{q} = -\lambda \nabla T \] (heat flux density)

\( \lambda \): thermal conductivity (W/m K)

For the moisture:

\[ \frac{\partial \rho_G}{\partial t} + \text{div} \vec{g} = 0 \]  \[4.2\]

with \( \rho_G = \lim_{\Delta V \to 0} \frac{\Delta M_G}{\Delta V} \) (moisture quantity \( \Delta M_G \) contained in a volume \( \Delta V \))

\[ \vec{g} = -D \nabla (c) \] (diffusion flux density)

\( D \): diffusion constant (m\(^2\)/s)

These can be rewritten as the following differential equations:

\[ \rho \cdot c_k \cdot \frac{\partial T}{\partial t} = \lambda \Delta T + q_c \]  \[4.3\]

\[ \frac{\partial m_G}{\partial t} = D \Delta c \]  \[4.4\]

With \( q_c \): quantity of heat released per unit of volume and time by condensation or absorption

\( c_k \): heat capacity of the body (J/kg K)

\( \rho \): density of the body (kg/m\(^3\))

\( m_G \): amount of moisture per unit of volume

These equations are very complex as they depend on the three space coordinates as well as time. Therefore, they are usually simplified into one-dimensional or steady-state equations. The heat and mass transfer in materials is usually assessed according to these simplified equations, often neglecting the coupled processes such as mass condensation or evaporation.

### 4.1.1 Dry heat transfer

Dry heat transfer through porous materials is composed of heat conduction through the bulk material and the air trapped in between, (free or forced) convection in the borderline outer surface environment, and radiation.

**Heat conduction**

The one-dimensional, steady-state heat conduction in a plane material (thickness \( dx \), temperature difference between both surfaces \( dT \)) is given by Fourier’s law:
\[ q = -\lambda \frac{dT}{dx} \quad [4.5] \]

with \( \lambda \): thermal conductivity (W/mK).

A thermal resistance can be defined (after integration using Fourier’s law) for a material with thickness \( x \):

\[ R = \frac{x}{\lambda} \quad [4.6] \]

**Convection**

Convection is the heat transfer mechanism that occurs in a fluid as its movement transports energy. There is a differentiation between free convection occurring because of differences of density in the fluid and forced convection if the flow is due to other forces. If a fluid has a temperature \( T_F \) and is in contact with a solid (temperature: \( T_S \)), the convective heat flow can be described as follows:

\[ q = h(T_S - T_F) \quad [4.7] \]

The quantity \( h \) (W/m\(^2\)K) is known as the convective heat transfer coefficient and is a complex function of the solid properties and the state of flow of the fluid. In an analogy of heat conduction, a thermal resistance can be defined that may be added to other resistances:

\[ R_C = \frac{1}{h} \quad [4.8] \]

**Heat radiation**

Heat radiation is different from heat conduction and convection as it does not require a physical medium for the transport. Furthermore, the temperature dependence is non-linear. If a body (temperature \( T_S \); emissivity \( \varepsilon_S \)) is totally surrounded by another, much bigger surface (temperature \( T_e \)), the Stefan–Boltzmann law is applicable:

\[ q = \varepsilon \sigma (T_S^4 - T_e^4) \quad [4.9] \]

with \( \sigma = 5.67 \times 10^{-8} \) W/m\(^2\)K\(^4\)

In analogy to the two other heat transport types, Equation 4.9 can be written differently:

\[ q = \alpha (T_S - T_e) \quad [4.10] \]

and the thermal radiation resistance
\[ R_s = \frac{1}{\alpha} \]  
with \( \alpha = \varepsilon \sigma (T_s^3 + T_e^2 T_s + T_s^2 T_e + T_e^3) \)  

### 4.1.2 Moisture transfer

Moisture transfer through textile layers occurs through:

- water vapour transport (diffusion) through the pores of the materials and along the surfaces;
- liquid water transport in the pores (capillaries) of the material (wicking effect), in the inside of the material (absorption and migration) and along its surface (adsorption).

**Water vapour diffusion**

Water vapour transport through textile layers is based on diffusion processes. Water vapour flows from the higher water vapour partial pressure to the lower. This diffusion is described by the Fickian law (one dimension):

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \]  
with \( C \): concentration (kg/m³)  
\( D \): diffusion coefficient (m²/s)

After integration of the Fickian law, the water vapour resistance can be defined as:

\[ R_d = \frac{d}{\varphi \cdot D} \]  
with \( d \): length of the diffusion path (m)  
\( \varphi \): latent heat of evaporation of water (J/kg)

**Liquid moisture transfer**

Liquid moisture transfer is a process depending on hydrophilic properties of the material (fibres), the yarn, the fabrication process of the fabric as well as the finish and combination of different layers. A differentiation between wetting and wicking can be made. Wetting describes the replacement of a solid–air interface with a solid–liquid interface. Wicking is defined as the transport of a liquid into a textile by capillary action. Capillary forces are caused by spontaneous wetting.
The hydrophilicity of a textile is very important for the wickability, as it dominates the equilibrium contact angle, but the size of the pores also influences the wicking effects.

The liquid moisture transfer gets more complex as soon as different textile layers are combined to a clothing system. Layer to layer wicking is only possible if in one layer a threshold amount of moisture is reached (Spencer-Smith, 1977; Adler and Walsh, 1984; Crow and Osczevski, 1998). This amount depends on the kind of fabrics and starts at about 30% above regain (Adler and Walsh, 1984).

**Liquid moisture transfer**

Evaporation from a liquid surface takes place as long as the water vapour partial pressure is smaller than the saturation pressure at the same temperature. As soon as the partial pressure reaches the saturation pressure, condensation starts.

Evaporation from a completely wetted textile into air is assumed to equal the evaporation of a liquid surface with the same area into air and is defined by the Hertz–Knudsen equation:

$$m_{\text{evap}} = E \sqrt{\frac{W_{\text{H}_2\text{O}}}{2\pi R}} \left[ \frac{p_{\text{sat}}(T_{\text{surf}})}{\sqrt{T_{\text{surf}}}} - \frac{p_{\text{amb}}}{\sqrt{T_{\text{amb}}}} \right]$$  \[4.14\]

with $m_{\text{evap}}$: evaporative mass flux (kg/m² s)

$T_{\text{surf}}$: temperature at the liquid surface (K)

$T_{\text{amb}}$: ambient temperature (K)

$p_{\text{sat}}(T_{\text{surf}})$: saturation pressure at the liquid surface (mbar)

$p_{\text{amb}}$: ambient partial pressure of water vapour (mbar)

$R$: universal gas constant (J/mol K)

$W_{\text{H}_2\text{O}}$: molecular weight of water vapour (g/mol)

$E$: evaporation coefficient

**Heat of evaporation/condensation**

Heat and mass transfer are linked by the heat released during evaporation, which is given by:

$$\Delta Q_{\text{evap}} = \varphi_{\text{evap}} m_{\text{evap}}$$  \[4.15\]

with $\Delta Q_{\text{evap}}$: heat released during evaporation (W/m²)

$\varphi_{\text{evap}}$: latent heat of evaporation (J/kg)
4.2 Testing heat transfer

4.2.1 Measurement of the thermal resistance and thermal transmission

The measurement of the thermal resistance with the sweating guarded hot plate according to ISO 11092 assesses the intrinsic resistance of the specimen plus a transition resistance from fabric to air. This transition resistance is dependent on the convective and the radiant heat loss from the surface of the fabric to the atmosphere. If a fabric is worn as an undergarment, there will usually be no convection and only limited radiation between the layers. Spencer-Smith (1977) showed that internal convection between layers can be neglected if the air layer is smaller than 8 mm. Furthermore, as long as the fibre content in a fabric is higher than 9%, only thermal conduction needs to be considered within the fabric (Woo et al., 1994). It is therefore only important to assess the thermal conductivity for fabrics used as undergarments. ISO 5085-1 (1989) and ISO 5085-2 (1990) provide a method to determine the thermal resistance of fabrics. The specimen is placed on a heating plate and covered by a cold plate with a defined pressure. The principle is that the temperature drop across the heating plate of known thermal resistance is assessed as well as the temperature on the surface of the cold plate. The thermal resistance of the specimen can then be calculated from these figures. The SI unit of the thermal resistance is m²K/W, but a widely used unit is the ‘tog’ (1 tog = 0.1 m²K/W). Another unit used to quantify the overall thermal insulation of garments is the ‘clo’ defined by Gagge et al. (1941). One ‘clo’ is equivalent to the insulation required to keep a seated subject comfortable at an air temperature of 21°C with an air movement of 0.1 m/s, which corresponds to the insulation provided by an ordinary dress suit.

The new standard (ASTM D7024, 2004) describes a method to determine the overall (dynamic) thermal transmission coefficient of textile fabrics and measure the amount of latent energy in textiles. This method was developed to assess the thermal efficiency of phase change materials (PCM), which provide a temperature-regulating function by absorbing or releasing energy through aggregate state changes. It allows the measurement of the steady-state thermal resistance of a fabric as well as the determination of a ‘temperature-regulating factor’ (TRF). The TRF is used to compare fabrics that store or release energy.

4.2.2 Sweating guarded hot plate

The thermal insulation and the water vapour resistance of one or several textile layers can be assessed with the skin model (sweating guarded hot
plate (ISO 11092, 1999/EN 31092)). The skin model consists of an electrically heated plate, which is located in a climatic chamber. Square samples are put on the plate, and air at a defined temperature, relative humidity and velocity (1 m/s) is blown tangentially from a fan over the sample. The plate is heated to 35°C and the measuring surface is surrounded by a guard that is heated to the same temperature in order to avoid any heat loss.

The thermal resistance $R_{ct}$ (m²K/W) is assessed from the supplied steady-state heating power ($Q$), the temperature difference between the air in the wind channel ($T_a = 20\, ^\circ C$) and the skin model ($T_s$) and the size of the measuring surface ($A$):

$$R_{ct} = A \left( \frac{T_s - T_a}{Q} \right)$$  \[4.16\]

4.2.3 Cylinder

Electrical heated cylinder models exist since several decades (Meinander, 1992) and are used to measure heat transfer and in some cases also mass transfer. The results given by the measurement with the cylinders are different from the results given by the hot plate method owing to their different geometries. At lower wind magnitude, the total heat transfer is reduced due to a ‘chimney effect’ because the air is ascending from the lower to the upper part of the cylinder. The shape of the cylinder is closer to human shapes and hence a lower amount of energy is released than when using a flat plate calorimeter. The thermal resistance $R_{ct}$ (m²K/W) is calculated taking into account the heating power of the cylinder, the surface of the tested material, and the temperature difference between the cylinder surface and the surrounding air.

4.3 Testing mass transfer

4.3.1 Measurement of the liquid water permeation

The water-tightness of rain-protection materials is usually assessed with the hydrostatic pressure (water column) method according to ISO 811. Owing to its simple application and good reproducibility, this method is extremely popular. Nevertheless, it does raise some critical questions when it is considered more closely. Is it justifiable to select a method merely on the basis of its good reproducibility and relatively simple application? How does this method work in practice and how relevant are the results for real applications in the clothing field?

The water-tightness of fabrics can be tested in various ways:

- Hydrostatic head (EN 20811).
- Bundesmann (EN 29865).
• Centrifugal test (water-tightness under the influence of wind).
• Rain shower test (EN 14360).

**Hydrostatic pressure (ISO 811)**

The specimen is submitted to increasing hydrostatic pressure. When the third drop penetrates the specimen (drops on the edges are excluded), the actual height of the hydrostatic pressure is read and the test terminated. According to ISO 811, materials with a hydrostatic head of more than 150 cm can be designated, in general, as rainproof. In the marketing field, however, the manufacturers of rain-protection materials outbid each other with hydrostatic heads of 80 m and more even though the materials are stressed with a static water pressure of only 2–3 mm in use. The major drawback of this method is that rain is a dynamic and not a static process.

**Bundesmann rain-shower test (ISO 9865)**

The material sample is subjected to drops of water of 5 mm diameter falling from a height of about 150 cm. After a period of rain lasting 60 minutes, the amount of water that has penetrated the sample is collected in a dish and weighed. At the end of the test, the repellent effect of the material can be determined through the visual inspection of the sample.

Unfortunately, the Bundesmann test (ISO 9865) has some weak points. In particular, so-called ‘breathable’ materials appear to be permeable to water. However, water does not penetrate the material, but is conducted by capillary forces around the edge of the sample to the collecting dish. To overcome this wicking effect, EMPA has developed a new sample-clamping device for the Bundesmann apparatus, which prevents the water from being transported around the sample to the inside of the collecting dish. Comparative measurements have shown that water enters via the sample edge in more than 50% of the 36 tested samples. With the new clamping device, these samples have been absolutely watertight.

**Rain test with high impact velocity of the water drops**

There are numerous applications where raindrops are projected onto a garment at a high velocity, e.g. by riding a motorcycle or strong winds. These are highly dynamic processes and have to be considered differently. A new apparatus (see Fig. 4.1) has been developed in which a sample is mounted on a moving arm turning at a peripheral speed that can be varied between 0 and 145 km/h. This apparatus is placed in the rain tower and subjected to rainfall from a height of over 10 m. The water penetrating the sample is absorbed by blotting paper, which is weighed prior to and after the test.
This apparatus is designed especially for the testing of motorcycle clothing, cycling apparel or mountaineering clothing.

Materials which have a hydrostatic head of more than 20 metres can be damaged by the raindrops having a velocity of 65 km/h, resulting in loss of water-tightness. On the other hand, materials have been tested with a hydrostatic head of 30 cm, and remained absolutely watertight when they were subjected to velocities of more than 130 km/h in this test. With certain types of material, there is a tendency towards increased water penetration at higher velocities of projection, even though the material remains intact.

Rain test on jackets (rain-shower test according to EN 14360)

The water-tightness of jackets can be assessed with an anatomically formed and jointed manikin as shown in Figs. 4.2 and 4.3. It is dressed with the jackets to be tested and exposed to an artificial rain in a rain tower. Twenty-two conductivity sensors are arranged over the upper extremity of the manikin. The system is exposed to an artificial rain for a specified time and the conductivity sensors register where and when water penetrates through the jacket.

Cotton underwear is put on the manikin underneath the jacket. The water absorbed by the underwear changes the electrical conductivity, and is registered as water penetration by the sensors. Furthermore, on completion of the measurement (i.e., normally after a rain for one hour), the wet area of the underwear is assessed visually. The jacket is then rated from 1 to 5, depending on the size of the wet area. Three jackets per type are measured,
4.2 The ‘James’ manikin developed at EMPA with the distribution of the 22 sensors (sensors 3, 4, 6 and 7 indicate moisture).

4.3 The original EMPA rain tower with one of the ‘James’ manikins.
and the mean value of the wet area is indicated so that the result is not only valid for the measured jacket, but will also enable a number of conclusions to be drawn for each respective type. Damage of the materials are sometimes observed.

The weather-protection clothing on the manikin is subjected to a cloudburst of rain: 2000 ‘drop-formers’ create a shower of rain equal to 450 l/m²h over an area of 2 m². The raindrops fall onto the sample from a height of 10 m, and correspond in quantity and drop size (diameter about 5 mm) to those of the Bundesmann rain shower test according to EN 29865. However, in contrast to the Bundesmann test, the raindrops show similar dynamics as in real life thanks to the higher fall height. In fact, the velocity of the drops in real weather depends on their diameter, at about 2 to 9 m/s. The drops created in the rain tower correspond to the upper limit.

Any test using this form of rain is very stringent, and only the best jackets remain watertight. Two other types of rain have been developed to be able to assess not only watertight, but also water-repellent jackets. These precipitations in the rain tower simulate steady rain and drizzles. In order to perform the test, rainfalls of 100 and 40 l/m²h respectively are created – rainfalls are thus very high in all cases. The raindrops have a diameter of about 1 mm in the case of the steady rain, and 0.5 mm in the case of the drizzle, which is close to real conditions where raindrops have a diameter of 0.5 to 5 mm. Raindrops in a drizzle have a diameter of 0.1 to 0.5 mm. In the case of these two forms of precipitation in the rain tower, the drops fall from a height of 3 m. Thus with steady rain they reach a velocity of about 2 m/s.

Only tests using the manikin can determine if the jacket is sufficiently watertight. According to the tests in the rain tower, the most frequent weak points of jackets are:

- seams (collar seams, hood attachment seam, zip-fastener seam);
- ventilation openings;
- wicking of the lining at the hem and the lower end of the sleeves;
- draw-strings;
- pockets;
- hood.

The intensity of the rain and the time factor, i.e. how long a person can remain outdoors under a specific rain intensity, have a decisive influence on the choice of the rain-protection material for a particular activity.

4.3.2 Measurement of the water vapour transmission rate

The water vapour transmission rate (WVTR) is frequently measured by means of a ‘cup’ method (ASTM E96 E, DIN 53122, ISO/WD
(106) or with the skin model according to ISO 11092. These methods are used for quality control of the surface materials but are of limited use to predict the overall water vapour permeability of a ready-made garment.

With light physical activity, the small amount of moisture produced by the body evaporates in the perspiratory glands, and is eliminated more or less as water vapour through the first layers of clothing. At lower temperatures, part of this water vapour may condense in the outer layers of clothing. In the case of intense physical activity, the wearer will inevitably perspire mainly in the form of liquid moisture to be able to dissipate the large quantities of heat (up to about 700 Wh per liter of sweat evaporated) efficiently. The evaporative heat loss prevents an excessive increase in body temperature. However, where the sweat evaporates is important. If it evaporates near the skin (e.g. in underwear), the thermal energy will be extracted from the body but if the liquid sweat is transported to outer layers and evaporates there, part of the evaporative cooling efficiency will be lost. Depending on the application, garment combinations that cool to greater or lesser extents can thus be designed.

In the case of excessive body heat loss, when for instance the insulation of the clothing is too low, the moisture should not contribute to a further heat loss. At the end of a strenuous activity, the sweat produced should be transported quickly in a liquid state to the next layers to avoid a post-exercise chill of the body. On the other hand, in the case of body heat gain, the liquid sweat secreted by the body should be evaporated efficiently and near the body to maximize the evaporative heat loss. The better the evaporative cooling, the less the body has to perspire.

There are a large variety of methods to measure the WVTR of fabrics, i.e. the quantity of water vapour that goes through the fabrics for a given surface and a given time thanks to a water vapour partial pressure difference. These test methods are either isothermal or non-isothermal measurements. Most of the techniques are based on gravimetric measurements, and a few of them are based on optical and thermal measurements. It is difficult to compare the results even between standard methods since the methods are not operated under the same conditions. For instance the temperature, the relative humidity and the ventilation of the samples can be different depending on the measurement method. Furthermore, the physical properties of the fabrics, including the WVTR, also depend on the temperature and the relative humidity during the testing (Gretton et al., 1998). Some polymers constituting the membrane or coating have a glass transition temperature ($T_g$) which can be below or above the temperature of the test and may affect their permeability. Additionally, hydrophilic materials display a dependency of the WVTR upon the humidity conditions (Farnworth et al., 1990).
‘Cup method’ is a denomination for gravimetric measurements performed on textiles, films, membranes or coatings, which are sealed on cups filled with water or a desiccant and placed in an environmental climatic chamber. The water vapour transmission takes place from the inside of the cup to the climatic chamber if the cup is filled with water, whereas the contrary is observed if the cup is filled with the desiccant. Among these cup methods, the most common ones are the ASTM E96 and the ISO 15496 methods.

The samples to be measured with the ASTM E96 are placed on vessels (cups) filled with pure water, letting an air gap between the water surface and the sample, and subsequently sealed on the cup. The cups are then placed in a climatic chamber with controlled relative humidity and temperature and are periodically weighted. The WVTR is calculated directly from the weight loss of the water in the cup divided by the interval of time of this weight loss and the surface of the sample. ASTM E96 comprises three variants described as ASTM E96 A (or desiccant method), B (or upright cup method) and ASTM E96 BW (or inversed cup method), depending on the orientation of the cup in the climatic chamber. The ASTM E96 BW method is obviously reserved for the characterization of waterproof materials, as the material is in direct contact with water. It is strongly recommended to operate the ASTM E96 when the air flow in the climatic chamber is homogeneous since there could be some disparities of the relative humidity sensed by the cups depending on their location in the chamber. It is also possible to have a rotary plate that allows the cups to receive the same air flow on average.

Hu et al. (2001) discussed the pertinence of ASTM E96 for films with a very high permeability, i.e. higher than $10000 \text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. They found that the measurements performed with ASTM E96 underestimated the permeability of these films. Owing to the very high permeability of these films, the relative humidity in the cup has much lower values than the 100% as shown in Fig. 4.4.

Nguyen et al. (2001) observed the same discrepancy for the determination of the WVTR of very permeable films with ASTM E96 owing to the resistance of the air layer near the film. They used a pervaporation technique where the vessel is inverted, i.e. where the sample is sandwiched between two chambers and the liquid water is on the upper chamber, and vacuum was applied on the downstream chamber while the liquid in the upper chamber was stirred. Accordingly to the authors, the set-up reduces the resistances of the air layer and the values of the WVTR were much higher.

We recently developed a modification to the ASTM E96 method in order to measure water vapour transmission rate in the presence of different...
4.4 Distribution of the relative humidity in the cup for films with (a) low WVTR, (b) high WVTR, (c) open cup without sample (Hu et al., 2001).
humidity gradients (Crespy et al., 2008a). The conventional ASTM E96 technique only allows the gradient of relative humidity to be around 50%. Moreover, even if it is possible to vary the relative humidity of the climatic chamber, the relative humidity in the cup cannot be changed. Since the measured relative humidity inside the cup for typical textiles is almost 100%, it corresponds in reality only to situations where the wearer sweats severely. In normal conditions, the relative humidity is much below this value as stated before. We varied the relative humidity inside the cups through using aqueous solutions saturated with inorganic salts. The cups filled with the saturated solutions display different relative humidities depending on the nature of the salt. It is then possible to measure directly the influence of the relative humidity on the WVTR with this simple method.

The ISO 15496 method, which is derived from JIS L 1099 B2, is also commonly used to determine the WVTR of textiles and membranes, especially since the values of water vapour permeability obtained with this technique are very high. Note that ISO 15496 is operated in isothermal conditions, i.e. at 23°C, whereas the air and water temperatures for JIS L 1099 B2 are 23 and 30°C respectively. The values of WVTR given by ISO 15496 are high owing to the large difference of relative humidity that drives the water vapour transmission compared with other methods (ΔRH ~ 67%). In fact, the sample to be tested is sandwiched between two microporous Teflon films, one being in contact with water and the other in contact with a saturated solution of potassium acetate as shown in Fig. 4.5.

Another gravimetric isothermal method was developed to measure the WVTR of porous membranes (Schmidt et al., 2005). The sample is continuously submitted to a tangent flow of dried air, leading to a
relative humidity difference of almost 100% between the two sides of the membrane.

Non-gravimetric isothermal methods can also be used to determine the water vapour transmission rate of membranes and coatings. Thus, the WVTR of polymer membranes and coated materials can be measured with an infrared sensor with ASTM F1249. The membrane or film to be characterized separates two distinctive chambers. A wet nitrogen gas flow is applied in one chamber, whereas a dry nitrogen flow is applied to the other one. An infrared sensor analyses the content of water vapour that permeated through the membranes.

A quick test method for the determination of the water vapour diffusion resistance properties of polymer membranes was introduced recently by Huang (2007b). The measurement time is only 5 min and the test requires small samples (10 cm × 4 cm). The water vapour diffusion resistance is calculated by determination of the concentration of water vapour by a humidity sensor.

Non-isothermal measurements

The methods cited above are performed only in static conditions, i.e. without significant evolution of the temperature and relative humidity with time. As stated before, this situation does not correspond to what is observed in practice, especially for sports applications. In fact, during a sports activity the temperature and the relative humidity vary greatly depending on the period of activity (rest or effort) or the intensity of the effort performed.

Finn et al. (2000) proposed a non-isothermal gravimetric method to measure the WVTR of textiles. The fabrics are placed on dishes, and the temperature of the water-filled dishes is controlled with a heating electrical plate. The whole system is placed in a climatic chamber with controlled humidity and temperature. A very similar apparatus was used by Nefzi et al. (2004) to study the effect of the temperature and the humidity gradients on the WVTR of textiles. Both methods are very similar to the cup methods described above.

Gibson et al. (1997) proposed the dynamic permeation cell method to determine both the steady-state and the transient regime of the water vapour permeability for fabrics (see Fig. 4.6). The method is now standardized (ASTM F2298, 2003). Two different mixtures of dry and water-saturated nitrogen streams with controlled temperatures are passed over the top and the bottom surfaces of the cell containing the sample. The WVTR is deduced from the measurements of temperature and relative humidity of the streams. This method is particularly useful since it is possible to regulate humidity and temperature at both faces of the sample, allowing a near real simulation.
The apparatus proposed by Gibson et al. is expensive and its use has not yet become routine. Therefore, we recently developed the double chamber technique, which allows the measurement of the water vapour transmission rate of textiles and membranes placed between two climatic chambers (Crespy et al., 2008b). The two climates can be set independently and therefore the WVTR can be measured in a large range of climatic conditions. The method was developed to assess new commercial membranes claiming to be highly sensitive to environmental stimuli (temperature, relative humidity) and to change their permeability properties depending on the climate. Even plastic membranes from the same class (here polyurethanes) have different climate adaptive properties, i.e. different permeability behaviours depending on the climate.

4.3.3 Protection against chemicals

Protective clothing against chemicals is divided into six categories, depending on their level of protection (gas-tight, liquid-tight, protection against solid particulates). For all these types of clothing, different standards were developed:

- EN 943 for ventilated and non-ventilated ‘gas-tight’ (Type 1) and ‘non-gas-tight’ (Type 2) clothing.
- EN 14605 for liquid-tight (Type 3) or spray-tight (Type 4) clothing.
- EN ISO 13982–1 for protective clothing against solid particulates (Type 5).
- EN 13034 for chemical protective clothing offering limited protection against liquid chemicals (Type 6).

All these standards contain different leakage, permeation or liquid penetration tests, either for the whole garment or for the surface materials. In ISO
6529, the test principle is to place the material to be tested between two chambers or a permeation test cell. The first chamber contains the test chemical, which can be either a liquid or a gas and the second is filled with the collection medium which can also be liquid or in gaseous form. The collection medium is analysed quantitatively for its concentration of the chemical and thus the amount of permeated chemical can be determined as a function of time.

The penetration of liquid chemicals is assessed according to ISO 6530 by placing a material sample onto a gutter that has an inclination of 45°. A piece of blotting paper is placed underneath the sample. A defined amount of liquid chemical (10 ml) is poured onto the sample in a defined time (10 s) from a fixed height from a pipette. The chemical that runs off the sample is gathered in a recipient and 60 s after the beginning of the test, the weight increases of the recipient, the sample and the blotting paper are assessed. The penetration index is then determined as the percentage of the weight increase of the blotting paper divided by the overall weight of the poured liquid.

Other methods to characterize the penetration of chemicals are still under development. In ISO/DIS 17491-3 and 17491-4, a jet-test and a spray-test are being developed which consist of spraying a defined amount of water containing a dye with a pressure of 150 and 300 kPa respectively onto a person wearing the chemical suit. The person wears an absorbing overall underneath and any penetration of the liquid has to be recorded.

### 4.4 Coupled heat and mass transfer testing

#### 4.4.1 The sweating guarded hot plate

The sweating guarded hot plate method (see Section 4.2.1) or skin model is one of the most commonly used techniques to determine the water vapour resistance \( R_{et} \) and/or the thermal insulation (i.e. the thermal resistance \( R_{ct} \)) of fabrics. The method is standardized (ISO 11092, 1999; ASTM F1868), and relatively fast to operate. However, the overall required equipment is relatively expensive. Samples to be measured are placed on a plate heated to 35°C and are submitted to a tangential wind to ensure the homogeneity of the humidity concentration in the air. The plate is kept at the same temperature by a guard that regulates the heat loss as shown in Fig. 4.7. The whole system is placed in a climatic chamber with controlled relative humidity (40%) and temperature (35°C). The porous plate is covered by a waterproof cellophane film permeable to water vapour to prevent wetting the sample, and the measurements are done in isothermal conditions to avoid condensation on the sample. \( R_{et} \) can be calculated with the following equation:

\[
\frac{1}{R_{et}} = \frac{1}{R_{ct}} + \frac{1}{R_{cl}}
\]
where $A$ is the surface of the sample, $p_s$ and $p_a$ the water vapour partial pressure respectively in the skin model and of the surrounding air. $Q$ is the steady state heating power. The water vapour transmission rate is calculated by the following equation:

$$WVTR = \frac{1}{R_{et}} \cdot \frac{\Delta p}{\varphi}(g m^{-2} h^{-1})$$

where $\varphi$ is the latent heat of vaporization of water at the test temperature ($\varphi = 0.672 \text{Wh g}^{-1}$ at $35^\circ \text{C}$), and $\Delta p$ the difference of water vapour pressure.

Huang (2006) reviewed the influence of the different parameters on the measurements with sweating hot plate method. He proposed also that the method could be improved to perform measurements under transient conditions. In fact, he stressed that the human body more often experiences dynamic situations, i.e. dynamic climates near the skin and outside, than static conditions. Therefore, it is more relevant to measure under transient conditions for comfort studies. There is no doubt that the sweating guarded hot plate method will be used in the near future to measure the dynamic water vapour and heat transfer.

Kim et al. (2006) developed a vertical type of skin model with two adjacent climatic chambers. The two climates of the two chambers could be separately controlled. The measured fabrics were first set in a warm climate and then the climate was changed quickly to a cold climate in subzero conditions in order to assess the transient effect of the microclimate variation. The authors studied the influence of the fabrics on the microclimate change in time and the drying out of the simulated sweating (with water).

EMPA developed a similar method to the skin model destined to simulate the sweating around the arm (Weder et al., 1995). The artificial arm is able to move during the measurements of water vapour and thermal...
resistance. Measurements with this technique compared with the skin model showed the importance of forced convection when the arm was moved and condensation effects at low temperatures (Rossi et al., 2004), thus indicating that the measurements with the sweating arm were more useful for the practice.

4.4.2 Sweating torso

A method to simulate the geometry of the human body is to use a cylindrical test device. The heat and moisture transfer are simulated by heating the surface to skin temperature and releasing water through nozzles. Different cylindrical systems were used for heat and mass transfer measurements through fabrics (Lamb, 1992; Anttonen and Oikarinen, 1997).

EMPA also developed a sweating cylinder (‘sweating torso’) (Rossi, 2000; Psikuta et al., 2008) which was taken over by several institutes around the world. As shown in Fig. 4.8, the measurement cylinder consists of an inner aluminium tube with a wall thickness of 30 mm and a polyethylene layer with a thickness of 7 mm, covered by a 0.1 mm polytetrafluoroethylene
(PTFE) foil. This Teflon foil acts as a protective layer. The polyethylene layer is purposefully made to slow the reaction time of the measurement cylinder. These three layers have similar thermal capacities and thermal conductivities to those of the respective layers of the human skin, such as epidermis, dermis and fat tissue. Owing to this combination of materials, transient processes can be modelled. Furthermore, the cylinder can be filled with water to obtain approximately the same heat capacity as the human body. A slow-rotating motor-driven stirrer ensures a homogeneous core temperature in the torso cylinder. It will respond much more slowly and be much heavier when filled with water.

On the upper end of the upright torso sits an aluminium dome, which is thermally separated from the measurement cylinder by an insulating connection flange between. In the same manner, an aluminium cover is fitted to the lower end of the upright torso. The two guards are regulated to the same temperature as the cylinder and have the function of shields to avoid any heat loss axially from the cylinder to the environment via conduction. The lower shield covers all the valves and some of the electronics, while the upper dome allows jackets to be put on the torso conveniently.

4.4.3 Microcomputer tomography

Microcomputer tomography (μCT) can be used to investigate the moisture transport of multilayered textiles under realistic boundary conditions. The dynamics of the moisture transport can be recorded without disturbing an ensemble during measurement. Quantitative moisture measurements for a given layer, and within a layer, can be obtained, including a full, three-dimensional visualization of the lateral moisture distribution. A similarly applicable non-contact method, magnetic resonance imaging (MRI), has been applied to investigate moisture transport in carpets (Leisen and Beckham, 2001). These were mainly one-dimensional studies, although Carr et al. (1998) also made two-dimensional MRI measurements to completely map the transplanar moisture distribution similarly to the visualization in Carr et al. (1998). Samples could be investigated with a resolution of 74 μm in all three dimensions (Weder et al., 2006). The sample was lying on a heating sample holder. In the middle of this holder was a sweat nozzle, which fed 5.5 g water during 36 min to the first layer. To estimate the absorbed water volume per layer, the μCT image data were analysed using a suitable intensity threshold, in order to compare the wet samples with the dry ones.

To illustrate the power of the technique for imaging water content, Fig. 4.9 shows a processed image of the water distribution in one sample. This image was derived from the raw data by subtracting the data of the dry sample. The location of the liquid moisture in Fig. 4.9 can be seen quite
clearly. Although the contributions of the dry wool fibres were removed, the structure of the moisture-containing fibres is readily apparent.

We have established that μCT is capable of rapid, quantitative imaging of water location and transport in complex textile systems. In addition, the moisture transport processes of multilayered materials and their interactions can be studied relatively cost effectively and precisely. The advantages of the μCT method over the traditional gravimetric approach are therefore obvious. With μCT it is possible to scrutinize the structure of the fibre composite and study the transport phenomena under the most diverse conditions. Thus the method enables the development of specific moisture-optimized combinations with unique characteristics.

4.4.4 Thermal and sweating manikins

Thermal manikins for the assessment of thermal insulation of garments have been used since the early 1940s, and probably more than 100 are in use worldwide (Endrusick et al., 2001; Holmer, 2004; Huang, 2007a). Some of these manikins can additionally release moisture or use wetted underwear to assess the evaporative resistance of ensembles (Meinander, 1992; Burke and McGuffin, 2001; Richards and Mattle, 2001; Tamura, 2006; Kar et al., 2007; Li et al., 2007). Several standards have been developed to describe the measurement methods (ISO 15831; ASTM F1291; ASTM
The main advantage of manikin testing is probably the realistic simulation of the heat and moisture transfer from the body through the clothing to the environment. This method provides objective results and the repeatability is usually fairly high provided that the designs of the manikins are similar. In fact, an interlaboratory trial on different sweating manikins showed a relatively high variability among the systems in use (McCullough et al., 2002). Manikins can assess the effects of air layers between the skin and the clothing and, if the limbs are movable, the pumping effects through the fabrics as well as ventilation effects through the garment openings. They are a valuable tool to assess the effects of the clothing design on heat and mass transfer.

4.5 Future trends

There is a cornucopia of documents dealing with the term ‘smart’ in current academic and industrial research and development. However, nobody has yet assessed the amount of smartness of these materials. Indeed it does not appear to be a measurable value and is therefore widely used for marketing and advertising purposes. Smart textiles for instance can be divided in e-textiles and in adaptive or stimuli-responsive textiles. The first category can be measured easily via standard methods whereas the second requires more attention. To assess stimuli-responsive materials, one has to make at least two measurements, i.e. before and after the stimulus, in order to characterize the adaptive character of the material. Thus, in the case of a temperature-adaptive or temperature-responsive water vapour permeability, the water vapour transmission rate will be measured at two different temperatures. Moreover, the industry needs to characterize materials under their conditions of use. Since outdoor tests and tests with human subjects are very expensive and/or usually not reliable because of the lack of subjects, it is a real challenge to develop cheap and quick ‘smart’ methods to evaluate the heat and mass transfer of membranes and coatings. The new generation of testing methods for smart membranes and coatings can be performed in steady state conditions as well as in transient conditions. Novel methods will propose dynamic scenarios such as scenarios for marathon, skiing, raining, etc. under conditions of varying relative humidity and temperature over time. As shown above, some developments are already under way and there is no doubt that the adaptive character of the new materials will be assessed routinely in the near future.

4.6 Conclusions

Many tests are used nowadays to assess the water vapour permeability of membranes and coatings. However, as shown by McCullough et al. (2003),
the standard techniques display different values of WVTR and even the ranking between samples is not comparable. There are some exceptions since the skin model was found to be highly correlated with the JIS L 1099 B2 and the ASTM E96 B was highly correlated with the dynamic moisture permeation cell (DMPC) operated in isothermal conditions as calculated with the Spearman rank order coefficient. Therefore, the most suitable WVTR value for the customer is the one measured near real conditions. The DMPC and the double chamber technique are hence promising methods. However, current methods to evaluate heat and mass transfer still operate under experimental conditions that are trivial compared with real conditions. To assess the feeling of comfort with a certain clothing system is very ambitious. In future, more research is needed to develop more realistic assessments of the complex system (people in their environment).

4.7 Standards


ASTM E96 (2005), Standard Test Methods for Water Vapor Transmission of Materials, ASTM, West Conshohocken, PA

ASTM F1249 (2006), Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor, ASTM, West Conshohocken, PA

ASTM F1291 (1999), Standard Test Method for Measuring the Thermal Insulation of Clothing Using a Heated Manikin, ASTM, West Conshohocken, PA


EN 342 (2004), Protective clothing, Ensembles and garments for protection against cold, CEN European Committee for Standardization, Brussels

EN 943-1 (2002), Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles – Part 1: Performance require-
ments for ventilated and non-ventilated ‘gas-tight’ (Type 1) and ‘non-
gas-tight’ (Type 2) chemical protective suits, CEN European Committee
for Standardization, Brussels
EN 13034 (2005), Protective clothing against liquid chemicals – Perform-
ance requirements for chemical protective suits offering limited protective performance against liquid chemicals (Type 6 equipment), CEN European Committee for Standardization, Brussels
EN 14360 (2004), Regenschutzkleidung: Prüfverfahren für fertige Beklei-
dungsteile – Beaufschlagung von oben mit Tropfen von hoher Energie
EN 14605 (2005), Protective clothing against liquid chemicals – Perform-
ance requirements for clothing with liquid-tight (Type 3) or spray-
tight (Type 4) connections, including items providing protection to parts of the body only, CEN European Committee for Standardization, Brussels
EN20811 (1992), Textiles. Determination of Resistance to Water Penetra-
tion. Bestimmung des Widerstandes gegen Penetration Wasser. Hydro-
static pressure test Hydrostatischer Druck-Test
EN29865 (1993), Textiles. Determination of Water Repellency of Fabrics by the Bundesmann Rain-shower Test
EN ISO 13982-1 (2004), Protective clothing for use against solid particu-
lates – Part 1: Performance requirements for chemical protective clothing providing protection to the full body against airborne solid particulates (Type 5 clothing), CEN European Committee for Standardization, Brussels
ISO 811 (1981), Determination of Resistance of Water Penetration: Hydro-
static Pressure Test, ISO International Organization for Standardization, Geneva, Switzerland
ISO 6529 (2001), Protective clothing – Protection against chemicals – Deter-
mination of resistance of protective clothing materials to permeation by liquids and gases, ISO International Organization for Standardization, Geneva, Switzerland
ISO 6530 (2005), Protective clothing – Protection against liquid chemicals – Test method for resistance of materials to penetration by liquids, ISO International Organization for Standardization, Geneva, Switzerland

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JIS L 1099 B2, Testing Method of Water Vapour Permeability of Textiles

4.8 References


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RICHARDS M and MATTLE N (2001), ‘Development of a sweating agile thermal manikin (SAM)’, Fourth International Meeting on Thermal Manikins, St Gallen, Switzerland.


**Abstract:** Encapsulation is a technique in which a core material is completely enveloped by a membrane or wall material. This chapter begins with discussions of the history, benefits, types, preparation techniques, and release behaviors of microcapsules. The remaining portion of the chapter describes uses and examples of microencapsulation technology in coating, laminates and textiles.

**Key words:** microencapsulation, controlled release, colloids and interfaces, smart textiles, polymer chemistry.

### 5.1 Introduction

The word encapsulate derives from the Latin *en* meaning in and *capsula* meaning a little box. Literally to encapsulate something means putting something in a box. As pointed out by Ghosh (2006) nature is filled with examples of encapsulation, including an egg in a shell, a seed in a coat, and a cell in a cell membrane or wall. An excellent contemporary definition of encapsulation is ‘enclosure in a sheath not normal to the part of the process or the formation of a capsule or a sheath about a structure’ (Taber, 1965). The word microencapsulation literally refers to the encapsulation of particles between 1 to 999 μm \((10^{-6}–10^{-3} \text{ meters})\), although in practice the term is used for particles between nanometers (nm) up through millimeters (mm).

The reason to encapsulate a material is to change the direct interaction of the encapsulated material with its environment. This change usually has to do with the time the material is in direct contact with the environment. The choice of material from which the shell of the capsule is made, the structure of the capsule, and material encapsulated allow three distinct modes of interaction with the environment. The encapsulated materials inside can be kept from directly interacting with their environment altogether, the contents of the capsule can be released all at once or the materials in the capsule can be slowly released over time.

As the capsule size decreases, the ability to spread and place the capsules as well as the control over the encapsulated material increase. This increase
in impact and utility as capsule size decreases has driven the technology toward microcapsules and continues to drive it toward nanocapsules.

5.2 History of microencapsulation

The use of commercial encapsulation and microencapsulation in coatings and laminates can be traced back to work at the National Cash Register Company in the 1930s (Ranney, 1969). This work was directed at carbonless transfer paper. In 1806 an Englishman, Ralph Wedgwood, received a patent for his ‘Stylographic Writer’ which used ‘carbonated paper’ (Adler, 1990). From that point on, copies could be made through the use of interleaved transfer sheets such as carbon paper. As technology progressed it became possible to make copies by simply coating the back of the top sheet with a carbon transfer composition or the equivalent. Improvements were still desired because a sheet coated on the back with an ordinary carbon transfer composition smudged and dirtied the undersheets and the operator’s hands. Moreover since the colored marking materials used for coating were ordinarily of dark appearance, sheets prepared from them were not felt to be attractive. These shortcomings were addressed by the development of rupturable transfer films which contained oily droplets of marking fluid (Green and Sandberg, 1951), these films were not composed of capsules. These transfer films consisted of a continuous film phase of gelled hydrophilic colloid material having fluid droplets of oil dispersed throughout. While these films alleviated some of the above-mentioned difficulties the fluid droplets inside the continuous film could escape through cracks in the film, especially because of the sponge-like texture of the colloid gel film surrounding the voids which held the oil. Cracks in the continuous films may have been caused by folding or rough handling of the material, or even by unusual environmental conditions. In order to eliminate this last difficulty, microencapsulated hydrocolloid transfer films were developed (Green and Scheicher, 1957). In these microencapsulated films cracks formed in the film did not run across the capsules, but around them, so that the oil was not released by random cracks produced in the film.

5.3 General benefits of microencapsulation

The choice to use microencapsulation technology has been expanding in both the number of companies which have chosen it and applications for which it is chosen. Additionally, the advantages of the technology are driving its use across different industries.

Although there are specific benefits for each particular application there are general benefits driving the technology. These general benefits can be gleaned by examining commonalities which arise across diverse
applications such as pesticides, agrochemicals, and drug delivery as well as food, textile, and paper additives. These benefits include the following:

- Controlled, predictable, steady-state release
  - better performance
  - lower costs due to need for less material
- Protection of the internal phase from degradation or evaporation
  - enhanced shelf-life
- Release targeted to a location
- Triggered release
  - time
  - temperature
  - pressure
- Control of odor or taste
  - release
  - absorption
- Improved or faster production capabilities due to ease of handling
- Conversion of liquid to free-flowing solids
- Protection from hazardous materials
  - safety for the user
  - protection of the environment.

5.4 Types of microcapsule

Spherical polymeric particles that range in size from 1 to 999 μm are technically polymer microspheres or microcapsules; however, the terms are often loosely used to describe particles ranging in size from about 50 nm to 10 mm. In the strictest sense microspheres refer to hollow or homogeneous solid polymeric particles (a and b in Fig. 5.1). In normal usage, the terms

![Microcapsules diagram](image)
microcapsules can be either reservoir or monolithic. The reservoir can be mono-nuclear or polynuclear (c and d in Fig. 5.1) while monolithic are a matrix composed of the encapsulated and encapsulating phases (Fig. 5.1).

5.5 Techniques of microencapsulation

Although there seems to be general agreement about techniques available for microencapsulation, there seems to be no agreement on how to categorize the techniques. Three different articles have characterized the techniques as follows:

- **Type of reaction** (Ranney, 1969) – phase separation techniques, interfacial reactions and physical methods.
- **Type of process** (Ghosh, 2006) – chemical processes, physico-chemical, physico-mechanical.
- **Type of encapsulating starting material** (Arshady, 1989) – monomeric starting materials, polymeric starting materials.

Two commercial facilities (Microtek Laboratories, www.microteklabs.com, and Southwest Research Institute, www.swri.org), which provide custom microencapsulation services ranging from R & D programs to large-scale product commercialization, simply characterize the techniques as chemical or physical. This seems the simplest way to break the techniques up, with the caveat that some physical methods rely on a chemical reaction and some chemical methods rely on physical events. The techniques in the above references and commercial facilities characterized as chemical or physical methods are included as Table 5.1. Particle size ranges for some of the commercially available materials are included.

The physicochemical steps in the microencapsulation process vary to some degree, based on what technique is being used (Arshady, 1989, 1990a,b; Thies, 1975). In the broadest sense the microencapsulation process involves three general steps.

1. **Capsule formation** – in some fashion getting the material which is to be the capsule outer wall to envelope the material that will be encapsulated (phase separation, spraying, dispersion, etc.).
2. **Capsule wall hardening** – changing the physical properties of the capsule wall such that it becomes a more permanent structure which is easier to handle (cross-linking, thermal change, solvent removal, etc.).
3. **Isolation of the capsules** – removal of the product capsule from the system and required post-processing.

The different techniques for microencapsulation allow for preparation of microcapsules with different sizes and wall thickness, as well as the
<table>
<thead>
<tr>
<th>Chemical methods</th>
<th>Physical methods</th>
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<tr>
<td>Technique</td>
<td>Capsule size range (μm)</td>
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<tr>
<td>Dispersion polymerization</td>
<td>1–500</td>
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<tr>
<td>Solvent evaporation</td>
<td>1–500</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>5–1000</td>
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<tr>
<td>Aqueous phase separation</td>
<td>1–500</td>
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<td>Organic phase separation</td>
<td>1–500</td>
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<tr>
<td>Simple coacervation</td>
<td>1–500</td>
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<tr>
<td>Complex coacervation</td>
<td>1–500</td>
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<tr>
<td>Interfacial polymerization</td>
<td>1–500</td>
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<tr>
<td>Suspension polymerization</td>
<td>100–500</td>
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<td>Emulsion polymerization</td>
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<tr>
<td>Sol-gel encapsulation</td>
<td>0.1–1</td>
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<tr>
<td>Layer-by-layer (L-B-L) assembly</td>
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<tr>
<td>In situ polymerization</td>
<td>1–500</td>
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The processing of a wide array of materials. There are many in-depth reviews of the different types of microencapsulation techniques (Ranney, 1969; Thies, 1975; Arshady, 1989; 1990a; Bourgeat-Lami and Duguet, 2006; Ghosh, 2006; Landfester, 2006; Shukla, 2006).

This chapter is focused more on the use of microcapsules in coatings, laminates, and textiles than the procedures for formation of the microcapsules themselves. Therefore rather than describing each method of preparation in detail only a description of phase separation/coacervation is included below.

### 5.5.1 Phase separation/coacervation

Torza and Mason (1970) published an in-depth discussion examining the equilibria to be expected after two immiscible liquid drops are brought into
intimate contact when they are suspended in a third immiscible liquid. The observations and mathematical modeling in this paper allow the description of the conditions for achieving encapsulation (complete engulfing) of a liquid core by a liquid encapsulating (wall) material while suspended in another liquid. This work was discussed and summarized by Thies (1975). These works describe spreading coefficients \( (S_1, S_2, S_3) \) based on the interfacial tensions between the three liquids \( (\sigma_{12}, \sigma_{23}, \sigma_{13}) \). The conditions are given in terms of each of the spreading coefficients. The condition for one of these spreading coefficients \( (S_3) \) is that the sum of the interfacial energy of the core and the capsule-forming wall material plus the capsule-forming wall and the solvent must be greater than the interfacial energy for the core material and the solvent. In general the conditions required for preparation of a completely engulfed microcapsule by these spreading coefficients is the thermodynamic minimum for the system.

As mentioned above, the first big use of microencapsulation, in a commercial product, was to make a carbonless copying or transfer paper. The work at the National Cash Register Company by B. K. Green (Ranney, 1969) resulted in many US patents during the 1950s; the first was to Green and Sandberg (1951) assigned to the National Cash Register Company. The first for microencapsulation was to Green and Scheicher (1957) assigned to National Cash Register Company. In 1953 the National Cash Register Company and Appleton Coated Paper Company (currently Appleton) made successful trials of NCR PAPER® (No Carbon Required – registered trade mark Appleton 2008). In 1954 NCR PAPER® was the first product of this type sold commercially.

Microcapsules in carbonless copying paper are made by coacervation. The word coacervate derives from Latin *co-* meaning together or with, and *acerväre* meaning to heap literally to heap together (*American Heritage Dictionary*, 2008). Bungenbergde Jong and Kruyt (1929) used the word coacervation to describe the phase separation technique, in which a solvated polymer is destabilized to the point at which it is no longer fully solvated.

The specifics of what occurs in a phase separation method vary somewhat depending on which method is used; however, all the techniques follow the general steps of capsule formation, capsule wall hardening, and isolation of the capsules mentioned above. A general schematic representation of the capsule formation and capsule wall hardening for phase separation techniques is shown in Fig. 5.2. Capsule formation for ‘simple coacervation’ is shown on the left and in the middle while ‘complex coacervation’ is on the right. The schematic for capsule wall hardening for both ‘simple coacervation’ and ‘complex coacervation’ is essentially the same.

Simple coacervation is the process where the solubility of a polymer in solution is decreased until it coalesces onto a material which becomes the
internal phase of the capsule. Complex coacervation is the process where two oppositely charged polymers are used to form the outer shell material.

Simple coacervation is performed with the encapsulating (shell) material dissolved in a solvent such that it is fully solvated. This can be done with just the shell material (homogeneous – left side) or with the shell material in the presence of the material to be encapsulated (internal phase – middle). A desolvating agent, which reduces the solubility of encapsulating polymer, is then added to the homogeneous dissolved polymer system or the dissolved polymer and internal phase system. The amount of desolvating agent added is not enough to cause the encapsulating polymer phase to completely precipitate but is enough that it is no longer completely solvated. Arshady (1990a) describes this as partial desolvation of polymer molecules as compared with exhaustive desolvation observed in precipitation. When the degree of solvation of the shell polymer in the presence of the internal phase is decreased the coacervation process begins. In the case of the partial desolvation of just the shell material (homogeneous – left side), the next step is the addition of the internal phase. The presence or absence of the internal phase at the time of partial desolvation, as well as
degree of agitation, temperature, and other variables for the system, impacts final capsule properties such as wall thickness and uniformity of encapsulation. Complex coacervaton is performed with the encapsulating (shell) material composed of two oppositely charged polymers. In the schematic for complex coacervation (right side of Fig. 5.2) it can be seen that initially a dispersion or emulsion of the core material is prepared with one of the charged polymers. The second and oppositely charged polymer is then added to the dispersion or emulsion of the core material and first charged polymer. The combination and coalescence of the two oppositely charged polymer shell materials onto the internal phase is then triggered by a perturbation to the system. The perturbation can take different forms, including the addition of salt, change of pH, temperature, etc. Complex coacervation using salt was the process used by Green and Scheicher (1957) to prepare microcapsules for carbonless copying or transfer paper.

Finally, the depiction of the coalescence of the polymer shell materials onto the internal phase followed capsule wall hardening is shown. As can be seen in the figure these two steps are conceptually the same for both ‘simple coacervation’ and ‘complex coacervation’.

5.6 Release behavior

Encapsulation of a material changes the direct interaction of the material with its environment. The internal phase is isolated from direct contact with the environment for some period of time. The choice of material from which the shell of the capsule is made, structure of the capsule, material encapsulated, and process used for preparation all affect the release behavior of the capsule. The encapsulated materials inside can be kept from directly interacting with their environment altogether, can be released all at once, or can be slowly released over time.

There are many companies involved in microencapsulation technology (Van Parys, 2006). Microencapsulated materials are commercially available from many sources, and custom microcapsule development is performed at many locations. In order to get a representative idea of materials, processes, and release mechanisms commercially available, five of these companies were examined. These companies included Microtek Laboratories, Southwest Research Institute (SWRI), Appleton (www.appletonideas.com), Ronald T. Dodge Company (www.rtdodge.com) and Thies Technology (www.thiestechnology.com). Microcapsules with a variety of release mechanisms and characteristics are commercially available, including:

- isolation (non-release);
- mechanical rupture;
- thermal release;
• permeation;
• dissolution;
• delayed and targeted release;
• pH and osmotic release;
• photolytic release;
• biodegradation;
• triggered release.

In certain applications it is desired that the encapsulated core materials do not release, diffuse from, or leach out of the microcapsule for the use life of the product. Phase change materials (PCM – discussed later) are required to take in heat and release heat over and over again. Microencapsulated PCMs have to remain encapsulated for the life of the product. Microcapsule walls need to be fully impermeable, durable, and resistant to mechanical and thermal stresses the capsule will encounter throughout the full range of use conditions.

There are a large number of product applications which require release of the core material when the capsule is subjected to a triggering stress. For these applications the capsule wall material is chosen such that it is susceptible to the appropriate trigger (mechanical pressure, osmotic pressure, temperature change, enzymatic degradation, etc.). In many of these applications the core material is a volatile liquid. Therefore, in addition to engineering the capsule wall to rupture at the appropriate time the capsule wall must retain the volatile core material until the trigger event occurs. If the core material leaks or diffuses out prior to the triggering event then the capsule will not perform its function when triggered. Additionally the longer the core material can be retained prior to the triggering event the longer the shelf-life of the product. Thies (1975) discussed some of the issues with and testing of premature release in capsules. He describes work (Thies et al., 1973) in which a variety of volatile liquids (toluene, xylene, isooctane, cyclohexane, and tetrachloroethylene) are microencapsulated (Bayless and Emrick, 1971). The resulting microcapsules were tested at three different temperature and humidity conditions (60°C, 90°C, 110°C/90% RH). The microcapsule parameters monitored were size (μm), internal phase content (%), and internal phase loss (%). The general trends observed in this study were:

• As microcapsule size decreases and surface area increases (400–600, 100–300, 50–100, 10–50 μm) the percentage loss of internal phase increases.
• At 60°C/90% RH after 28 days most capsules lost less than 10% of their internal phase.
• At 90°C/90% RH after 14 to 28 days most capsules lost less than 25% of their internal phase.
• At 110°C/90% RH after 14 days 10–50 μm capsules with isooctane and cyclohexane lost less than 20% of their internal phase.
• At 110°C/90% RH after 14 days 10–50 μm capsules with toluene lost most of their internal phase (98%).

Thies et al. (1973) performed the testing under different conditions to demonstrate that polymers, being relatively temperature sensitive, perform differently under different conditions. From these results one can glean that it is imperative to evaluate the microcapsules at environmental and test conditions to which a microcapsule might be exposed.

For applications where controlled release is desired the rate of release must be considered and materials are chosen which yield the desired release rate. A large body of literature is available in which the mechanisms and kinetics of controlled release are examined. Peppas and Ritger (1987) published a study deriving equations for Fickian and non-Fickian solute release from non-swellable devices of varying geometries. Work on specific applications has also been published (Dappert and Thies, 1978; Arshady, 1990a; Wang and Chen, 2005; Huang et al., 2006; Madene et al., 2006; Eldgren et al., 1993; Wilkins, 2008).

Release kinetics is a diffusion-controlled process and can be mathematically treated like reaction kinetics. A rate law which describes the behavior of the system can be derived. The three most discussed behaviors are zero order, first order, and square root order release behavior. The amount of material (core/internal phase) which needs to pass out of the microcapsule and be present in the environment at a given time is a function of the application in which a material is used.

An understanding of release rate and amount of material which has passed through the microcapsule wall can be gained by looking at the rate laws for these systems. Table 5.2 is a summary of the differentiated and integrated rate laws for zero, first, and square root order release. Additionally the general form for an nth order (except where n = 1) rate is given. Figure 5.3 is a generalized graphical representation comparing the total amount of the internal phase released as a function of time for the three different rate orders. From the rate laws it can be determined that for a zero order reaction material is released at a constant rate which is proportional to time. This can be graphically represented as the solid line in Fig. 5.3. The material is released at a constant rate until it is fully depleted. That is, the amount released during the first time period (0–1) is 12.5% which is the same amount released during each remaining time period until 100% release is reached. As during the first time period, 12.5% is released during the 7–8 (last) period. The amount of the internal phase that is released by a microcapsule which exhibits a first order release rate is depicted by the dashed and dotted line in Fig. 5.3. The rate of core material released
5.3 Graph of cumulative release vs time.

Table 5.2 Differentiated and integrated rate laws

<table>
<thead>
<tr>
<th>Release rate order</th>
<th>Differential rate law</th>
<th>Integrated rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>(- \frac{d[A]}{dt} = k)</td>
<td>([A] = [A]_0 - kt)</td>
</tr>
<tr>
<td>First</td>
<td>(- \frac{d[A]}{dt} = k[A])</td>
<td>([A] = [A]_0 e^{-kt})</td>
</tr>
<tr>
<td>General rate for (n)th order (except for (n = 1))</td>
<td>(- \frac{d[A]}{dt} = k[A]^n)</td>
<td>(\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)kt)</td>
</tr>
<tr>
<td>Square root</td>
<td>(- \frac{d[A]}{dt} = k[A]^{0.5})</td>
<td>(\sqrt{[A]} = \sqrt{[A]_0} + (0.5 - 1)kt)</td>
</tr>
</tbody>
</table>

initially is very large and decreases over time. During the 0–1 (first) time period approximately 40% is released, which decreases during the 1–2 (second) to about 25%. The rate of release continues to decrease, to less than 2%, through the 7–8 (last) time period. The final condition, depicted by the dotted line, is square root order. The change in release rate is between the first and zero order.

Like the first order there is a rapid (but smaller) initial release. During the 0–1 (first) time period about 35% of the core material is released, which changes to about 13% during the 1–2 (second) time period. This slower initial release rate is less than the first order situation. The rate decreases (much more gradually than in the first order rate) over time until the
amount released during the 7–8 (last) time period is about 6%, which is a faster rate than in the first order situation but slower than in the zero order. Therefore by knowing whether an application requires a steady release of material throughout the life of the product, a rapid release of the majority of the material with a small release after, or a rapid initial release with a slowly decaying rate of release one can choose the system which exhibits appropriate kinetics.

Most studies of release behaviour have been on populations of microcapsules. Lefenfeld et al. (2006) published a study on visualization of the release behavior, particularly focused on single microcapsules.

5.7 Main uses of microcapsules in coatings and laminates

Commercially available or previously developed microencapsulated materials can be obtained from many sources. Information about the spectrum of materials which have been used to prepare these microcapsules can be gleaned by examining the offerings of the five companies previously mentioned (Microtek, SwRI, Appleton, Ronald T Dodge, and Thies Tech). Capsule walls have been formed out of species from the many classes (genera) of materials including proteins, polysaccharides, starches, waxes, fats, resins, natural and synthetic polymers.

Internal phases (core materials) which have been encapsulated and commercially available are shown in Table 5.3. From the number of commercially available capsule wall and core materials it is clear that the number of material permutations and performance capabilities are tremendous. Table 5.4 is a list containing some of the large number of industries which have utilized microencapsulation to develop new products or solve problems with existing products. Representative applications are described below. Applications specific to textiles will be discussed in the next section.

5.7.1 Carbonless copy paper

When discussing the use of microcapsules in coating and laminates the discussion really must begin with carbonless copy paper (CCP) (Schulte, 2000). CCP is usually a multilayer material consisting of a microencapsulated colorless dye solution which, when capsules are broken, comes into contact with a developer. Figure 5.4 is a schematic for a three-part CCP system. The bottom surfaces of the top and the second sheet are coated with a layer of microcapsules that have a diameter of 3–6 μm. The top surfaces of the second and third sheets are coated with the clay or resin developer. The microcapsules are filled with a colorless solution, usually 2–6% dye dissolved in a high boiling point organic solvent (Fig. 5.4, left
### Table 5.3 Commercially available core/internal phase materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Acids</th>
<th>Activated carbons</th>
<th>Active metals Adhesives</th>
<th>Alcohols</th>
<th>Aldehydes</th>
<th>Amines Amino acids</th>
<th>Animal feed ingredients Antibiotics</th>
<th>Antibodies Antiseptics</th>
<th>Aqueous solutions Agrochemicals Antioxidants Bacteria Bases</th>
<th>Biocells Biocides Bleaches</th>
<th>Catalysts Chemiluminescent materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibitors</td>
<td>Corrosion</td>
<td>Cosmetic</td>
<td>Cosmetic oils Curing agents</td>
<td>Deodorants</td>
<td>Dietary supplements Dyes Dye solutions</td>
<td>Energetic material</td>
<td>Enzymes</td>
<td>Flame retardants Flavor oils</td>
<td>Flavorants Fragrance oils Food ingredients Fuels Fumigants</td>
<td>Fungi Fungicides Herbicides</td>
<td></td>
</tr>
<tr>
<td>Indicators</td>
<td>Cosmetic</td>
<td>ingredients</td>
<td>Curing agents</td>
<td>Liquid hydrocarbons</td>
<td>Liquid</td>
<td>Lubricating oils Dye solutions</td>
<td>Metal oxides and powders</td>
<td>Oils</td>
<td>Organometallic compounds</td>
<td>Oxidizers Peptides</td>
<td>Pesticides</td>
</tr>
<tr>
<td>Pigments</td>
<td>Inks</td>
<td>Activated carbons</td>
<td>Inorganic salts ion-exchange resins</td>
<td>Propellants</td>
<td>Additives</td>
<td>Radioprotectors Reactive chemicals</td>
<td>Metal oxides and powders</td>
<td>Oils</td>
<td>Organometallic compounds</td>
<td>Paints Peptides</td>
<td>Pharmaceuticals</td>
</tr>
<tr>
<td>Pigments dispersed in oils</td>
<td></td>
<td></td>
<td></td>
<td>Propellants</td>
<td>Lubricant additives</td>
<td>Radioprotectors Reactive chemicals</td>
<td>Moisturizing oils</td>
<td>Oils</td>
<td>Retinoids Salts</td>
<td>Paints Peptides</td>
<td>Phase change materials</td>
</tr>
<tr>
<td>Proteins</td>
<td></td>
<td></td>
<td></td>
<td>Propellants</td>
<td></td>
<td>Reflective products Resin-curing agents</td>
<td>Moisturizing oils</td>
<td>Oils</td>
<td>Retinoids Salts</td>
<td>Paints Peptides</td>
<td>Phase change materials</td>
</tr>
<tr>
<td>Preservatives</td>
<td></td>
<td></td>
<td></td>
<td>Propellants</td>
<td></td>
<td>Reflective products Resin-curing agents</td>
<td>Moisturizing oils</td>
<td>Oils</td>
<td>Retinoids Salts</td>
<td>Paints Peptides</td>
<td>Phase change materials</td>
</tr>
<tr>
<td></td>
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<td>Oils</td>
<td>Retinoids Salts</td>
<td>Paints Peptides</td>
<td>Phase change materials</td>
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<td>Paints Peptides</td>
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<tr>
<td></td>
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<td>Propellants</td>
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<td>Reflective products Resin-curing agents</td>
<td>Moisturizing oils</td>
<td>Oils</td>
<td>Retinoids Salts</td>
<td>Paints Peptides</td>
<td>Phase change materials</td>
</tr>
</tbody>
</table>

The microcapsules rupture under the pressure of writing and the released dye solution is transferred from the bottom surfaces of sheets one and two to the top surfaces of sheets two and three. The dye solution reacts with the clay or resin coating to form an image (Fig. 5.4, right side).

In the real system (not schematic) the microcapsule coating includes inert spacer particles called ‘stilts’ which are made from various materials such as floc, uncooked arrowroot, and/or wheat starch particles. These ‘stilts’ are larger than the microcapsules and are added to protect the microcapsules.
Table 5.4 Industries utilizing microencapsulation

<table>
<thead>
<tr>
<th>Industry</th>
<th>Adhesives</th>
<th>Agriculture</th>
<th>Automotive</th>
<th>Biomedical</th>
<th>Consumer products</th>
<th>Cosmetics</th>
<th>Composites</th>
<th>Dental</th>
<th>Drug delivery</th>
<th>Essences</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flavors</td>
<td>Food additives</td>
<td>Food supplements</td>
<td>Home care</td>
<td>Home improvement</td>
<td>Industrial chemicals</td>
<td>Lubricants</td>
<td>Medical</td>
<td>Military</td>
<td>Novelty</td>
</tr>
<tr>
<td></td>
<td>Nutraceutical</td>
<td>Paints</td>
<td>Paper systems</td>
<td>Personal care</td>
<td>Pharmaceutical products</td>
<td>Printing</td>
<td>Recreation</td>
<td>Sealants</td>
<td>Security</td>
<td>Textiles</td>
</tr>
</tbody>
</table>

5.4 Schematic for a three-part carbonless copy paper system.

from premature rupture. This configuration can be seen in the scanning electron micrograph (SEM) of Fig. 5.5 (courtesy of Appleton). This corresponds to the bottom surfaces of sheets one and two in Fig. 5.4.

The developer and reactive dye microcapsules can be coated onto the same paper surface; self-contained CCP. A representative process for producing CCP involves applying the appropriate coatings to paper (Apol and Thoburn, 1986). The coatings can be applied to a wet web of paper, during the paper formation process on, for example, a Fourdriner paper machine. The coatings can also be applied as the dry paper exits the machine. Once the coating is applied, the paper is put through a dryer and wound on a roll. The microcapsule coating may also be applied to the paper, in a separate step, as it passes through a series of dryers and is rewound on a roll.
5.7.2 Self-sealing/healing

In 2001 White et al. reported on and described a structural polymeric material with the ability to ‘autonomically’ heal cracks. Up to that point, while crack healing methods had been reported (Dry and Sotos, 1993; Dry, 1996; Wool, 1995), they required a manual intervention step. This ‘autonomic’ healing system was composed of an encapsulated monomer and a separate catalyst. The catalyst, as a particulate, and the microcapsules of monomer are distributed throughout the coating. However the wall of the microcapsule keeps the monomer from coming into contact with the catalyst. When the microcapsule ruptures, by a crack or cut in the coating, the monomer comes into contact with the catalyst in the bulk of the coating and thereby polymerizes.

In the work of White et al. (2001) endo-dicyclopentadiene (DCPD) monomer was microencapsulated as the uncured healing agent and a first generation Grubbs’ catalyst [(PCy₃)₂(Cl)₂Ru–CHPh – benzylidenebis(tricyclohexylphosphine)dichlororuthenium] was used. Both the microcapsules and the particulate catalyst were dispersed into an epoxy matrix. The crack initiates and then begins to propagate. As it propagates it runs into and ruptures a microcapsule as well as exposing some catalyst. While the crack continues to propagate the monomer begins to wick (capillary action) into the channel left by the crack. As the monomer wicks through the channel it contacts the exposed catalyst and this initiate the ring-opening metathesis polymerization (ROMP). Once the polymerization reaction is initiated it goes to completion and the polymerized material fills the crack and bonds the surfaces together. Recovery of up to 75% in fracture toughness was reported. Additional studies have been performed to examine effect of healing time (Brown et al., 2002) catalyst form (Rule et al., 2005; Jones et al., 2006), fatigue loading (Brown et al., 2005), and microcapsule size and concentration (Brown et al., 2004) on the healing efficiency. In addition to DCPD other monomers for the ROMP have

5.5 Microcapsules in carbonless paper with four large starch particles.
also been examined including 5-ethylidene-2-norbornene (ENB) and exo-DCPD (Larin et al., 2006).

5.7.3 Wound management/medicament delivery

The delivery of medicaments and use of dressings, or combination of the two, in wound care is meant to promote rapid wound healing with the best functional and cosmetic results. The properties of an ideal material to achieve the above objective include flexibility, durability, adherence, a capability of absorbing wound exudates, and protecting the lesion from dehydration. Controlled local release of medicaments from external dressings or implanted materials can provide high local concentrations of medicament for prolonged periods and avoid the risk of systemic toxicity.

The performance of these materials are characterized by in vitro (Latin – in glass, in laboratory) and/or in vivo (Latin – alive, in living system) studies. Representative recent studies looking at both wound dressings and drug delivery are included below.

In 2006 Huang et al. published a study looking at wound dressings containing basic fibroblast growth factor (bFGF). Growth factors play an important role in cell growth and in the process of wound healing. bFGF is among these growth factors; however, the in vivo half-life of bFGF is very short. Additionally, when bFGF is injected in soluble form it rapidly diffuses away from the site of injection and is also denatured and degraded enzymatically. Microencapsulation of bFGF has been used as a way to ameliorate the above-mentioned shortcomings. In this study bFGF microcapsules were prepared by a modified coacervation technique using gelatin for the encapsulation. Since gelatin is soluble in aqueous solution, it must be crosslinked before use in long-term biomedical applications. Glutaraldehyde was used as the cross-linking agent in this study. Gelatin sponges were used to house the bFGF, and made into a bilayer wound dressing. A control (gauze and Vaseline) was compared with bilayer wound dressings containing gelatin sponge, gelatin sponge with bFGF, and gelatin sponge with bFGF-loaded microspheres. The compatibilities of the dressings were designed and tested with a series of preliminary in vitro protein release and bioactivity experiments. In vivo experiments were then performed by applying the dressings on full thickness skin defects created on York pigs. During the in vitro portion of the study it was demonstrated that crosslinked gelatin microcapsules can serve as delivery vehicles for controlled release of bFGF and released bFGF can enhance proliferation of fibroblasts (in vitro). During the in vivo study, all configurations provided an improvement relative to the control. The degree of improvement in healing, relative to the control, progressed (least to most) from bilayer wound dressings.
containing gelatin sponge to gelatin sponge with bFGF and the most improvement in gelatin sponge with bFGF-loaded microspheres.

In 2006 Sayin et al. published a study looking at vancomycin-loaded microspheres blended with human/rabbit bone grafts. One of the risks and difficulties of bone surgery is bacterial osteomyelitis (inflammation of the bone marrow or of the bone and marrow). The condition requires high levels of antibiotics for prolonged periods. Parenteral (situated or occurring outside of the intestines, not oral) administration of antibiotics for this condition is largely unsuccessful because the vancomycin concentration, at systemically non-toxic levels, often provides insufficient concentration of the antibiotic at desired site. In this study glycopeptide antibiotic vancomycin was selected as a suitable antibacterial agent. Poly-lactide-co-glycolide (PLGA – a biodegradable polymer) was used to encapsulate the vancomycin. In this study bone was used as the carrier for the medicament as opposed to gelatin sponge. Vancomycin-loaded PLGA microspheres, vancomycin-impregnated bone grafts, vancomycin-loaded PLGA microsphere impregnated bone grafts were evaluated in vitro and in vivo over six weeks for drug release behavior. It was felt that the formulations containing vancomycin-loaded microspheres might offer the possibility of providing a long-acting formulation for implantation with allografts (a transplant which is sourced from a genetically non-identical member of the same species). It was concluded that combination of antibiotic-loaded microcapsules with bone allografts provided a bioactive drug carrier system for the treatment of infected bone defects. Additionally, the formulations were appropriate for increasing patient compliance and local antibiotic concentration, reducing the systemic toxicity of the antibiotic, shortening the hospitalization of the patients and avoiding secondary surgery.

In 2007 Adhirajan et al. published a study looking at development and characterization of doxycyclin-loaded microspheres. Healing of chronic wounds is negatively impacted by expression of elevated levels of proteases, in particular matrix metalloproteinases (MMPs). These MMPs degrade granulation tissue (fibrous connective tissue that replaces a clot in wound healing) and endogenous biologically active proteins. Doxycycline, a potent broad-spectrum antibiotic of the semi-synthetic tetracycline family, is known to inhibit MMPs and has been used for many MMP-associated disorders, including chronic wounds. Topical application of drugs are preferred over systemic administration for chronic wounds, because of lack of blood supply to the surface of the chronic wounds. In 2003 Chin et al. reported that 1% doxycycline gel applied topically, once daily, proved effective in the treatment of chronic and diabetic foot ulcers, in particular, by reducing the levels of MMPs. It was noted that controlled delivery over a long period would be even more beneficial. In the work by Adhirajan et al. (2007) doxycycline was encapsulated in gelatin microcapsules which
were prepared by an emulsification solvent extraction method. The gelatin was then cross-linked with 1-ethyl-3-(3-dimethylaminopropyl) carbodi-imide hydrochloride (EDC). The drug release behavior and the biodegradability of microcapsules with varying degrees of crosslinking were studied in vitro. Altering the EDC concentration and crosslinking time periods yields microcapsules with various degrees of crosslinking. This in turn influences the mechanical stability, swellability, and drug release behavior of gelatin microspheres. It was demonstrated that an increase in the extent of crosslinking decreased drug release and decreased the rate of degradation. It was concluded that the crosslinker EDC can be considered as a potential alternative for crosslinking gelatin microspheres used in drug delivery. Further it was felt that it could be inferred from the results of this in vitro study that control over the release profiles of these materials will provide an approach to enhance in vivo drug delivery.

As stated above, the number of material permutations and performance capabilities are tremendous. Therefore the number of applications is also quite large. Some areas other than textiles in which microencapsulation have been used are included for the information of the reader.

5.7.4 Wear-resistant – self-lubricating

Composites consisting of a metal matrix and ceramic particulates or liquid-containing microcapsules have been developed and used in industry as wear-resistant (Liquin et al., 2004) or self-lubricating (Alexandridou et al., 1995) coatings. Liquin et al. (2004) prepared liquid-containing microcapsules by the phase separation in an aqueous solution method. Alexandridou et al. (1995) prepared liquid-containing microcapsules by the interfacial polymerization method. Because of the metal matrix present in both cases the microcapsules were applied to the substrate by electrolytic co-deposition (Liquin, 2006).

5.7.5 Phase change materials

Phase change materials (PCM) have been utilized for thermal energy storage in construction products, building materials, electronic components, insulating coatings, automotive components, textiles (to be discussed later), and numerous other areas. A PCM works by absorbing heat as it changes state from solid to liquid (heat of fusion – melting), and giving off the stored heat as the material changes back from liquid to solid. The temperature to which a material in contact with PCM is exposed is moderated by the absorption and release of heat from the PCM. That is, as the environment heats and the PCM changes from solid to liquid it absorbs some of the heat, thereby shielding the substrate to which it is attached. Con-
versely, as the environment cools, the PCM changes from liquid to solid and releases the stored heat, thereby warming the substrate to which it is attached. In the broadest sense there are two classes of PCM materials, namely organics and salt-based materials. Within these two classes there are a large number of PCM materials available (Van Parys, 2006). One of the larger applications for PCMs is in construction products and building materials. Su et al. (2005) examined and published results looking at the preparation and characterization of PCMs used in building materials. The choice of the PCM material is made based on the requirements (temperature range, length of time, etc.) of the application for which it is used. Boh et al. (2005) looked at the microencapsulation of higher order hydrocarbon phase change materials with three different melting points (25, 40 and 50°C) by *in situ* polymerization.

Some works which describe additional areas in which microencapsulation has been utilized include flavor (Madene et al., 2006) and fragrance (Wang and Chen, 2005) control, pharmaceutical (Eldgren et al. 1993), agricultural (Wilkins, 2001), adhesion enhancement (Charmeau et al., 1997), and microparticle-based electrophoretic image display for use in microparticle-based paper-like display systems (Yoshizawa, 2004).

### 5.8 Applications of microcapsules in textiles

The successful use of microencapsulation in textile materials requires that the microcapsules survive the multiple washing and drying cycles to which they are subjected. Additionally, the microencapsulation process cannot have too large a negative effect on textile tactile properties. That is, the handle and comfort of the textile must still remain acceptable. The microcapsules must also perform sufficiently long, relative to the lifetime for the textile product, that the consumer is satisfied. The range of textile applications in which commercially available microcapsules have been used can be gleaned by examining the offerings of the five companies previously mentioned (Microtek, SwRI, Appleton, Ronald T Dodge and Thies Tech). Additional applications can be found in reviews of the technology (Pause, 1995; Nelson, 2002; Van Parys, 2006; Mukhopadhyay and Midha, 2008). These applications include temperature regulation PCMs, delivery system (fragrances, deodorants, insect and animal repellents, antimicrobials, etc.), flame retardants, and thermochromic and polychromatic dyes.

#### 5.8.1 Temperature regulation phase change materials

Like the discussion of the use of microcapsules in coating and laminates with CCP, the discussion of use of microcapsules in textiles must begin with PCMs. The use of microencapsulated PCMs was pioneered by the
US National Aeronautics and Space Administration (NASA) in the early 1980s. Microencapsulated PCMs were examined for thermoregulation in space suits, in particular, to provide improved thermal protection against the extreme temperature fluctuations in outer space. More than 500 different PCMs are described in the book published in 1971 by NASA entitled *Phase Change Materials Handbook* (Hale *et al.*, 1971). Although the concept never yielded materials which satisfied the needs of this application and was not put into use by the space program, the work led to interest in other high tech areas. Outlast Technologies licensed the technology from NASA and controls the production of PCM-based microcapsules for textiles and other materials. Outlast has and does license other companies to produce and sell PCM microcapsules (Nelson, 2002; Van Parys, 2006).

PCMs (*Hale et al.*, 1971; Adamson, 1979; Pause, 1995, 2003; Kim and Cho, 2002; Nelson, 2002; Choi *et al.*, 2004; Chung and Cho, 2004; Van Parys, 2006; Mukhopadhyay and Midha, 2008) take advantage of the latent heat absorption associated with a phase change. Figure 5.6 is an example showing the energy associated with phase change of water. It is a schematic representation, in which it can be seen that below 0 °C and above 100 °C water exists as a solid and vapor respectively. From 0 to 100 °C it exists in liquid form. A calorie (measurement of heat) is defined as 4.184 joules. It can also be thought of as the amount of heat required to raise the temperature of 1 gram of water from 14.5 to 15.5 °C. Looking at Fig. 5.6 one can clearly see that the amount of heat required to cause the phase change of 1 gram of water from liquid to solid at 0 °C (\(\Delta H_{\text{fusion}}\)) is 80 times the amount of heat required to raise the temperature 1 gram of water one degree (insert). This
A large difference between the amount of energy to change the temperature of a material within a phase and the amount of energy required to change the phase of a material (at the same temperature) is what makes PCMs effective. Heat must be absorbed by the ice when it melts and heat is given off by the liquid water as it freezes.

A PCM is chosen for an application by determining which material undergoes a phase change near the temperature for the desired application. In a textile application as the system drops below the desired temperature the PCM gives off heat (warms the wearer) and as the temperature goes above the desired value the PCM absorbs heat (cools the wearer). The most commonly used materials in the temperature range for textile applications are paraffin materials (Pause, 2003). Some paraffin materials are shown in Table 5.5.

It is clear from Table 5.5 that octadecane (Kim and Cho, 2002; Pause, 2003; Choi et al., 2004; Chung and Cho, 2004; Mukhopadhyay and Midha, 2008) is especially useful in clothing textiles because of the combination of the high heat absorption capacity and its melting point. It has a heat storage capacity more than 20 joules/gram higher than nonadecane and an MP of 28.2°C. This means the large heat uptake and release associated with the phase change (and therefore the temperature-moderating effect) occurs right near the mean skin temperature of 33.3°C.

The microcapsules for textile applications (Kim and Cho, 2002; Choi et al., 2004; Chung and Cho, 2004) are often made by interfacial polymerization. The shell material is chosen such that it can withstand the rigors of laundering and drying and is often a polyurea or melamine formaldehyde. The microcapsules can be permanently embedded in the fibers, applied (coated) on the surface of the textile or added as a powder after the application of a coating (Van Parys, 2006). Many common coating application techniques can be used for microcapsules, including knife-over-roll, knife-over-air, pad–dry–cure, gravure, dip coat, transfer coat, etc. In 2004 Choi et al. published a study entitled ‘Thermal storage/release and mechanical properties of phase change materials on polyester fabrics’ in which the application by knife-over-roll and screen printing was examined. Among
other observations it was noted that the mechanical properties, including durability, were better by knife-over-roll coating while the tactile properties of the fabric were better with screen printing.

5.8.2 Flame retardants

Flammability of textiles has always been a concern. The US Flammable Fabrics Act of 1953 and its amendment by Congress in 1967 led to high safety standards for children’s sleepwear and growth in research on flame resistance of textiles (Vail et al., 1982). Burning is a combination of chemical and physical processes. The chemical process occurs in the bulk of polymeric materials (condensed phase) and above the surface (gas phase). The physical process is that of heat transfer from the gas phase back to the condensed phase (Bugajny et al., 1999, 2000).

Many different approaches and fire retardant materials have been used in textile applications. Because of questions regarding the use of bromine-containing systems, halogen-free flame retardant systems are now receiving the most interest. Without commenting on whether the arguments against bromine are valid or not the two primary concerns are stated below. Concerns have been raised about the potential for generation of polybrominated dioxins from incineration of organobromine compounds. The second and more recent concern regards antimony–bromine (Sb-Br) finishes, in particular the potential role of Sb III oxide in sudden infant death syndrome (SIDS) (Horrocks, 2004). Phosphorus-containing materials are heavily represented among the halogen-free fire retardants, and will be discussed here. These systems function as intumescents. The mechanism of action for an intumescent is the formation of a char layer on the surface of the burning material, thereby protecting the underlying material from heat flux and flame. Intumescent formulations contain three active ingredients: an acid source, carbonization agent (material which forms a char), and blowing agent. Ammonium phosphates mixed in polyurethane (PU) coatings have been used in textiles to achieve fire retardant behavior, but these mixed coated materials are not permanent. In 2001 Giraud et al. published work that examined the FR behavior of cotton with microcapsules of di-ammonium hydrogen phosphate (DAHP) in a PU shell, prepared by interfacial polycondensation. Samples of the cotton coated with polyurethane and neat DAHP as well as samples coated with polyurethane and microencapsulated DAHP performed better than the cotton coated with just the polyurethane. In 2008 Wu et al. published work that examined the fire retardant behavior of polypropylene with microcapsules of ammonium polyphosphate (APP), in a melamine–formaldehyde (MF) resin, prepared by in situ polymerization. Additionally these materials were studied with and without the presence of the carbonization agent pentaerythritol.
(PER). In this study the materials were mixed directly into the polypropylene and prepared in a Brabender-like apparatus. Polypropylene composites were prepared with APP, APP/MF microcapsules, APP–PER, and APP/MF microcapsules with PER. The composites that contained PER showed a remarkable improvement in flame retardation over the composites without PER. The polypropylene composites with APP/MF microcapsules and PER had a thermal stability of higher than that of the APP–PER only composites, as determined by thermogravimetric analysis (TGA). In 2006 Liu and Wang published work that examined the FR behavior of polyamide-6 with microcapsules of red phosphorus (RP), in melamine cyanurate (MCA). RP has been widely applied in many flame retarded polymers and shows some distinct advantages such as low cost, little smoke, and low toxicity. The RPMC microcapsules were prepared by a self-assembly reaction. The self-assembly of the MCA on the RP surface was accomplished by pre-dispersing fine RP powder in the fluid suspension of the reactants and the MCA-encapsulated RP was obtained. In this study the fire retardant materials were mixed directly into the polyamide-6 to prepare the fire retardant composite. It was concluded that MCA-microencapsulated RP flame retardant PA6 shows enhanced flame retardancy and mechanical properties compared with conventional microencapsulated RP.

5.8.3 Deodorizing and fragrance-enhancing additives

There has been an ongoing use of deodorizing and fragrance-enhancing additives in cleaning processes for textiles. The major drawback of this technology has been its lack of durability. Usually the treatment does not survive more than one or two wash/dry cycles. Microencapsulation can play an important role in an effort to achieve greater durability and efficacy in elimination of bad odours and delivery of pleasant fragrances (Nelson, 2002; Yoshizawa, 2004; Wang and Chen, 2005; Van Parys, 2006). There are many materials which can be used as the encapsulating (capsule wall) materials. The choice of materials is largely defined by the physical properties which are required in the environment in which the microcapsule is used. The use of gelatins, (Versic, 1989; Charbonneau and Relyea, 1997) is sometimes called the National Cash Register (NCR) process and seems to have a lower likelihood of interacting with and changing the scent of the fragrance. The use of polyureas (Versic, 1989; Charbonneau and Relyea, 1997) is sometimes called the 3M process and includes polyoxymethylene urea (PMU) and urea–formaldehyde. These processes seem to give rise to a stronger capsule and minimize premature release. When considering issues of human safety, cyclodextranes (Wang and Chen, 2005) seem to be best. In an effort to provide improved durability and as an alternative to microencapsulation during 2008 Liu et al. described the

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addition of the fragrance directly to a polymer fiber. Scent was infused into the polypropylene chips, the scented chips were then melt spun, as the core of a sheath core fiber, with polylactic acid as the sheath. Microcapsules can be applied by most conventional textile coating processes. For applications which require precise placement of the capsules, such as ‘scratch and sniff’, printing (e.g. screen printing) is favored. There are specific advantages to microencapsulation for deodorants and antiperspirants, which have the potential to be toxic to the wearer and environment (Bilbrey, 1994; Van Parys, 2006). Microcapsules for use in textile products which deliver medicaments such as antibacterial agents have also being prepared (Hu et al., 2008).

**Aromatherapy**

In addition to deodorizing and fragrance enhancing, microcapsules can be used to deliver scents for specific purposes. Among the embodiments for these specific applications are as agents for aromatherapy (Nelson, 2002; Wang and Chen, 2005; Van Parys, 2006; Liu et al., 2008). Fragrance and scents have been used in folk medicine for a substantial period of time. The term aromatherapy dates to the late 1920s and is attributed to R. M. Gattefosse (Buchbauer, 1994). In 1982 the study of the interrelationship between psychology and fragrance to elicit specific feelings and emotions was coined aromachology (Jellinnek, 1994). The belief at the heart of aromatherapy is that through stimulation of the olfactory pathways in the brain, specially the limbic system, certain aromas produce feelings of relaxation, exhilaration, sensuality, happiness, and well-being.

**Insect and/or animal repellant**

Scents are used in other applications to repel insects and/or animals (Boh et al., 1999; Van Parys, 2006). Boh et al. (1999) published a study examining the application of microcapsules of the animal repellent ‘Daphne’ to various substrates including nonwoven textiles. Results of this study were very positive and included the observation that the repelling effect of all formulations with microcapsules lasted longer than those with non-encapsulated Daphne. The repelling effects of Daphne were weaker during the winter. However, in the trials where pastes or nonwoven textile strips (impregnated with microcapsules) were applied to tree bark, good repellency against deer and rabbits was achieved even during the winter.

5.8.4 **Liposomes**

Among the other applications that are being performed or examined are the use of liposomes for dyeing textiles (de la Maza et al., 1998; Coderch
et al., 1999; Nelson, 2002). Liposomes are an artificial microscopic vesicle consisting of an aqueous core enclosed in one or more phospholipid layers (The American Heritage® Stedman’s Medical Dictionary, 2008). Liposomes have been and continue to be examined as a carrier capable of reducing the degradative effects of conventional wool dyeing.

5.8.5 Polychromic and thermochromic dyes

Thermochromic dyes are materials that change color with changes in temperature and are used in novelty products (T-shirts, logos, garments, etc. (Nelson, 2002; Van Parys, 2006; Ronald T. Dodge Co.)). Polychromic dyes are materials that change color in response to some other stimuli. Currently most widely used, also in novelty materials, is the photochromic material which changes color with light, in particular UV light.

5.9 Sources of further information and advice

Books


Journals

Polymer Engineering and Science
Polymer-Plastics Technology and Engineering
Journal of Colloid Interface Science
Journal of Controlled Release
International Journal of Food Science and Technology
Journal of Industrial Textiles
Journal of Microencapsulation
Journal of Membrane Science
Nature
5.10 References


Microencapsulation technology for coating and lamination


Conductive coatings for textiles

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Abstract: Having electrical conductivity is often a prerequisite for many smart and intelligent textiles. Conventional textiles are non-conductive materials. One of the approaches to make a textile item electrically conductive is conductive coating. This chapter introduces some practical methods to impart conductivity to textiles, including metal coating and conducting polymer coating. It highlights the principles, coating methods, performance and applications of textile materials coated with conducting polymers such as polypyrrole.

Key words: conductive coating, electronic textiles, conducting polymers, polypyrrole, surface resistivity.

6.1 Introduction

Human intelligence requires efficient transfer of electrical signals amongst a complex network of nerve cells within our brain: having electrical conductivity is often a prerequisite for many smart and intelligent textiles also. However, conventional textiles are non-conductive materials. One way to make a textile item electrically conductive is through the use of a conductive coating.

For conventional non-conductive textiles, build-up of static charge is very undesirable. Static electricity is generated when two unlike materials make contact and are then separated from each other, for instance by friction or rubbing of garments. If textiles are insulators (surface resistivity >1000 MΩ/square), very high static charges may build up, meaning that the materials could pick up excessive dust, possibly ignite a flammable or explosive atmosphere, damage electronic equipment, or induce a charge on a nearby non-earthed object. Electrostatic discharge from textiles has been a concern in a wide range of situations (Rizvi et al. 1995). Textiles with a certain degree of electrical conductivity are thus desired for many antistatic applications (Holme et al. 1998; Pionteck and Wypych 2007).

The demand for electroconductive fibres and textiles is growing rapidly not only in antistatic applications but also in other areas such as sensing, data transfer, monitoring, corrosion protection and electromagnetic...
interference (EMI) shielding. Depending on applications, fabrics or yarns may be required to have different levels of electrical conductivity. For example, highly conductive flexible yarns may be required to fabricate textile-based electronic circuitry and user interface elements, which offer an alternative to traditional printed circuit boards. Relatively low conductivity textiles may be used for static dissipation. Textiles of high electrical conductivity are of great interest in innovative product development.

Embedding electronic circuits and wearable devices into garments, or smart electronic textiles, is a growing trend for improving the quality of life (Carpi and De Rossi 2005; Dhawan et al. 2005; Locher and Troster 2008). Such garments integrate embedded electronics and sensing devices for a range of functions including physiological monitoring, communications, harvesting of energy, passive/active thermal management, casualty care, protection and entertainment (Carpi and De Rossi 2005; Dhawan et al. 2005; Winterhalter et al. 2005; Locher and Troster 2008). Dhawan et al. (2005) reviewed fibre and textile-based electrical and optical devices and systems including some commercial products and product concepts of electronic textiles, which demonstrated that research in this area is paving the way for the development and commercialisation of fully integrated electronic textiles with intelligent built-in features.

Improving the quality and efficiency of healthcare, both at home and in hospitals, is becoming more and more important for patients and society at large. Many smart sensors and first aid and communication devices can be integrated into clothing for monitoring, reporting and enhancing the comfort and security of patients. Apart from smart textiles in healthcare, sportswear and functional fabric-based products that incorporate integrated electronics have also been developed and commercialised. Such products are capable of interfacing with or accommodating entertainment and communications devices including iPods, mobile phones, laptop computers, and interactive jackets, bags, business suits and fabric keyboards.

The aesthetic quality is an important factor when integrating smart materials and devices into conventional textiles. The electronic textiles should be flexible, lightweight, comfortable, economical and durable, and more importantly they require electroconductive materials, such as conductive yarns and fabrics. To make flexible substrates conduct electricity, many methods have been developed (Gregory et al. 1991; Dietzel et al. 2000, 2008; Akbarov et al. 2005, 2006; Carpi and De Rossi 2005; Wang et al. 2005; Kaynak et al. 2006; Gan et al. 2008; Roh et al. 2008; Sen 2008; Wei et al. 2008). This chapter briefly introduces some practical methods to impart conductivity to textiles, including metal coating and conducting polymer coating. It highlights the principles, coating methods, performance and applications of textile materials coated with conducting polymers such as polypyrrole.
6.2 Methods for imparting conductivity on textiles

Metal filaments and yarns made from brass, stainless steel, aluminium, copper or nickel are commonly used in electronic fabrics, in particular as part of embedded electronic circuitry (Post et al. 2000; Dhawan et al. 2004a,b; Winterhalter et al. 2005; Locher and Troster 2008; Roh et al. 2008) because they are low cost, widely available and have a good strength, biological inertness and reliable electroconductive properties. However, metal fibres are heavier than polymer-based textile fibres, and fabrics containing metal fibres are not as flexible as fabrics made from conventional fibres. Once they are deformed, they are unlikely to recover, like most conventional fabrics do, to their initial shape without applying a force. Metal fibres add bulk and weight to a garment, which makes the garment uncomfortable to wear.

Carbon filaments have reasonable electrical conductivity. They can be incorporated into fabrics mainly for antistatic purposes. Conductive yarns can also be made by wrapping a metallic ribbon or foil around a high strength fibre in a helix shape. The metallic ribbons, such as copper, silver or gold foil, impart high conductivity to fibre-based materials, while the helix arrangement provides a certain degree of flexibility and extensibility for the ribbon, and the core filament provides the strength while in service. Fabrics made from such yarns have better flexibility than metal wires. However, the fragility of metal foil may lead to breaking of the electrical continuity.

Adding conductive particles, such as silver particles or carbon nanotubes, during filament spinning can modify the filament electrical property. The conductivity of the modified filament depends on the weight ratio of the conductive particles. When the adjacent conductive particles are far apart, the filament cannot effectively conduct electricity. Although composite fibres containing carbon nanotubes can be spun by dispersing and properly orienting them in polymers, producing highly conductive fibres would require boosting the nanotube percentage to as much as 20% due to structure homogeneity problems and the aggregation of conductive materials. Similarly, fibres containing conductive carbon/graphite can be spun, but the carbon content in the fibre needs to exceed 30% for good conductivity. The inclusion of conductive particles in the fibre spinning process is not an ideal approach. The conductive materials can be more effectively utilised if they are confined to the fibre surface. Instead of using a metal fibre or a filament, coating fibres with high percentage carbon and/or metallic compound inclusion is also cost effective because the conductive substance needed for coating is small in quantity, especially when expensive metals such as gold, platinum or silver are used. In addition, the multifunctional properties needed for intelligent textiles are mainly determined by the...
surface properties; thus coating conductive materials on the fibre surface is most desirable.

Another practical technique to make electroconductive fibre materials is to coat conducting polymers onto fibre or fabric surface. Conducting polymers can be produced to have a wide ranging modulation of their electrical conductivity, from insulating to highly conductive, i.e. $10^{-10}$–$10^5$ S/cm (MacDiarmid 2001). Their conductivity value can be adjusted by incorporating specific concentrations of dopant during polymerisation. Conducting polymers are brittle and insoluble, and cannot be readily melted for fibre extrusion. Hence, it is not practical to spin conductive fibres and textiles from these conducting polymers. Instead, coating is more commonly used to impart conductivity to non-conductive fibre materials, including both natural fibres and synthetic materials. Conducting polymers can combine the electronic characteristics of metals with the engineering properties of polymers.

6.3 Main types of conductive coating

6.3.1 Metal coating

Most methods for imparting conductivity to flexible substrates rely on coating a conductive layer of metals, conducting polymers or other conductive materials such as conductive paints and lacquers onto their surface. Coating precious metals on textile surfaces have had a long history for aesthetic or protective purposes. The metal layer on fibres can also find new applications in electrical conductivity, in addition to protective and decorative effects. Textile metallisation technologies, which include vacuum deposition, ion plating, electroplating and electroless plating, deposit metallic particles on the textile surface and create metallic-coated textiles (Dietzel et al. 2000, 2008; Akbarov et al. 2005, 2006; Lee et al. 2005; Gasana et al. 2006; Jiang et al. 2006, 2007; Jiang and Guo 2008; Wei et al. 2008). Vacuum metallisation and ion plating are processes that deposit evaporated metal particles onto the substrate surface. The former method deposits metal vapour on substrates in vacuum, and the materials to be vaporised can be solids in any form and purity. The ion plating evaporates the molecules of metal materials and accelerates the ionised metal particles onto the substrate surface in an inert gas. The ion plating technology has higher density and stronger adhesion when compared with vacuum deposition.

An electroplating process, also referred to as electrodeposition, coats textile materials with a layer of metal particles such as copper, silver, gold, nickel, cadmium, chromium, zinc and alloy by means of an electrical current. It is performed in an electrolytic cell which contains an electrolyte and two electrodes. The anode (positive electrolyte) is the metal source, while the
cathode (negative electrolyte) is the material to be coated. Under a low-voltage current, ions in the electrolyte move towards the cathode, and they are converted into metal form electrochemically and deposited onto the textile surface.

Electroless plating, also known as chemical or auto-catalytic plating, is a plating method that does not involve the use of external electric energy. It involves several simultaneous chemical reactions in an aqueous solution to reduce metallic ions to metal on non-conductive textile materials. Electroless plating can be performed by autocatalytic plating or ion exchange plating depending on the metal to be coated.

Metal-coated textile materials are breathable and lightweight compared with metal fibre fabrics. Their electrical conductivity can be tailored by controlling the coating thickness and choosing the right metals. They provide functions such as antistatic properties, shielding against EMI and radiofrequency interference, conducting electricity and presenting a brilliant decorative effect. The conductive fabrics can be used by the military for camouflage applications. As some metals resist microbial attacks, metal coated textiles are good materials for antimicrobial applications, such as wall coverings and barrier curtains. Non-conductive yarns and fabrics chemically coated with gold or silver nanoparticles also offer very high levels of electrical conductivity and silver metallised fabrics are ideal for making fabric circuitry. Metallised fabrics can also be used in protective clothing for protection against intense radiant heat, as textile surface coated with aluminium provides a high degree of heat reflection.

Wei et al. (2008) reported that copper sputter coating on the surfaces of polypropylene (PP) nonwovens reduced the surface electrical resistance significantly, and the resistance decreased as the coating thickness increased. Tested at 1 cm longitudinal intervals, a 20 nm coating can give a surface resistance of about 157 Ω, and a 100 nm coating reduces the resistance to below 8 Ω on average. Gan et al. (2008) coated polyethylene terephthalate (PET) fabrics with Cu–Ni–P alloy using the electroless plating method, and demonstrated that the plating parameters affect the properties of alloy-coated fabrics. Conductive fabrics with high EMI shielding effectiveness could be prepared at an optimum condition. A Cu–Ni–P alloy deposit weight of 40 g/m² produced a shielding effectiveness of more than 85 dB over the 100 MHz to 20 GHz frequency range.

For electronic equipment and wiring in aeronautics and space applications, low weight, improved flexibility and high strength are paramount. With electronics confined to small spaces and subject to severe stress, copper wire is prone to break (Slenisky and Walz 2006). A hybrid metal–polymer filament can replace copper wire for signal wiring. The polymer wire is manufactured by covering a high performance polymer filament such as PBO (poly-phenylene benzobisoxazole), which has a tensile strength
higher than 7 GPa and decomposition temperature in excess of 600°C (Hearle 2001), with a metallised coating (nickel, copper, silver or gold), resulting in an electro-conductive and yet flexible polymer/metal hybrid yarn. The polymer wire is more than two times stronger and seven times more resistant to dynamic cut-through at high temperature (200°C), and approximately 27% lighter than the current comparable size of state-of-the-art high strength CS-95 beryllium–copper alloy wire (Lee et al. 2005). Although the conductive PBO yarn shows 67% the electrical conductivity of beryllium–copper, it can carry 9 A of current for over 5 minutes without failure. The polymer–metal hybrid wires would increase the life and reduce the maintenance costs of commercial and military aircraft and spacecraft. Compared with the tin-plated beryllium copper, the PBO conductor shield RG393 cables showed very similar shielding effectiveness over the frequency ranged from 0.1 to 10 GHz (Fig. 6.1). It is expected that the metallised fibres will have many potential applications where conductive properties are required and low weight, durability and flexibility are of critical importance.

6.3.2 Conducting polymer-coated textiles

Conducting polymers are polymeric materials that conduct electricity. They combine the electronic characteristics of metals or semiconductors with the engineering properties of polymers, hence are often referred to as 'synthetic metals'. Electroconductive polymers have attracted a great deal of interest because of their unusual electrical properties. The sensitivity of electrical properties to external effects such as radiation, temperature and chemicals makes these polymers candidate materials for various applications includ-
Conductive coatings for textiles

...ing static electric charge dissipation (Lekpittaya et al. 2004), gas sensors (Kincal et al. 1998), biomechanical sensors (Wu et al. 2005), electrotherapy (Oh et al. 2003; Kim et al. 2004b), heating devices (Boutrois et al. 1997; Håkansson et al. 2004; Bhat et al. 2006), microwave attenuation (Kuhn et al. 1995), EMI shielding (Kaynak 1996; Kim et al. 2002; Håkansson et al. 2006, 2007), electronic textiles (Carpi and De Rossi 2005) and recovery of precious metals (Wang et al. 2007; Ding et al. 2008). Even though melt spinning of electroconductive fibres is possible by blending up to 40 wt% polypyrrole with polypropylene, the conductivity of resultant filament is only $2.88 \times 10^{-7}$ S/cm (Kim et al. 2004a), which is several orders lower than a desired conductive fibre. Coating conducting polymers onto fibres and fabrics results in materials which possess good mechanical and structural properties whilst retaining the electrical properties of conducting polymers. As conducting polymer coated textiles have many advantages over metal coated ones, this chapter introduces coating fibre materials with conducting polymers, and highlights some properties of the coated textiles, as well as applications of such conductive materials.

### 6.4 Principles and procedures of conducting polymer coating

As shown in Fig. 6.2, the most commonly used conducting polymers are polypyrrole (PPy), polyaniline (PANI), polythiophene and their derivatives. Of all known conducting polymers, PPy is the most frequently used in the commercial area due to its high electrical conductivity and preparation techniques to form homo-polymers or composites that have optimal mechanical properties. It is also one of the most suitable conducting polymers for textile coating. Therefore, PPy is the focus of this chapter.

A thin PPy film can be formed on fabrics by an electrochemical polymerisation process, which involves the chemical oxidation of a solution containing the pyrrole monomer and a specific electrolyte salt. This process offers greater control of the resulting polymer thickness, morphology and degree of doping due to the \textit{in situ} deposition of the polymer at the electrode surface. However, the PPy layer can easily be detached from the...
substrates, and electrochemically polymerising conducting polymers onto textiles substrates is not practical for bulk production.

It is common that insulating textile materials are coated with a conducting polymer from a diluted solution or through interfacial polymerisation techniques to yield a composite material with a surface conductivity as low as a few ohms per square. Figure 6.3 shows a basic process of making conductive textiles through either a solution polymerisation method or a chemical vapour deposition method. The polymerisation of pyrrole by chemical oxidation usually is achieved in organic solvents or water. From an economic point of view, the large surface associated with fabrics is better handled through conventional dyeing and finishing processes. Therefore, for textile conductive coating, polymerisation in water is usually preferred, though coating in solvents may produce better products. After polymerisation, the coated material should be thoroughly rinsed to remove excess deposition and oxidants from the fibre surface. Further treatment may be conducted to improve the coating stability.

An aqueous method of conductive textiles coating can be achieved by either in situ polymerisation or two step polymerisation. When in situ polymerisation is employed, fibre materials and all the reagents are added at the same time. Chemical polymerisation occurs in the bulk of the solution, and the resulting polymers either deposit spontaneously on the surface of the immersed fibre materials in the polymerisation solution, or precipitate as insoluble solids. For a better coating result, it is desirable to deposit the bulk polymerisation on fibre surface as much as possible. This can be usually achieved by choosing an optimal reaction condition, like the reactant’s concentration and ratio, reaction temperature, and an appropriate treatment of the material surface to be coated (Kaynak et al. 2002; Hosseini and Pairovi 2005; Beneventi et al. 2006).

In two-step polymerisation, fibre materials first adsorb certain reagents, and then begin polymerisation with the addition of the rest of reagents. In the first step, the textiles are normally subjected to heating, agitation, ultrasonic vibration or padding treatment to promote the penetration of the reagents into the textile structure. As the surface to be coated is enriched either with a monomer or an oxidising agent, a distinct advantage of this process is that the polymerisation occurs almost exclusively at the surface and possibly inside the fibre structure. However, this process may not suit some textile materials that cannot be sufficiently enriched with a layer of either monomer or oxidant in a separate stage preceding the
surface polymerisation. Regardless, this method is more popular than *in situ* polymerisation.

Coating fibre materials with PPY has been widely reported in the literature. PPY is produced by the polymerisation of the pyrrole monomer with chemical oxidants, such as FeCl₃. Figure 6.4 shows schematically the process of oxidative polymerisation of pyrrole. First an electron is withdrawn from the pyrrole monomer by an oxidant, followed by the recombination of two radical pyrrole monomers to a dimer. The electron withdrawing step is repeated at the dimers with the subsequent growing of the chain to a polymer, yielding consecutively PPY as the end product of oxidative polymerisation (Malinauskas 2001).

The electrical conductivity of conducting polymer involves the movement of charge carriers along polymer chains and hopping between polymer chains. The intra-chain charge transfer occurs when there is a rearrangement in the polymer chain producing the charge carriers, and an inter-chain charge transfer occurs between neighbouring polymer chains. The charge transfer allows the movement of electrons to occur over a larger distance (Bredas and Street 1985). It is generally believed that the electrical resistance of intra-chain hopping is much greater than that of inter-chain transport, as the conducting polymer film/coating is an aggregation of nano-conducting polymer particles (Fig. 6.5).

When in the reduced form, dopants influence the conductivity by modulation. Doping is the creation of defects in the structure of polymer without destroying the chain. These defects in the polymer, which can be radicals, anions, cations or combinations of these, are the charge carriers. High electrical conductivity can be achieved by doping the conductive polymer with an appropriate dopant (Lekpittaya* et al.* 2004), for example, polymerisation in the presence of a sulphonate dopant yields better conductivity. Owing to the numerous types of conducting polymers and their vast molecular differences, simple modifications of the monomers or specific polymerisation conditions allow the conducting polymer coated textiles to suit different applications.
PPy shows good affinity with both natural and manufactured fibres. Textile substrates can be easily covered with a PPy layer by immersing them in a solution containing pyrrole, an oxidant and a doping agent. As polymerisation occurs in the solution, insoluble PPy polymers are deposited onto the fibre surface as shown in Fig. 6.6. The physical properties and mechanical properties of the conductive textiles may be affected by monomers, dopant anions, oxidants and synthesis parameters such as time, temperature, pH and liquor circulation in the coating vessel. During the process of the chemical oxidative polymerisation, there are usually visible changes in the colour of the polymerisation solution, and the precipitation of a dark blue or black solid polymer. Hence, the coated textile materials normally have a dark shade.

Conducting polymer coating can be conducted in the presence of excess dyes and conductive textiles with a certain colour can be produced (Kaynak

6.5 Polypyrrole powder obtained by *in situ* polymer precipitation.

6.6 Conducting polypyrrole coated polyester fabric (left) and excessive deposits of polypyrrole on polyester fibre during *in situ* polymerization (right).
Certain dye molecules can be substituted as dopant anions and hence contribute to the improvement of electrical conductivity to the polymer. At the same time, dyes impart colour to the substrates, but the resultant colour will be darker than what the dye recipe intended. The coating procedure depends on the conductivity and colour of the coated fabric. It is recommended that fabric substrates be scoured before coating. Figure 6.7 shows an example of coating PPy onto scoured polyester fabrics. The advantage of adding monomer and dopant at the start of dyeing is to allow them to migrate into the fibres, enhancing the adhesion between fibres and PPy. The polymerisation is performed at a low temperature to minimise the formation of side products that inhibit the continuation and completion of the polymerisation reaction. This coating procedure can easily be achieved with conventional dyeing facilities. It could produce dark coloured conductive fabrics with a surface resistivity of as low as hundreds ohms per square.

Chemical vapour deposition (CVD) is another method for conducting polymer coating. This method involves two steps for PPy coating to produce electroconductive composites. The first step is impregnating a fabric with an oxidant and a doping agent and then drying it. The second step is applying pyrrole vapour to the oxidant pre-loaded surface/substrate, yielding conducting polymer coated composite material. Kaynak et al. (2006) immersed a dyed wool fabric into a FeCl$_3$/ethanol solution and dried at 20°C for 10 min, followed by exposing the treated fabric to a pyrrole/nitrogen vapour for 3 minutes. The finished fabric has a surface resistance of 1.2 kΩ/□.

The vapour deposition process is economical, and allows the recovery of the dopant and oxidant solutions, as well as the unreacted monomer (Dall’Acqua et al. 2006). Vapour phase coated fabrics show a highly uniform coating on the fibre surface, as the dopant and oxidant have been applied evenly on the fibre surface where the polymerisation occurs. This process generates nanoparticles with less aggregation, which maximises the surface area coverage and causes greater contact between polymer chains, thus resulting in a net increase in conductivity compared with aqueous coating for the same level of weight gain of conducting polymer.
6.5 Substrates for conductive coating

In the literature, a wide variety of materials were coated with a thin layer of conducting polymer, and pyrrole, aniline and a number of oxidants were commonly involved in the polymerisation. Among these materials, many types of fibres have been attempted for producing conducting textiles, including polyester (Kincal et al. 1998; Kim et al. 2002; Håkansson et al. 2004; Lekpittaya et al. 2004; Lin et al. 2005; Molina et al. 2008), nylon (Oh et al. 2003; Wu et al. 2005; Ferrero et al. 2006), Lycra (Wu et al. 2005), nylon–Lycra (Håkansson et al. 2007), cotton (Lekpittaya et al. 2004; Hosseini and Pairovi 2005; Bhat et al. 2006; Varesano et al. 2009), wool (Bhadani et al. 1997; Wang et al. 2005), silk (Bhadani et al. 1997; Hosseini and Pairovi 2005; Boschi et al. 2008), cellulose derivatives (Dall’Acqua et al. 2004, 2006; Beneventi et al. 2006), polyaramide (Gasana et al. 2006) and glass (Genies et al. 1991; Kincal et al. 1998), as well as biomaterials (George et al. 2005; Ponce de Leon et al. 2008). All these materials have an affinity for conducting polymers, and a conducting polymer coating permits the production of composite textiles with improved electrical properties. The conductivity of the composite materials depends on the nature of the fibres and the coating procedure. The fibre selection may be determined by the intended applications and desired properties of the coated materials. For example, a conducting polymer coated polyaramide woven substrate has excellent mechanical properties and thermal resistivity.

The bonding between conducting polymers and fibres determines the tendency for the coating to delaminate. Animal fibres may be a better choice as a substrate material for conducting polymers to attach to its surface due to the abundance of functional groups, to which the polymer molecules and dopant anion can attach themselves through ionic hydrogen and even bonds. Moreover, the scalar surface morphology of wool fibres offers sites for adsorption of the conducting polymer. When polypyrrole was chemically polymerised onto wool fibres and polyester monofilaments under the same coating conditions, the adhesion of the coating layer to the wool surface improved considerably; in particular, wool has better conducting polymer coverage as polyester surface is smooth and has poor adhesion to the conducting polymer. Tavanai and Kaynak (2007) reported that the amount of deposited polypyrrole on the surface of PET fabrics increased as a result of the rough surface topology obtained by weight reduction through aqueous sodium hydroxide treatment. Hence fibre surface morphology affects coating performance.

The process of adsorption of pyrrole at the substrate–liquid interface dictates the resulting structure of PPy. The carboxyl groups on nylon backbones can provide a template for pyrrole monomers via hydrogen bonds, which yield a higher ordered and coherent PPy (Martin 1994). Lee and
Hong (2000) suggested that nylon polymer backbone provides a higher affinity to pyrrole monomers, and thus was accountable for its higher conductivity and superior adhesion.

6.6 Testing of conductive coatings

6.6.1 Conductivity

It is ideal that conductive textiles have adjustable electrical properties and maintain those properties while being used. The electrical characterisation of the conductive composites is usually carried out by DC electrical conductivity measurements according to a standard, or a modified method based on the standard. The conductivities of conducting polymer films can be determined by the four-probe technique (ASTM test method D4496). The technique employs four equally spaced electrical contact points on a line with a polymer film on an insulating surface. Between the outer pair of these points, a constant current is applied while the potential difference arising from this current is measured at the two inner contacts. The conductivity ($\sigma$) can be calculated from the constant current ($I$, ampere) across the two outer points, the voltage drop ($V$, volt) across the two inner points, and the sample thickness ($t$) according to the following equation:

$$\sigma = \frac{\ln 2}{\pi t} \frac{I}{V}$$

The resistance of a fibre, yarn or narrow strip fibre materials over a given length may be measured with the four-probe method, or using the fundamentals of a division measurement over a known resistor and an unknown one (the sample). It can also be simply measured with a multimeter. The resistivity is normally expressed as the resistance per unit length of the test specimen, usually in $\Omega$ cm$^{-1}$. Fibres and yarns are irregular materials and their dimensions vary; the coating thickness of the conducting polymer layer on the fibre materials is not uniform and the fibre contacts to the electrodes at different measuring points are not the same. Because of this the resistance of a fibre or yarn is not proportional to the length of the materials, as shown in Fig. 6.8. Hence, it is often that the conductivity of these materials are characterised as resistance with an indication of distance between the electrodes for resistance measurements.

AATCC Test Method 76 is often used to test the surface resistivity of a conductive fabric. The surface resistivity is expressed as the square resistance, which is the resistance between two measuring points on a piece of fabric, and the unit for which is frequently expressed as $\Omega$ per square ($\Omega/\square$), to emphasise the fact that the resistance measured is independent of the distance apart of the contact points. According to the AATCC Test Method...
The surface resistivity of coated conductive fabric samples can be measured by placing two rectangular copper electrodes on the surface of the fabric specimen, then measuring the electrical resistance \( R \) between the electrodes, or applying a DC voltage \( V \) between the electrodes and recording the current \( I \) as shown in Fig. 6.9. The surface resistivity \( R_s \) can be calculated according to the following formula:

\[
R_s (\Omega/\square) = \frac{W}{D} \cdot R = \frac{W}{D} \cdot \frac{V}{I}
\]

where \( W \) and \( D \) are the width of the conductive sample and the gap distance between the electrodes, respectively. Other methods, such as BS 6524:1984 76-1995, the surface resistivity of coated conductive fabric samples can be measured by placing two rectangular copper electrodes on the surface of the fabric specimen, then measuring the electrical resistance \( R \) between the electrodes, or applying a DC voltage \( V \) between the electrodes and recording the current \( I \) as shown in Fig. 6.9. The surface resistivity \( R_s \) can be calculated according to the following formula:

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R_s (\Omega/\square) = \frac{W}{D} \cdot R = \frac{W}{D} \cdot \frac{V}{I}
\]

where \( W \) and \( D \) are the width of the conductive sample and the gap distance between the electrodes, respectively. Other methods, such as BS 6524:1984
method for determination of the surface resistivity of a textile fabric and ASTM D257-07 standard test methods for DC resistance or conductance of insulating materials, may also be used.

Gasana et al. (2006) have observed that the electrical conductivity of PPy coated polyaramide fabrics depends on current signals. The fabrics have a higher conductivity when alternating current signals were applied than the direct currents. This is because the mechanism of charge transport in PPy is electron hopping rather than electron conducting (Sato et al. 1991; Abthagir and Saraswathi 2004). The end user of conducting polymer coated fabrics should be aware that in most publications the electrical conductivity or resistivity was measured under DC power supply. The electrical properties may be different for AC signal applications.

6.6.2 Coating thickness

Coating thickness and evenness affect the electrical properties of the coated material. Uneven coating will have a lowering effect on the DC conductivity while thicker polymer coating will normally lead to a higher conductivity and better electromagnetic attenuation. The coating thickness may be determined from a transmission electron microscopy (TEM) image (as shown in Fig. 6.10) of the cross-section of the coated fibre, which was further coated with gold vapour before it was embedded in resin. Although TEM is a direct and a more precise way of measuring the coating thickness, the scope of TEM images is too small, and TEM imaging is too expensive to get a meaningful statistical result. To quickly estimate the coating thickness...
thickness, commercial instruments for fibre diameter measurement such as Laserscan or OFDA (optical-based fibre diameter analyser) instrument may be used to measure and compare the mean fibre diameter before and after coating.

Through OFDA measurements, Lin et al. (2005) revealed that the thickness of PPy coating on PET fabrics increases with pyrrole concentration and the PPy deposition is faster at low pyrrole concentrations than high pyrrole concentrations, as shown in Fig. 6.11. Coating thickness can also be controlled by coating time. Shorter deposition times lead to a thin inhomogeneous coating layer and poor surface coverage. Longer deposition times will improve the surface coverage and increase the coating thickness. To further thicken the coating layer, a coated substrate may be coated repeatedly, allowing more conducting polymer to attach to the fibre surface. However, there is a limitation to improving the conductivity of heavily coated textiles, and thick conducting polymer coating will reduce the flexibility of the substrate.

It is worth noting that the vapour phase polymerisation shown in Fig. 6.10 took place from the exterior to the core. The diffusion and the polymerisation of pyrrole into the fibre core are slow and inhomogeneous because of the obstruction of the already present polymer. Nevertheless, the coating thickness is just an indication of polymer add-on to the fibre. To determine the actual amount of conducting polymer attached to the fibre/fabric, weight gain after coating may be used.

6.11 Effect of pyrrole concentration on the coating thickness during aqueous polypyrrole polymerisation (the molar ratio of the monomer, dopant and oxidant (FeCl₃) was 1:0.6:2.5).
6.6.3 Coating fastness evaluation

It is important that conductive textiles not only have the desired electrical conductivity properties, but also acceptable quality characteristics, as well as the durability to retain acceptable conducting performance during deployment. Coatings are subjected to heat stress when they are conducting electricity, resulting in thermal expansion between the coating and substrate. Thus, the coating material should exhibit high ductility so that it is able to expand and contract without cracking or delaminating. When used as apparel materials, it is inevitable that the electronic textiles will be subjected to laundry and abrasion. The coatings may also be subjected to polymer degradation and ageing, which may result in significant loss of conductivity, and reduction of the material’s effective service life. It is essential to evaluate the fastness of the conductive layer as well as the effect of conducting coating on textile performance for some applications.

The coating fastness can be simply evaluated with abrasion and washing assays, and the textile industry standards or similar procedures specified in the standards may be followed. Changes in conductivity, colour and surface morphology are usually tested as well. The Martindale abrasion tester has been reported for abrasion resistance measurements. By abrading a 38 mm diameter conductively coated fabric sample against an abradant fabric for a number of specified cycles under a given pressure, the differences before and after abrasion can be used to quantitatively specify the abrasion fastness of the coated samples. Washing fastness, lightfastness, colourfastness, thermal stability, etc. may also be determined using their respective textile standards, or modified versions.

6.7 Properties of conducting polymer coated textiles

Conducting polymer coating not only changes the material’s conductivity but also modified its physical, chemical and mechanical properties, which are important to the end products. In general, apart from imparting electrical conductivity, the negative impact of conducting polymer textile coating on other properties should be minimised.

6.7.1 Electrical conductivity and antistatic performance

Antistatic materials exhibit a conductivity in between not conductive and conductive, which is sufficient to eliminate or at least to diminish static charging. Conventional textile fibres are non-conductive materials and can easily accumulate charges, which could produce sparks to ignite flammable gases and vapours (Wilson 1977; Kathirgamanathan et al. 2000). Dissipating
the electrostatic charges deposited on textile products will prevent these risks. Conventional textile fabrics, such as wool, cotton and polyester, have a surface resistivity of more than $10^9\ \Omega/\square$, and are thus non-conductive materials. To make them antistatic materials for dissipation of static charge, they need to increase the conductivity to an adequate level.

To demonstrate antistatic performance, PPy was chemically synthesised on fabrics to produce conductive textiles. Three pairs of coated and uncoated fabrics as listed in Table 6.1 were evaluated for electrical performance. The results in Table 6.1 show that uncoated fabrics do not have a measurable conductivity (their surface resistivity exceeded $10^9\ \Omega/\square$), while fabrics coated with PPy can easily achieve a conductivity in the $k\Omega/\square$ region, reducing the static voltages by several orders, though fabric constituents (such as fibre used, fabric thickness and weight) may affect the electroconductive effectiveness.

The surface resistivity of a PPy coated fabric can be reduced below $20\ \Omega/\square$ by using optimised synthesis parameters for chemical polymerisation. Therefore, coating textiles with conducting polymers is an easy approach for many antistatic applications, as conducting polymer coating can be simply carried out using most dyeing machines.

### Table 6.1 Fabric information and electrical performance

<table>
<thead>
<tr>
<th>Fabric sample</th>
<th>Thickness (mm)</th>
<th>Weight (g/m²)</th>
<th>Coating</th>
<th>Surface resistivity (kΩ/□)</th>
<th>Static voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45% wool–55% polyester</td>
<td>0.49</td>
<td>170</td>
<td>No</td>
<td>$\infty$</td>
<td>10000</td>
</tr>
<tr>
<td>100% wool</td>
<td>1.05</td>
<td>300</td>
<td>Yes</td>
<td>33.3</td>
<td>110</td>
</tr>
<tr>
<td>80% wool–20% polyester</td>
<td>0.45</td>
<td>225</td>
<td>Yes</td>
<td>6.0</td>
<td>30</td>
</tr>
</tbody>
</table>

#### 6.7.2 Frictional properties

Coating causes conducting polymer nanoparticles to cover and smooth the fibre surface, which tends to reduce the coefficient of friction of the fibres that have a rough morphology. Wang et al. (2005) examined the effects of conducting polymer coating on the fibre frictional properties of wool and alpaca fibres. They coated the fibres with conducting PPy by vapour polymerisation, and measured the degree of fibre friction. The changes in coefficient of friction of the single fibres upon coating with the conducting polymer are presented in Fig. 6.12. It can be seen that the coefficient of friction is statistically significant between coated and uncoated fibres; con-
Conductive polymer coating decreases the coefficient of friction. This is because the conducting polymer coating layer partially covers the scales and forms a transition hump at the scale tips, which smooths the fibre surface.

The conducting polymer coating also reduces the directional friction effect (DFE) of wool and alpaca fibres as shown in Fig. 6.13. This also suggests that the conducting polymer coating layer smooths the surface of animal fibres.

6.7.3 Durability

The electrochemical stability of organic conductors is crucial especially when being used in electro-driven devices. Coating durability affects the service life of conductive textiles, as any loss of conductivity will alter the application effectiveness, in particular in situations where the electrical resistance of the conductive materials is required to be in a defined range. Figure 6.14 shows that the tested conductive specimens have poor abrasion.
6.13 Directional friction effect of vapour coating on the wool and alpaca fibres.

6.14 (a) Change of fabric colour due to 2000 cycles abrasion under 9 kPa of pressure using a Martindale abrasion tester. (b) Detachment of conducting polypyrrole layer after laundering.

performance. The coated fabrics were obtained from a two step polymerisation process. After 2000 cycles of the Martindale abrasion test, the black conducting polymer coated fabric became lighter and the conductivity in the abraded area decreased by approximately 26%. Also due to abrasion, weak bond formation between conducting polymer and fibre, and possible hygral expansion difference in moist conditions, the conducting polymer coating layer was partially removed during washing.

Huang and Liu (2006) reported a method of producing polyaniline/PET conductive composite fabrics using a multi-stage polymerisation process. They repeatedly immersed the PET fabrics in a 0.75 m solution of aniline monomer in 1 m hydrochloric acid, padded and dried the fabrics. They then
initiated the polymerisation by immersion of the fabrics in a 0.17 m oxidant solution containing 1 m HCl, squeezed the fabrics with a padder and allowed the polymerisation at ambient temperature for some time. They further washed the composite fabrics with a 1 m HCl solution and then with distilled water; doped the dried fabrics with a 1 m aqueous solution of dodecylbenzene sulphonic acid (DBSA) as secondary dopant with ethanol as a cosolvent for 20 min; followed by rinsing and drying. They claimed that such method improved the coating fastness to washing. Their results in Fig. 6.15 show that the surface resistivity of most PANI/PET composite fabrics increased 10 to several hundreds of times after repeated machine washing at 40 °C. Even for the best performed conductive fabrics they produced, the increase in resistance was at least five times. This suggests that the
washfastness of conducting polymer coated fabrics is one of the major problems that hinder them from successful commercialisation.

For the coated conductive fabrics that are subjected to severe abrasion and washing during deployment, advanced coating methods may be used to improve the abrasion performance (Tessier et al. 2000; Garg et al. 2007). Surface treatment techniques can increase the fibre surface energy and enhance binding interaction between the conducting polymer and the fibre. Adequate chemical uptake and adhesion before coating can change the fibre wettability and surface texture, and generate cross-linking radicals. The presence of free radicals induces secondary reactions, enabling the deposition of solid polymeric materials with desired properties onto the substrates. Garg et al. (2007) demonstrated that atmospheric plasma glow discharge treated fabrics exhibit better hydrophilicity and increased surface energy. Plasma treatment is able to improve the ability of the substrate to bond with conducting PPy coating, resulting in better coating uniformity, abrasion resistance and conductivity.

When in use, the surface resistivity of a PPy coated fabric increases with time, as shown in Fig. 6.16. This change is almost linear for this instance. Hence, the surface resistivity of the conductive fabric may be predicted while in service, which gives a fair indication of the service life of the conducting polymer coated fabric-based electronic system.

It should be mentioned that the conductivity decay of the PPy coated fabrics will accelerate under elevated temperatures. Since the mechanism of conductivity degradation involves the diffusion or reaction of oxygen, an inert atmosphere will lower the rate of the conductivity loss compared with air, and the stability of the coatings can be dramatically improved by coating an encapsulating barrier, which isolates the conducting polymer from atmospheric oxygen (Kuhn et al. 1995). For example, to prevent the
oxidation of conductive textiles prepared with PPy coating, silicon-based coatings (polydimethylsiloxane oil) can be applied to minimise direct air contact after polymerisation (Dall’Acqua et al. 2006). The encapsulating barrier improves not only the electrical stability but also the washfastness of conductive coatings.

Conductivity decay is also due to the loss of charge carriers on the polymer backbone. Lee and Hong (2000) revealed that the exchanged counterions can stabilise the conjugated chains of PPy and local charge carriers against electrochemical oxidation. Using diluted acid can confer a coinciding structural enhancement. Such a stabilisation method may be achieved through product care, such as washing.

For high levels of fastness to washing, polymerisation may take place in the internal fibre structure. Dall’Acqua et al. (2004) applied monomer and reagents to a cellulose substrate in an aqueous solution so that it penetrates uniformly into the core of the fibre as it swells similarly to a non-reactive dye. Therefore, subsequent polymerisation occurred inside the fibre, leading to improved washfastness and lightfastness (Dall’Acqua et al. 2006).

6.7.4 Tensile properties

Coating methods and substrates used affect the mechanical properties of coated fabrics. Dall’Acqua et al. (2006) evaluated pure viscose fabrics coated with PPy in vapour phase and two-step liquid phase polymerisation respectively. For vapour polymerisation, they impregnated the fabrics in aqueous solution containing both oxidant and dopant for 1 hour, dried the treated fabric for 24 hours at room temperature, followed by exposing the fabric to pyrrole vapour for 8 hours. To coat fabrics by aqueous polymerisation, they soaked the fabrics in catalyst and dopant aqueous solution for only 30 min, then added pyrrole for polymerisation. The tensile testing results in Fig. 6.17 show that the strength and elongation at break of the fabrics dropped significantly for the vapour phase coated fabrics, while the change for the liquid phase polymerisation fabrics was relative small. This is because the FeCl₃ oxidises the cellulose structure more effectively in vapour phase coating than in liquid phase coating. The mechanical properties of vapour phase coating samples sharply decreased by the long time treatment of oxidant and increased concentration of catalyst after drying, which damaged the fabric from the oxidation reaction.

Polymerisation mainly occurs at the outermost layer of the fibre substrate. Thus, coating of conducting polymer on fibres, filaments, yarns and fabrics should not lead to very significant changes in their tensile properties if the damage of oxidant to fibre is negligible. In most cases, coating may enhance material mechanical properties. Figure 6.18 shows an example. Conducting polymer coating on wool fibres and yarns improved the
tenacity and breaking elongation of the fibre materials. This is attributed to the modification of the surface morphology of the wool fibres by the deposition of PPy. The thin layer of conducting polymer has a reinforcing effect. The reduction in the initial modulus of the yarns upon PPy coating may be attributed to the change of frictional properties of wool fibres due to coating (Fig. 6.12).

Evaluation of a wide range of fibre materials suggested that the use of a textile substrate represents a convenient method for introducing mechanical strength, flexibility and processability to conducting polymers for practical applications. Fabrics coated with a thin layer of PPy with an optimised procedure have essentially similar mechanical properties as the textile substrate, with minor variations depending on processing conditions and fibre types. Subjective handle assessment has indicated that the tactile properties of the textiles were not significantly affected by a thin coating of conductive PPy, though the coated fabrics tend to be harsher owing to the

![Graph showing change in mechanical properties of polypyrrole coated viscose fabrics](image1)

![Graph showing tensile properties of polypyrrole coated wool fibres and yarns](image2)
brittleness of conducting polymers and possible bonding between fibres. However, a thick coating of PPy caused the fabric to become stiff, resulting in a poor handle.

6.8 Applications of conductive textiles

Conducting electroactive polymers have various application fields such as metallisation of dielectrics, batteries, antistatic coatings, shielding of electromagnetic interferences, sensors and sensor arrays. Using textiles as the substrate materials, a thin conducting polymer coating layer is able to combine both the conductivity and the flexibility. Since the conducting polymers have a comparable degradation lifetime to textile materials, the conductive coated substrates are often employed for engineering conductive textiles. Applications of conductive substrates are varied and numerous. Fabrics coated with PPy can easily achieve high conductivity in the kΩ range. They reduce the static voltages by several orders. Such materials can be used for many antistatic applications. In addition to antistatic applications, they may also have other potential applications such as sensing, heating, EMI shielding, medical and sports gears, microwave filters and absorbers, etc. Some example applications are briefly introduced here.

6.8.1 Electromagnetic interference shielding

EMI can be defined as the impairment of the functioning of an electronic device caused by electromagnetic radiation emanating from other nearby electronic devices. It has been found that strong electromagnetic waves hinder the normal operation of sensitive electronic devices and navigation systems. For instance, some personal electronic devices must be switched off during aeroplane taking off and landing. EMI may also cause health problems for the human body. Therefore, EMI shielding is important to protect people and electronic devices from harmful interference. In addition, the reflection of microwaves can be used to discover and locate certain objects, which has been used as a tool in military intelligence gathering. Materials absorbing microwaves can provide camouflage effects.

In order to reduce EMI, the radiated EMI (disturbance propagated through space) needs to be filtered. When an incident electromagnetic wave reaches a material, it is transmitted partially through the material. The rest of the wave is attenuated by reflection and absorption of the material. The relative shielding efficiency of reflection and absorption is an important determinant of its practical application. The EMI shielded by absorption rather than reflection is more important for most applications at the present time.
Metals or metal coated surfaces possess very high EMI shielding efficiency based on surface reflection, which is not ideal in some applications. On the other hand, textiles coated with electroconductive polymers are capable of not only reflecting but also absorbing the electromagnetic waves and therefore exhibit a significant advantage over the metallic shielding materials. EMI shielding by absorption can be enhanced by changing the electrical conductivities or the dielectric constants of electroconductive polymers (Kaynak 1996; Kim et al. 2002; Håkansson et al. 2006, 2007). In addition to strong absorption to the EMI signals, conducting polymer coated textiles also maintain their excellent permeability to air and moisture. Therefore, flexible conductive textiles have found wide potential applications in military as camouflage material, in industry for shielding EMI and microwaves, and in daily life for blocking electromagnetic waves from electronic appliances such as mobile phones, microphones, microwave ovens and wireless communication devices (Kuhn 1997).

6.8.2 Conductive fabric circuits

Textile-based circuits offer opportunities to deploy sensors and other devices, and create large-area electrical and electronic systems. An outstanding advantage of textile circuits over traditional circuit boards is their flexibility. They can be easily embedded in fabrics and replace conventional printed boards in electronics applications (Locher and Troster 2008). Figure 6.19 demonstrates a facile technique for patterning conducting polymer on a fabric by quenching the polymerisation reaction that occurred in the protected areas (Kaynak et al. 2006). The patterning technique can be used to fabricate patterned electronic circuits for wearable electronic textiles. The conducting pattern has a resolution of about 2 mm. This will allow a margin for chemical migrating along the pattern boundaries and reduce the

![Flow diagram of patterning conductive textiles.](image)
possibility of loose conductive fibres to short the circuit. Therefore, this method best suits a circuit on a large fabric area.

Conducting polymer coating and patterning enable integration of soft circuitry into fabrics, thus eliminating the need for hardwiring and hence increasing flexibility and wearability of the electronic textiles. As conductivity is integrated into the fibre itself, there is no need to incorporate metallic loadings. Figure 6.20 shows an example of applying the technique for a light-emitting diode (LED) display. The LEDs will be lit up when a potential is applied through the fabric conducting areas.

6.8.3 Temperature regulation

Conducting polymer coated fabrics can be used for heat generation. Garments with a heating function are desired in cold outdoor environments to keep the human body warm. The generation of heat is due to resistive heating of the conductive fabric on the passage of a current. Compared with other heating devices, the advantages of the conductive fabrics are their flexibility, softness, temperature homogeneity, low power density on large surfaces and suppleness (Boutrois et al. 1997; Håkansson et al. 2004). They can be sewn up, cut off or pasted on substrates for a large range of applications, such as aircraft de-icing, heating winter sports wear, car seats, gloves, curtains and buildings.

Increasing thermal conductivity is important for wool fabrics used in a warm environment. Wang et al. (2006) reported that by coating wool fabrics with conducting PPy improved the thermal conductivity of the PPy coated fabrics. The PPy coating parameters influenced the thermal conductivity of
the coated wool fabrics. Overall, thermal conductivity increased with the increase of electrical conductivity.

As heat can be simply generated by batteries, active cooling is more of a challenge for thermo-regulating garments than heating. Hu et al. (2005) proposed a concept of cooling with conducting polymer coated fabrics by applying the ‘Peltier effect’. It occurs whenever electrical current flows through two dissimilar conductors; depending on the direction of current flow, the junction of the two conductors will either absorb or release heat. A noticeable amount of temperature difference has been achieved using the conductive PPy coated fabric. This cooling technique is still in its infancy.

6.8.4 Substrates for metal deposition

Using the electroless metal plating method, non-conductive substrates can be deposited with metals. In the deposition process, the metal ions are reduced to metal only on specific areas where catalysts are present. With this method, when an aqueous [Au(III)Cl₄]⁻ gold ion solution is exposed to PPy nanoparticles or passes through PPy-coated fibre substrates, the conductive PPy demonstrates an outstanding ability to reduce the gold ions electrolessly into Au(0) and deposit the Au particles on the substrates (Wang et al. 2007; Ding et al. 2008). This technique can be used for electroless gold recovery as shown in Fig. 6.21. As nanofibres have a large surface area and excellent permeability, PPy-coated electrospun nanofibre membranes can filter out gold from the aqueous solution stream that continuously passes through the membranes. Wang et al. (2007) found that the recovery efficiency of the PPy-coated nanofibre textiles is affected by

![SEM image of polypyrrole coated nanofibre membrane with gold deposits.](image)
the membrane thickness, the permeate flux rate and the $[\text{Au(III)}\text{Cl}_4]^{-}$ concentration. A higher gold recovery yield can be achieved by using a thicker nanofibre membrane or by reducing the solution flux rate.

The metallisation of textile materials also provides functionality of high electrical conductivity. Gasana et al. (2006) found that the conductivity of PPy coated polyaramide fabrics is poor under a DC current. To achieve better conduction, they further coated the PPy coated structures with a layer of metallic copper through electroless deposition. The DC electroconductive polyaramide structures obtained after depositing copper on top of the prior deposited PPy layer showed excellent electroconductive properties, which was comparable with metallic conductivity.

6.9 Conclusions

There are many situations where conventional textile materials are required to conduct electricity. Garments with wearable electronics/devices/systems highlight the applications of such conductive textiles. Many approaches can be used to impart electroconductive properties to conventional textiles, including metallisation, conductive particles inclusion, electroless deposition, electrodeposition and chemical coating. Metallised high performance hybrid polymer yarns can be stronger and lighter than metal wires, and have similar electrical performance as metal fibres, making them an ideal replacement of metal wires for signal wiring and electronic textile applications.

Conducting polymer coated textiles are an economical, flexible and lightweight alternative to traditional conductive materials. By coating textile substrates with conducting polymers, the electrical properties of conducting polymers can be combined with the strength and flexibility of the textile substrates. The brittleness of the conducting polymer coating layer does not have a significant negative impact on the flexibility and handle of coated textile materials. PPy, PANI and polythiophene are the most commonly used polymers for conductive textile coating.

Conducting polymer coating can be easily prepared by either an aqueous method or chemical vapour phase deposition method. The simplest polymerisation process is to mix the fibre materials and all the reagents in one bath at the same time. While the fibre materials are coated with the conducting polymer, the in situ polymerisation process also produces precipitate of insoluble conducting polymer in the polymerisation solution. Two-step polymerisation involves allowing fibre materials to first adsorb certain reagents, before adding the rest of the reagents for polymerisation. This has an advantage in that the polymerisation occurs almost exclusively at the surface and possibly inside the fibre structure. Chemical vapour phase coating is another suitable process to produce electroconductive textiles with low reagents wastes. The coating is highly uniform on the fibre surface.
A desired coating result can usually be achieved by optimising a coating procedure. Conducting polymers can be coated onto a wide range of fibres, yielding new composite materials with a wide range of electrical conductivities. The conductive textiles have numerous potential applications in various fields such as antistatic, fabric circuits, electromagnetic interference shielding, heating and precious metal recovery, though most of the technologies are still at the developmental stage. The conductivity of coated fabrics decreases gradually when in use. In particular, the electrical conductivity drops dramatically when the conductive coating is directly exposed to atmosphere, or is under severe service conditions such as abrasion, washing and high temperature. Though measures can be taken to slow the loss of conductivity, the environmental stability and durability of electrical properties of the conducting polymer coated textiles should be considered when estimating the material service life.

The mechanical properties of conducting polymer coated textiles are affected by the oxidant treatment and polymerisation process. For fibres that are not sensitive to oxidant, the effect of conducting polymer coating is generally small. On the other hand, if the oxidation reaction damages the fibre structure, the mechanical properties of conducting polymer coated textiles will drop accordingly. Conducting PPy coating on animal fibres covers the fibre scales and smooths the fibre surface, resulting in a reduction in the fibre coefficient of friction and directional friction effect.

6.10 References


Conductive coatings for textiles


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Conductive coatings for textiles


Malinauskas, A. (2001), Chemical deposition of conducting polymers, Polymer, 42(9): 3957–3972. DOI: 10.1016/S0032-3861(00)00800-4.


Intelligent breathable coatings and laminates for textile applications

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Abstract: In this chapter, breathable textiles based on passive and active hydrophilic coatings are discussed. The chapter includes an introduction of breathable textiles, their importance and a brief description of methods to make breathable coatings. Usually breathable textiles are made up of hydrophobic microporous coatings and laminates. These coatings tend to show lower water vapor transmission values and therefore do not form the ideal approach for breathability. In contrast, suitably crosslinked hydrophilic polymer-based breathable coatings can provide high water vapor permeability. Further, the use of stimuli-sensitive polymers can have additional benefits in creating environmentally responsive textiles. This chapter covers intelligent breathable coatings for various applications for protective/specialty applications.

Key words: temperature responsive textile, transition temperature, poly(N-tert-butylacrylamide-ran-acrylamide), coated yarn, water vapor transmission rate.

7.1 Introduction: breathable textiles

Breathability is a desirable property for a fabric, especially for all-weather fabrics, which are permeable to water vapor, while showing protection against wind and resistance to rain.1 This allows perspiration to be transmitted from the wearer’s body, making it possible to use these garments in extreme weather conditions.1–4 This property is expressed as ‘water vapor transmission rate’ (WVTR). It is defined as the steady water vapor flow in unit time through unit area of body, normal to specific parallel surfaces, under specific conditions of temperature and humidity at each surface. The value is expressed in number of grams per square meter over a given period of time. Breathable fabrics find application as comfort fabrics in active sportswear, protective fabrics, survival suits, divers’ suits, mountaineering suits and special military clothing. Other areas include tents, transport cargo wraps, and sleeping bag covers.
7.2 Methods of making breathable textiles

There are several approaches to designing a breathable fabric depending on its end use application, such as tightly woven fabric using microfibers, creating membranes based on microporous polymer coating and laminated films, and finally coating of the fabric with solid polymer film. These solid polymers may be of hydrophobic coatings or hydrophilic coatings.

In the past 15 years, tremendous scientific contributions have been made towards the understanding and development of breathable textiles for different end applications. Methods of production of breathable textiles have described in detail in a number of publications.5–10

7.2.1 High density woven textiles

Ventile was the first waterproof breathable fabric developed by the UK Ministry of Defence in the 1940s to protect air crews from the severe conditions of the North Atlantic Ocean. The finest types of long staple cottons were used to design densely woven fabrics. In this fabric, when the surface is wetted with water, the transverse swelling of cotton fibres reduces the size of pores in the fabric. Ventile fabric has a pore size of about 10 μm when dry and 3–4 μm when wet.6 Such densely woven fabrics can also be made from synthetic microfilament yarns. Fabrics made from microfilaments have a soft handle and are windproof, but not truly waterproof as synthetic filaments do not swell on wetting. Hence, these are mostly used in ski clothing where water vapor permeability and windproofing are required rather than water impermeability.

7.2.2 Polymeric coatings

Microporous coatings

Some garments are made water resistant by coating the outer surface with a layer of hydrophobic (‘water hating’) chemical or wax. When water droplets fall onto the fabric they ‘bead’ due to the surface tension of the water, and then roll off. The disadvantage of this method is that the coating can be damaged during repeated washing and flexing.

Microporous coatings can be developed by two methods:

1 The foam made out of aqueous polymer dispersion is pressed after being completely dried.

2 Phase separation to achieve microporous coatings. In this method there are two types of coagulation: (i) wet coagulation – this method involves the precipitation of the coagulated polymer using salts – and (ii) dry coagulation – an emulsion containing solvent and non-solvent is
applied to the textile. During the evaporation of the solvent, the polyurethane will be coagulated in the non-solvent, forming a microporous structure.

**Hydrophilic coatings**

Hydrophilic coatings are achieved by evaporating the solvent in the polyurethane solution, leaving a compact film behind. The water vapor can transmit through the film with the help of hydrophilic groups.

### 7.2.3 Polymeric membranes

A more durable method is to use a waterproof breathable film or ‘membrane’, which lies inside the garment. Socks and gloves incorporate a film in this way. It lies between the inner and outer textile fabrics. The film is both waterproof and breathable, and will never be washed away.

In this chapter, breathable textiles based on passive and active hydrophilic coatings are discussed.

### 7.3 Hydrophilic breathable coatings

Generally, breathable coatings are made up of hydrophobic microporous coatings and laminates having pores of size 0.1–50 μm, which allow the passage of water vapor but resist the liquid water. These micropores are created using any of the various methods\(^{11}\) such as wet-coagulation, phase separation, solvent extraction and mechanical fibrillation. Because of their hydrophobic character, these types of membranes tend to show lower water vapor transmission values and therefore are undesirable.

Mostly, hydrophilic coatings are not highly hydrophilic. They are copolymers of hydrophilic and hydrophobic segments, where hydrophobic moieties provide water resistance property and facilitate adherence of the coating to the substrate, while the hydrophilic part, which is a soft segment, allows the water-vapor permeability.\(^{12-14}\) The absence of open spaces and macro-pores in the coatings/laminates provide protection against wind and water. The chemical structures of the polymer and film thickness are the main determinants of permeability in a monolithic film.\(^{15}\) However, such coatings have limited water vapor transmission.

Different hydrophilic coatings\(^{8,16-23}\) that form a non-porous layer on the fabric are Ucecoat NPU series of UCB Specialty Chemicals/B, Witcoflex/Staycool of Baxenden/GB and Impraperm of Bayer/D, while hydrophilic laminates are Sympatex, BION II and EXCEPOR-U. Hydrophilic coatings have advantages over other kinds of coating in terms of price, simplicity of process and higher production speeds.\(^{24}\)
Hydrophilic films are totally solid, without pores, pinholes, microcracks and other defects. It is therefore physically impossible for droplets of liquid water to pass through. The transmission of water vapor molecules occurs by absorption of water vapor at the surface of higher concentration of the vapors, diffusion through the film (from molecule to molecule) at the rate controlled by the concentration gradient, and desorption at the surface of lower concentration.²⁵ The driving forces are the differences in humidity and temperature between the atmospheres on each side of the film. The internal climate, next to the skin, is hot and humid because the body is generating heat and moisture as it exercises. The external climate is much drier and cooler. Consequently, water vapor is driven from the inside of the garment to the outside. As the skin gets hotter during an activity, so the film becomes more efficient at expelling moisture. The mechanism of breathability is shown in Fig. 7.1.

These membranes are able to achieve varied degree of water vapor permeation and protection. However, the hydrophobic segments are present in significant proportions to obtain required durability and, therefore, WVTR values are sacrificed. Further, many of the coating materials and the additives are toxic.⁵,¹⁶

Therefore there is a need to develop lightweight, durable and functionally efficient coatings to address some of the above concerns. Ideally, a highly hydrophilic system may provide highly efficient vapor transmission properties. Such systems include coatings with poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAAc), poly(ethylene oxide), etc. However, such systems are not used because they are water-soluble and cannot provide durable
coating onto a fabric for normal wash and wear use. Durability has to be imparted by introduction of cross-links. In this chapter, hydrophilic, highly efficient yet durable breathable coatings are discussed. The polymer was covalently bonded to cotton fabric using crosslinking agents. The crosslink density was optimized to provide sufficient integrity to coating while maintaining the necessary hydrophilicity for good water vapor transmission.

7.3.1 Polyacrylamide as a breathable coating on cotton fabric

Polyacrylamide (viscosity average molecular weight of ~420 000 Da) synthesized by free radical polymerization and citric acid was used for coating cotton fabric. The high molecular weight was necessary in order to obtain uniform and mechanically strong coating of the polymer. Citric acid was found to give significant crosslinking among polyacrylamide chains and between polymer chains and hydroxyl group of fabric.

Predetermined quantities of selected crosslinker (citric acid) and catalyst (sodium hypophosphite) were added to the above polyacrylamide solution for coating. Different samples were prepared with single, double and triple coatings and with different crosslinker contents. The crosslinker content was calculated based on desired crosslinking density in the polymer coating. The various samples with different crosslinker content along with the number of coatings and resultant add-ons are described in Table 7.1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Crosslinking density (mol%)</th>
<th>Quantity of crosslinker used (g 100 ml⁻¹)</th>
<th>Number of coats</th>
<th>Coating add-on obtained (wt% of fabric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AMCIT50</td>
<td>50</td>
<td>1.971</td>
<td>Single</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Double</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Triple</td>
<td>29.0</td>
</tr>
<tr>
<td>AMCIT20</td>
<td>20</td>
<td>0.7917</td>
<td>Single</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Double</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Triple</td>
<td>15.0</td>
</tr>
<tr>
<td>AMCIT10</td>
<td>10</td>
<td>0.3947</td>
<td>Single</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Double</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Triple</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Note: Catalyst concentration was kept at 0.3 g per 100 ml of polymer solution samples.
For the single coating, the samples were dried at 90 °C for 6 min, and then cured for ~20 min at 150 °C. For the double and triple coatings, drying was carried out after each application of the coating, while the curing was carried out in the end, i.e. after drying the last coating. The integrity of the coatings was evaluated as a percentage of weight loss of the original add-on after washing. The first wash showed a weight loss of around 20–28% for the samples with high crosslinker concentration of 10–50 mol%. In the second wash, the loss of coating for AMCIT50 and AMCIT20 samples was negligible. The role of crosslinker in providing integrity to the polyacrylamide coating is evident from these results. The negligible loss in the coating after the second wash cycle, suggested that the initial loss in coating material consisted of uncrosslinked low molecular weight polymer and other soluble additives. The resultant coating after the first wash appeared to be permanent.

In a dry coating, the water-soluble catalyst, sodium hypophosphite, forms 5–7% of the total add-on weight. Therefore, about one-fourth of the loss in weight was accounted for by the loss of catalyst alone on washing. Similarly, unreacted citric acid may also be lost during washing accounting for other significant portion of weight loss.

**Hydrostatic head**

The hydrostatic head values for the coated samples are given in Table 7.2. Triple coated fabric samples with high crosslinker concentration gave high values of hydrostatic head. Interestingly, values as high as 1280 mm were

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Hydrostatic head (mm)</th>
<th>WVTR (g m⁻²24 h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As coated</td>
<td>Washed</td>
</tr>
<tr>
<td>Control</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>AMCIT50 triple</td>
<td>1280</td>
<td>800</td>
</tr>
<tr>
<td>AMCIT50 double</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td>AMCIT50 single</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>AMCIT20 triple</td>
<td>1200</td>
<td>680</td>
</tr>
<tr>
<td>AMCIT20 double</td>
<td>800</td>
<td>80</td>
</tr>
<tr>
<td>AMCIT20 single</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>AMCIT10 triple</td>
<td>760</td>
<td>60</td>
</tr>
<tr>
<td>AMCIT10 double</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>AMCIT10 single</td>
<td>120</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 7.2 Hydrostatic head and WVTR values for the samples before and after wash treatment of coated samples
observed for AMCIT50 triple-coated samples. All single coated samples showed a low hydrostatic-head, indicating that sufficient amount of material could not be coated in single application to give a good continuous film. The triple-coated sample with higher amount of polymer on the surface provided good barrier to the water pressure. A higher number of coatings are more likely to form a continuous, defect-free film with good barrier properties. Further, it can be observed from Table 7.2 that the role of the crosslinker in keeping the integrity of the coated film is of prime importance. There was a drastic reduction in the hydrostatic head as the amount of crosslinker was reduced. A crosslinker concentration of at least 20 mol% with triple coating was found to be necessary to provide reasonable resistance to water penetration.

The hydrostatic head values were lower after the samples were washed. The loss of weight of coating appeared to create weak regions in the barrier film, through which water could penetrate at relatively lower pressures.

**Air permeability**

The air permeability values for the coated samples were found to be several orders of magnitude lower than the control (uncoated) fabric sample. This was reduced by about two orders of magnitude for AMCIT50 triple-coated fabric. The air permeability values for coated and coated washed samples are given in Table 7.3. The consistent reduction in the air permeability values as a function of the crosslinker content suggests that the higher crosslink density plays an important role in keeping the continuity of the film. The second factor affecting barrier properties was add-on or number of coatings. The higher add-on values gave better barrier to air penetration as expected.

The air permeability values of the wash samples are also reported in Table 7.3. As expected, the extent of the integrity of the coating had a direct influence on the air permeability values upon washing, suggesting continuous, well-crosslinked coating is important in obtaining good barrier properties.

**Water vapor transmission rate**

The water vapor permeability is not affected significantly even on increasing the coating add-on with polyacrylamide. The AMCIT50 triple-coated sample gave a WVTR value of 2016 g m\(^{-2}\) 24h\(^{-1}\), which was only 23% less than that of the control fabric (2640 g m\(^{-2}\) 24h\(^{-1}\)). In general, it was observed that, as the number of coatings were increased, the WVTR values dropped. This was expected, as the barrier created by the coating was responsible for the lower transmission values of coated samples compared
Table 7.3 Air permeability values of samples before and after washing treatment

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Air permeability values after harsh wash (cm³ cm⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As coated</td>
</tr>
<tr>
<td>Control</td>
<td>249.20</td>
</tr>
<tr>
<td>AMCIT50 triple</td>
<td>1.14</td>
</tr>
<tr>
<td>AMCIT50 double</td>
<td>1.27</td>
</tr>
<tr>
<td>AMCIT50 single</td>
<td>4.20</td>
</tr>
<tr>
<td>AMCIT20 triple</td>
<td>2.17</td>
</tr>
<tr>
<td>AMCIT20 double</td>
<td>3.79</td>
</tr>
<tr>
<td>AMCIT20 single</td>
<td>4.83</td>
</tr>
<tr>
<td>AMCIT10 triple</td>
<td>2.39</td>
</tr>
<tr>
<td>AMCIT10 double</td>
<td>3.51</td>
</tr>
<tr>
<td>AMCIT10 single</td>
<td>85.70</td>
</tr>
</tbody>
</table>

Note: Air permeability values for coated samples measured at pressure of 2400 Pa, and for control sample measured at 200 Pa.

Water vapor transmission tests were also performed on the washed samples. It was observed that although laundering removed around 28% of the coating, the water vapor transmission values were nearly the same. The water vapor transmission values for selected samples before and after washing are given in Table 7.2.

Water vapor permeability tests values reported by different researchers cannot be compared unless determined under identical test conditions. In the literature, the suggested value, as a standard for the water vapor permeability is 2000 g m⁻² 24 h⁻¹ with inverted disk (ASTM E96 B&W), with a hydrostatic head greater than 1500 mm.

Water vapor transmission values for commercial hydrophilic membranes have been reported for hydrophilic membranes following the ASTM E96 B method for evaluation. Sympatex, based on polyester co-block polymer,
with a thickness of 12 μm thick, has been reported to have a value of 2700 g m\(^{-2}\) 24 h\(^{-1}\). Munro, with a value of 1500 g m\(^{-2}\) 24 h\(^{-1}\), is a specialty application membrane, having greater strength and toughness used in the medical applications. Microporous films are based mainly on polytetrafluoroethylene (PTFE) and polyurethane. The Tetratex film based on PTFE gives a value of 1000 g m\(^{-2}\) 24 h\(^{-1}\), as determined by the ASTM E96 B method.\(^1\)

Coatings based on di-block polymer of polyurethane and polyester polyol showed values of 1094 g m\(^{-2}\) 24 h\(^{-1}\) for coating with isophorone block and 1864 g m\(^{-2}\) 24 h\(^{-1}\) with methane diisocyanate block. The samples were tested by the cup method,\(^3\) by evaporation of water using BS 7209:1990. The breathable polyurethane coated nylon fabric samples with water vapor permeability values in the range of 2952–4200 g m\(^{-2}\) 24 h\(^{-1}\) at 90% relative humidity have been reported\(^3\) against a value of 9833 g m\(^{-2}\) 24 h\(^{-1}\) for an uncoated control fabric (58 g m\(^{-2}\) fabric density). This shows a reduction of water vapor permeability by a value of 57–70% due to the application of the polyurethane-based coating. In the present study, the hydrophilic polyacrylamide coated fabrics showed only 5–23% reduction in the water vapor transmission values compared with the values shown by control cotton fabric.

A Gore-tex fabric of density 178 g m\(^{-2}\) investigated by the method described in this study, simultaneously with AMCIT50 Triple coated fabric, was observed to give a 10% lower WVTR value. The air permeability value as compared with AMCIT50 Triple coated fabric stood 56% lower, while the hydrostatic head value for the Gore-tex fabric exceeded 1400 mm, compared with the 1280 mm (value for the AMCIT50 Triple coated fabric).

The considerable retention in the moisture permeability values even on coatings as high as 29% (AMCIT50 triple coated) show that the water molecules diffuse through the coating by binding with the amide pendent groups in polyacrylamide. The dependence of moisture permeability on the number of coatings and the crosslinking density shows that the hydrophilicity of the polyacrylamide coating can be varied by varying the crosslinker content. In a polyacrylamide system, rapid transfer of water is observed due to high hydrophilicity of the polymer although integral coatings could be obtained due to crosslinking by citric acid.

**Increase in stiffness due to application of coating**

Coating led to an increase in the stiffness of the fabrics, which is observed to be related to both the crosslinking density as well as the number of coats. The percentage increase in the stiffness of control fabric (the cotton fabric used in this experiment) is 167.6% in the warp direction, and 162.5% in the weft direction.
The higher increase in the stiffness in the weft direction, as compared with the warp, is expected, since the continuous film is crosslinked evenly irrespective of the machine direction (warp).

The combination of Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) and solubility studies\textsuperscript{30} confirm the crosslinking in polyacrylamide through condensation. The results offer potential for the application of such carboxylic acids for coating of acrylamide on cotton and also explain the improved durability of such coatings.

7.3.2 Polyvinyl alcohol-based breathable textiles

As discussed above, highly hydrophilic poly(acrylamide) was used to develop good breathable fabrics.\textsuperscript{30} This polymer coating was chemically integrated onto a cotton fabric using polycarboxylic acid compounds, such as citric acid, as crosslinkers and sodium hypophosphite as a reaction catalyst. This coating provided a high degree of water vapor transmission values along with high level of integration to the cotton substrate. However, only a moderate level of water head protection could be obtained. Additionally, the coated fabrics were stiff when tested in dry condition. These undesirable properties were the result of high glass transition temperature (165 °C) of poly(acrylamide) and its copolymers, due to which the coated films developed microcracks upon washing, giving only a moderate level of water head protection.

The same authors have also reported\textsuperscript{33} breathable cotton fabrics based on an alternate hydrophilic polymer system that could overcome the above-mentioned drawbacks shown by poly(acrylamide). For this, high molecular weight PVA was used as the hydrophilic polymer and was integrated to cotton substrate using a low molecular weight PAAc as a crosslinker.\textsuperscript{34} Using this approach, a hydrophilic coated textile with high level of breathable characteristics could be obtained.

Several coated samples were prepared using the PVA-based coating solutions as described in Table 7.4. The PAAc is reported to act as a crosslinking agent in which its carboxylic groups would condense with the hydroxyl groups of PVA and cellulose to give chemically integrated, highly durable, breathable coatings. The model is schematically shown in Fig. 7.2.

The PVA solution and partially neutralized PAAc solution were mixed at different ratios at 80 °C as given in Table 7.4. The coated fabrics were dried at 90 °C for 10 min, and then cured for 25 min at 160 °C. For double-coated samples, drying was carried out after each application of the coat, and the curing was carried out in the end. The percentage change in the weight of the dried coated fabric over the dried uncoated fabric was referred to as ‘dry coating add-on’ and is given in Table 7.4.
Table 7.4 Details of coated sample

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Total polymer concentration in coating mixture (%)</th>
<th>Molar ratio of PVA to PAAc</th>
<th>Dry coating add-on (wt% of the fabric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA–PAAc1.5/37</td>
<td>20</td>
<td>1.5</td>
<td>37</td>
</tr>
<tr>
<td>PVA–PAAc5.0/48</td>
<td>20</td>
<td>5.0</td>
<td>48</td>
</tr>
<tr>
<td>PVA–PAAc10/41</td>
<td>20</td>
<td>10</td>
<td>41</td>
</tr>
<tr>
<td>PVA–PAAc15/59</td>
<td>20</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td>PVA–PAAc20/66</td>
<td>20</td>
<td>20</td>
<td>66</td>
</tr>
<tr>
<td>PVA–PAAc25/61</td>
<td>20</td>
<td>25</td>
<td>61</td>
</tr>
<tr>
<td>PVA–PAAc30/63</td>
<td>20</td>
<td>30</td>
<td>63</td>
</tr>
<tr>
<td>PVA–PAAc1.5/66</td>
<td>25</td>
<td>1.5</td>
<td>66</td>
</tr>
<tr>
<td>(concentration 25%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA–PAAc1.5/66</td>
<td>30</td>
<td>1.5</td>
<td>66</td>
</tr>
<tr>
<td>(concentration 30%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA–PAAc25/34</td>
<td>20</td>
<td>25</td>
<td>34</td>
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<tr>
<td>PVA–PAAc25/24</td>
<td>20</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>PVA–PAAc25/18</td>
<td>20</td>
<td>25</td>
<td>18</td>
</tr>
</tbody>
</table>

7.2 PVA crosslinked network structure with cotton.
Effect of crosslinker poly(acrylic acid) concentration

In order to determine the minimum amount of carboxylic groups that is required for making a stable wash resistant network of PVA with cellulose, coatings with varying molar ratios of PVA to PAAc were used. The molar ratio of PVA to PAAc was increased from 1.5 to 30. The sample codes can be explained with the help of PVA–PAAc1.5/37. Here 1.5 refers to the molar ratio of PVA to PAAc, while 37 indicated dry coating add-on on the fabric. The dry coating add-on was found to increase as the molar ratio of PVA to PAAc was increased from 1.5 to 30, as given in Table 7.4. This was attributed to the difference in molecular weights of the two polymer components. The fastness to washing or integrity at harsh conditions was determined as per the standard procedure. For all combinations, the coating integrity was found to be excellent except for PVA–PAAc30/63 for which it was a bit lower. Since it was desirable to have higher number of free hydroxyl groups in PVA for facilitating efficient diffusion of water vapors, the PVA to PAAc molar ratios of 25 was determined to be a suitable ratio for making well-integrated breathable structures.

The as-coated as well as the washed samples showed excellent protection against hydrostatic head. The resistance to hydrostatic head in most cases was more than 1460 mm, which was the highest reading obtainable by the instrument (Table 7.5). The number within the bracket indicates the number of droplets that came to the other side of the fabric during the test.

The molar ratio of PVA to PAAc of 1.5 was expected to give at least as good protection against hydrostatic head as other samples. However, owing to the low viscosity of the coating solution at this molar ratio, a good film structure could not be achieved. Coating solutions for this molar ratio at slightly higher total polymer concentration of 25 and 30 wt% (Table 7.6) gave very high resistance to hydrostatic head similar to the samples of other molar ratios.

As given in Tables 7.5 and 7.6, the WVTR values of the washed samples were significantly better than those of the as-coated samples. The reported values of WVTR were attributed the result of the combined effect of crosslinking density as well as the coating thickness.

Effect of coating add-on

The effect of coating add-on on breathable parameters was evaluated by varying add-on values from 18% to 61 wt% for a molar ratio of PVA to PAAc of 25. These coatings also showed good integration to cotton. This is evident from the low weight loss of 2.9 to 5.7% on normal washing for all the samples (Table 7.7).

The harsh wash test, under ISO 4 standard test method, on PVA–PAAc25/34 resulted in a weight loss of 9.6% only. This was slightly more
than the 3.8% obtained in the regular washing conditions (Table 7.5). Weight loss was calculated as the percentages of the coating add-on values of the samples. Subsequent washing did not result in any noticeable loss. This indicated that the coatings were well integrated to the cotton substrate.

The hydrostatic head values for samples were found to be high, suggesting that a good polymer network was formed for all add-ons. Only the sample with add-on value of 18% showed a comparatively lower hydrostatic head value of 1400 mm after washing (Table 7.5).

The air permeability values for the coated samples were found to be several orders of magnitude lower than that of the control uncoated fabric sample. The air permeability value for the control fabric was 140 cm$^3$ cm$^{-2}$ s$^{-1}$. This value was reduced to 0.664 cm$^3$ cm$^{-2}$ s$^{-1}$ for PVA–PAAc25/61 washed
sample. The air permeability values of all samples are given in Table 7.7. The coating add-on of 18% was found to improve the barrier properties sufficiently. The higher add-on values gave only a marginal improvement as mentioned in the table. High barrier properties of the as-coated and washed samples suggested that the coatings were continuous and well integrated to the substrates.

The WVTR increased from 1368 g m\(^{-2}\) 24 h\(^{-1}\) to 2165 g m\(^{-2}\) 24 h\(^{-1}\) as the coating add-on was decreased from 61% to 18% at the molar ratio of 25. The fabric WVTR value of 2165 g m\(^{-2}\) 24 h\(^{-1}\) for 18% add-on is 50% that of uncoated cotton substrate at 4335 g m\(^{-2}\) 24 h\(^{-1}\). The value indicates that the coated fabric had high permeability to water vapor though it had a capacity to provide high protection against water head and air permeability. There was a small difference between the water vapor permeability of the as-coated and the washed samples. Unwashed samples showed relatively lower WVTR values as given in Table 7.7.

The PVA coating increased the stiffness of the resultant fabrics. The bending length value of the coated samples were found to be only moderately higher than the control samples. The percentage increase in bending value of the coated samples in the warp direction was comparatively higher than that of the weft direction. The stiffness of the fabric increased with the increase in the coating add-on. The sample with the coating add-on of 18 wt% showed an increase of 106% and 79% in the bending length value compared with that of the control sample in warp and weft way, respectively. These values were found to be significantly lower than poly(acrylamide)-based breathable fabrics with similar add-ons.\(^{30}\)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Weight loss (%)</th>
<th>Hydrostatic head (mm)</th>
<th>Air permeability (cm(^3) cm(^{-2}) s(^{-1}))</th>
<th>WVTR (g m(^{-2}) 24 h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As coated</td>
<td>washed</td>
<td>As coated</td>
<td>washed</td>
<td>As coated</td>
</tr>
<tr>
<td>Control</td>
<td>–</td>
<td>0</td>
<td>140</td>
<td>4335</td>
</tr>
<tr>
<td>PVA–PAAc25/61</td>
<td>2.9</td>
<td>&gt;1460</td>
<td>&gt;1460</td>
<td>0.530</td>
</tr>
<tr>
<td>PVA–PAAc25/34</td>
<td>3.8</td>
<td>&gt;1460</td>
<td>&gt;1460</td>
<td>0.674</td>
</tr>
<tr>
<td>PVA–PAAc25/24</td>
<td>5.7</td>
<td>&gt;1460</td>
<td>&gt;1460</td>
<td>0.864</td>
</tr>
<tr>
<td>PVA–PAAc25/18</td>
<td>4.6</td>
<td>&gt;1460</td>
<td>1400</td>
<td>1.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Possible mechanism of breathability

The study was aimed at developing nonporous, continuous, breathable coating based on a hydrophilic polymer system. In order to verify the possible mechanism of breathability in these coated fabrics, the hydrophilicity and surface characteristics of the coatings were investigated.

The water retention by the coating is a good indication of the extent of free hydroxyl groups, and thus the hydrophilicity, of the breathable film. The average water retention value of the uncoated control sample after centrifuging was around 9.4% (Table 7.8). The water retention was significantly higher for the coated samples. The increased values indicate that the coatings were highly hydrophilic even after they were crosslinked using polycarboxylic acid.

The samples coated with different mole ratio but with similar add-ons were compared. The water retention value of coated samples with add-on of 66% changed from 36.0% to 62.1% as the molar ratio of PVA to PAAc was changed from 1.5 to 20. The sample with higher molar ratio of 20 showed higher WVTR. Clearly, the increase in mole ratio of PVA to PAAc is able to significantly enhance the availability of a number of hydroxyl groups or hydrophilicity of the coating.

Surface morphology of the as-coated fabric as well as the harsh washed fabrics of PVA–PAAc25/24 and PVA–PAAc25/34 were studied under SEM at the magnification of 100 and 1000 times (Fig. 7.3). The surface features of the as-coated fabric showed that the coating obtained was smooth except for some superficial impressions left from the air bubbles that might be present in the solution during coating.

The film on the sample appeared to be continuous and adhered well to the substrate. There was no indication of micro-cracks or pinholes even after the harsh wash. The high protection against hydrostatic head and air penetration appears to be the result of the formation of a well-integrated continuous film and the high water vapor transmission values are the result of efficient diffusion of water vapors through the highly hydrophilic crosslinked film.

Table 7.8 Water retention values of control and washed samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Water retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 1</td>
<td>9.3</td>
</tr>
<tr>
<td>PVA–PAAc1.5/66</td>
<td>36.0</td>
</tr>
<tr>
<td>PVA–PAAc20/66</td>
<td>62.1</td>
</tr>
<tr>
<td>PVA–PAAc25/17</td>
<td>28.0</td>
</tr>
<tr>
<td>PVA–PAAc25/34</td>
<td>52.7</td>
</tr>
</tbody>
</table>
The above-mentioned approaches (hydrophilic breathable coatings) produce breathability designed to a particular application. These coatings are passive and they do not adapt to changing environmental conditions such as temperature. A breathable fabric with temperature dependent response may be desirable for certain specialized applications where high variations of temperature are encountered over a short period. One of the approaches may be to use stimuli-sensitive polymers (SSP) to develop breathable coatings.

Temperature responsive polymers\textsuperscript{35–42} (or smart polymers) that show a reversible transformation from one state to another as a response to temperature stimulus from the environment provide a big opportunity for creating intelligent materials. In their hydrogel form, they exhibit a rever-

![Scanning electron micrographs of PVA-PAAc25/24](image)

7.3 Scanning electron micrographs of PVA-PAAc25/24: (a) as coated at 100×; (b) as coated at 1000×; (c) harsh washed at 100×; (d) harsh washed at 1000×.

### 7.4 Smart temperature responsive breathable coatings for textile structures

The above-mentioned approaches (hydrophilic breathable coatings) produce breathability designed to a particular application. These coatings are passive and they do not adapt to changing environmental conditions such as temperature. A breathable fabric with temperature dependent response may be desirable for certain specialized applications where high variations of temperature are encountered over a short period. One of the approaches may be to use stimuli-sensitive polymers (SSP) to develop breathable coatings.

Temperature responsive polymers\textsuperscript{35–42} (or smart polymers) that show a reversible transformation from one state to another as a response to temperature stimulus from the environment provide a big opportunity for creating intelligent materials. In their hydrogel form, they exhibit a rever-
sible change from hydrophilic to hydrophobic form at the transition temperature; this lies at the lower critical solution (LCST). The SSPs have both hydrophilic and hydrophobic groups in their structure. For example poly(N-isopropylacrylamide) (PNIPAm) has hydrophobic backbone and a pendant group which has a hydrophilic amide moiety and a hydrophobic isopropyl moiety (Fig. 7.4a). Depending upon which among the hydrophilic or hydrophobic interactions dominate, the polymer exists as an extended chain or a collapsed chain. The transition temperature of the PNIPAm hydrogel is about 33 °C. Below the transition temperature the polymer gel absorbs water and exhibits swelling. An abrupt conformational change occurs from a state of extended chains to a state of coiled chains as the temperature approaches the LCST. As this transformation occurs at a particular temperature and is reversible, the hydrogel becomes useful as an intelligent actuator. The huge difference in water-holding capacity, which transforms reversibly according to the transition temperatures, has the potential of being exploited for different applications. Very recently, these polymers have been used in the form of hydrogels as smart breathable coatings.\textsuperscript{35,43}

7.4 Hydrophilic and hydrophobic moieties in NIPAm polymer.
(b) Chemical structure of copolymer.
The transition temperature can be tuned by

- using additives
- designing monomer Structure
- copolymerization.

Generally, the temperature-sensitive polymers are used in the hydrogel form because these polymers are soluble in water at temperatures below the LCST. The major drawback of SSPs when polymerized in the gel form is their slow response at transition and weak mechanical properties; hence they cannot be applied in thin dimensions. Also, the main challenge is to integrate them chemically and still retain the responsive behaviour.

In order to obtain fast transitions, high functional efficiency and exploit new potential applications, stimuli-sensitive polymer systems have been developed which can be processed into structurally strong and thin desirable shapes. This has been achieved by converting the linear copolymers (containing reactive groups) into desirable shapes and subsequently crosslinking (using suitable crosslinkers) them without adversely affecting the stimuli-sensitive response of the material. The presence of reactive side groups in the monomer has been utilized to introduce crosslinks with the help of polyfunctional crosslinkers. This approach of incorporation of responsive polymers in the form of thin film/coating on reactive flexible substrate provides active polymer layers on top of substrates. Such a structure also results in mechanically strong SSP composites with large surface area.

For this, temperature responsive copolymers based on poly(acrylamide)³⁵,⁴³ were used to develop smart breathable coatings,⁴³ where the breathability changes with the change in environmental temperature (due to a change in the hydrophilicity of coating). The SSP poly(N-tert-butylacrylamide-ran-acrylamide) (NTBA-ran-acrylamide) was coated on a cotton fabric and temperature-dependent breathability was observed.

Recently, the synthesis⁴⁴ and processing⁴⁵ of a series of linear temperature sensitive copolymers of poly(NTBA-ran-acrylamide) into thin films have been reported. A selected copolymer from this series (SSP50 with 27 mol% NTBA) with a sharp transition at 37 °C was used for the purpose of processing into thin films and coating of yarn and fabric to overcome the above-mentioned drawbacks of SSP hydrogels and to develop smart textile materials (Fig. 7.4b). Also, this copolymer has a large fraction of acrylamide side groups desirable for crosslinking and hence was selected for coating. 1,2,3,4-Butanetetracarboxylic acid (BTCA) was found to be an appropriate crosslinking agent for carrying out reactions with amide side groups of the acrylamide moiety. Carboxylic acid was found to condense with amide side groups to form imide linkages. The feasibility of crosslinking polymer chains using amide side groups and polycarboxylic acid crosslinking agents in the presence of catalyst sodium hypophosphite has been established.⁸
7.4.1 Coated yarn structures

The add-on percentage for the coated cotton yarn was found to be 670% with a percentage coefficient of variation (CV%) of 10.73. The integrity of copolymer coating to yarn was found to be excellent. The coated yarns showed no weight loss on either hot or cold washing, suggesting that the polymer chains are chemically bound to the cotton substrate. The good integrity at high add-on of the stimuli-sensitive copolymer on the yarns can be attributed to the penetration of copolymer into the porous structure and crosslinking with the high internal surface area of the spun yarn.

Transition behaviour of coated yarn

The transition behaviour of the coated yarn was studied with respect to temperature of the surrounding water bath. The coated yarn was first conditioned by subjecting it to swelling at low temperature (6 °C) and then its transition behaviour was evaluated by placing the sample in water and measuring the change in yarn diameter with temperature. The diameter was also measured after keeping the yarn for 5 min which is sufficient for attaining the equilibrium swelling at any temperature. The swelling percentage was calculated on the basis of change in diameter using the following equation:

\[
\text{Volumetric swelling (\%)} = \left( \frac{d_{\text{scy}}^2 - d_{\text{yarn}}^2}{d_{\text{dcy}}^2 - d_{\text{yarn}}^2} \right) \times 100
\]

where \(d_{\text{scy}}\) is the mean diameter of swollen coated yarn; \(d_{\text{dcy}}\) the mean diameter of dry coated yarn; and \(d_{\text{yarn}}\) the mean diameter of dry yarn. The diameter values were measured in μm at ten different places along the length of the yarn.

Both the swelling and deswelling behaviour were studied to determine hysteresis. The rate of transition during swelling and deswelling was studied by observing the change in diameter of the sample with time after the sample was subjected to 6 °C for swelling and 80 °C for deswelling. The yarn shows volumetric swelling of 4500% at 6 °C and collapse to a swelling percentage of 800 at 80 °C.

Figure 7.5 shows a clear transition in the temperature range 15–35 °C with a mean transition temperature of about 25 °C. When the coated yarn was subjected to deswelling, the deswelling curve with temperature followed the swelling curve with a small hysteresis. The transition was found to be reversible to repeated swelling and deswelling cycles. The rate of swelling and deswelling of the coated yarn was studied to understand the dynamics of transition. During swelling, equilibrium was achieved within 5 min (Fig. 7.6), while during deswelling equilibrium was attained in less than 10 s.
The transition observed in coated yarn was broader than that observed in pure copolymer thin films or gel disks, showing a sharp transition at 21 and 37 °C respectively. The broad transition may be a result of localized heterogeneity in the crosslink density of the coated yarn structure. The shift in transition temperature of processed linear copolymers (21–25 °C in coated yarns and thin films) using crosslinker compared to polymerized gel disk (37 °C) is due to the decrease in hydrophilicity of the copolymer on processing. The decrease in hydrophilicity is caused by the decrease in number of amide groups as some of these are used in the crosslinking reaction.

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Alternate methods for integration of stimuli-sensitive polymers to textile substrate or films have been reported in the recent literature. PNIPAm has been integrated to cotton fabric/substrate by radiation grafting.\textsuperscript{46,47} Similarly, integration has been carried out using photo irradiated grafting (@ $\lambda < 300$ nm).\textsuperscript{48–50} In all these cases, the transitions of the integrated PNIPAm remains similar to the pure PNIPAm; however, it is shown to become significantly broad over a wide temperature range.

\textit{Transition behaviour of model fabric}

In order to simulate the fabric structure, the cured coated yarns were glued on a square support made of copper wire in warp configuration, with a spacing of 1.3 mm as shown in Fig. 7.7. The model fabric composed of coated yarns was studied for the transition in terms of percentage cover of the fabric with temperature. Figure 7.8 shows optical micrographs of the model fabric at different temperatures. The change in percentage cover corresponds to the transition, which is a response of the copolymer coated yarn. The model fabric shows no open spaces at 6 °C where the copolymer existed in a completely swollen state. The area of the model fabric opens up to an extent of 5% (percentage cover of 95%) at 15°C, 21% (percentage cover of 79%) at 20°C and around 39% (percentage cover of 61%) at 30°C. Thereafter, the opening of the fabric continues gradually due to further collapse of the coatings at still higher temperatures of up to 80°C. The open spaces of the fabric finally reach a value of 57%, i.e. percentage cover of 43%. When the change in percentage cover of the model fabric is plotted against temperature (Fig. 7.9), a clear transition in fabric structure is observed between 15 and 30°C. The model fabric shows a stability of transition for over many cycles.

This experiment was simulated to present an extreme situation where the cover factor changes by a large value. In applications, such large changes
7.8 Optical micrograph (×10) of the model fabric undergoing transition in a water bath at (a) 6 °C, (b) 20 °C and (c) 40 °C.

7.9 Change in percentage cover of the model fabric with temperature.
may not be necessary. The extent of change may be tailored by altering the add-on of copolymer and the crosslinker concentration. The lower add-on and higher crosslinker concentration is expected to result in low values of change as has been observed in films of this copolymer.

Unlike the above tests in water baths, where an ample supply of water is available for transition, the transitional behaviour of the fabrics made from the above-mentioned coated yarns was studied in air with the change in environment temperature and humidity. Because the supply of water in the atmospheric air is limited at any relative humidity (RH), comparatively lower change in diameter of the coated yarns and consequently in the open spaces of the fabric was expected. At a temperature of 10 °C and 95% RH (below the transition temperature), the volumetric swelling of the integrated copolymer was estimated to be 120% in 24 h. When this swollen yarn/fabric was subjected to atmospheric conditions of 45 °C and 95% RH (i.e. above the transition temperature), the structure collapsed to a volumetric swelling of 46%. These values are calculated on the basis of dry volume of the copolymer as shown in Table 7.9.

### 7.4.2 Temperature-responsive breathable textile by modification of fabric

The performance of temperature-responsive breathable textile based on (poly(NTBA-ran-acrylamide) 27:73) with BTCA as a crosslinker was studied. The add-on percentage obtained for the various coated samples is given in Table 7.10. A poly(acrylamide) coated (non-responsive) sample was also prepared with add-on similar to SSP50-2 sample for comparison.

#### Rate of transition

It was found that the SSP coated samples showed a fairly quick response to swelling and even quicker response to deswelling. Samples SSP50-1 and

<table>
<thead>
<tr>
<th>Condition</th>
<th>Diameter of coated yarn (μm)</th>
<th>Volumetric swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured and dry coated yarn</td>
<td>309</td>
<td>–</td>
</tr>
<tr>
<td>10 °C, 95% RH, 24 h</td>
<td>383</td>
<td>120</td>
</tr>
<tr>
<td>45 °C, 95% RH, 24 h</td>
<td>339</td>
<td>46</td>
</tr>
</tbody>
</table>

Note: Diameter of spun cotton yarn: 231 μm.
SSP50-2 attained their equilibrium values (swelling %) in approximately 5 and 20 minutes, respectively, while SSP50-3 took a substantially longer time of about 1440 minutes (Fig. 7.10).

The significantly longer time taken by SSP50-3 can be explained on the basis of thicker coatings due to substantially higher add-on (43.21%), as compared with 22.76% and 13.36% for the double and single coated samples, respectively.

### Table 7.10 Temperature-responsive breathable textile: details of samples prepared

<table>
<thead>
<tr>
<th>Sample</th>
<th>BTCA conc. (mol% of available amide groups in polymer)</th>
<th>Weight of BTCA (g 100 g&lt;sup&gt;-1&lt;/sup&gt; of solution)</th>
<th>Number of coatings</th>
<th>Add-on (%) (dried weight)</th>
<th>Wt loss (%)</th>
<th>1st wash</th>
<th>2nd wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SSP50-1</td>
<td>50</td>
<td>4.961</td>
<td>Single</td>
<td>13.36</td>
<td>2.3</td>
<td>Zero</td>
<td></td>
</tr>
<tr>
<td>SSP50-2</td>
<td>50</td>
<td>4.961</td>
<td>Double</td>
<td>22.76</td>
<td>11.93</td>
<td>Zero</td>
<td></td>
</tr>
<tr>
<td>SSP50-3</td>
<td>50</td>
<td>4.961</td>
<td>Triple</td>
<td>43.21</td>
<td>6.53</td>
<td>Zero</td>
<td></td>
</tr>
<tr>
<td>PAM50-3</td>
<td>*</td>
<td>0.9922**</td>
<td>Triple</td>
<td>24.00</td>
<td>11.95</td>
<td>Zero</td>
<td></td>
</tr>
</tbody>
</table>

Note: Control = uncoated cotton fabric.  
* Crosslinker concentration on molar basis was maintained similar to SSP50-2.  
** BTCA concentration on the basis of 4 wt% poly(acrylamide) solution.

7.10 Swelling rate below transition temperature of the SSP coated fabrics.
samples. Because swelling and deswelling are diffusion-controlled processes, thicker films are expected to take a longer time for the transition. Samples SSP50-1, SSP50-2 and SSP50-3 showed identical swelling percentages at equilibrium irrespective of their add-on percentage (or thickness).

The deswelling time showed a similar trend to that observed for swelling time (Fig. 7.11). The samples with higher add-on percentage SSP50-3 took longest to deswell (i.e., 30 minutes), while SSP50-2 and SSP50-1 showed complete deswelling within 5 and 1 minutes, respectively.

**Reversibility**

Figure 7.12 shows a repeated swelling–deswelling of SSP50-1, SSP50-2 and SSP50-3 over five cycles. Samples SSP50-1 and SSP50-2 show a high swelling % of around 800% and 750% respectively, while SSP50-3 shows a value of about 450%. This should not be mistaken by the equilibrium value as this sample shows a very slow rate of swelling and a final value of 784% in 1440 minutes. The cycling experiment was carried out by placing the fabrics for only 30 minutes and therefore the complete swelling could not be reached for this sample. The deswelling of all the samples was nearly complete to about 50%. The results proved that the smart textile samples had good transition reversibility and can be used in applications with frequently changing environmental conditions.
Transition temperature

The response of the SSP coated samples with respect to temperature is shown in Fig. 7.13. The transition was found to be broad over a range of 15 to 40°C. In comparison, in our earlier studies, the films of the same copolymer cast on glass substrate had resulted in much sharper transition at around 21°C. The broad transition may be because of the heterogeneous composition of the structure. Since the crosslinking density between the polymer chains and the cotton substrate may vary locally in this composition, the multiplicity in the transition may result in the overall broad response of the SSP coated fabric.

Water permeability

The resistance to penetration by water under pressure was found to be highest for the triple-coated (SSP50-3) sample and lowest for the single-coated (SSP50-1) sample for both before and after washing (Table 7.11). This is expected because multiple coatings and higher add-ons result in formation of defect-free coating. Surprisingly, SSP coated fabric showed significantly lower resistance to water penetration compared with the equivalent poly(acrylamide) coating. Figure 7.14 shows the electron micrographs of SSP coated fabrics before and after washing. Before washing the coatings appear to be continuous with occasional occurrence of small pores (~50 μm diameter). These pores may have appeared during
The above pores may be responsible for lower values of hydrostatic head observed in these samples. Upon washing numerous cracks appear on the coating. These cracks are long, but with micro-level thickness. Also there appears to be a small increase in the pore size due to loss of water-soluble components. This may be the reason for further reduction in hydrostatic head values. However, there is no evidence of removal or separation of polymer coating.
Air permeability values are given in Table 7.11. The air permeability of the coated fabrics was found to be 1 to 3 orders of magnitude lower than the uncoated fabric sample. The air permeability of the coated fabric was found to reduce drastically with increase in the number of coatings or add-on %. Interestingly, the poly(acrylamide) coated fabric (PAM50–3) with add-on similar to SSP50-2 showed a value lower by one order of magnitude. This difference in air permeability may be attributed to the presence of pores as mentioned above. On washing the samples, only a small increase in the air permeability values was observed. This indicates the proper integration of
the SSP layer to the fabric. As expected the air permeability value could not be detected for the SSP coated samples with very high add-ons (SSP50-3). In these samples the air permeability value did not change even after washing treatment, indicating continuity of the coated film at a high add-on %.

**Water vapor transmission rate**

The WVTR values of control (uncoated fabric), poly(acrylamide) coated fabric and SSP coated fabrics are given in Table 7.12. The SSP coated sample selected for comparison with poly(acrylamide) coated sample had similar add-on % and crosslinker concentration. As expected the WVTR values for all samples were found to increase with the increase in the temperature and decrease with increase in the relative humidity of the environment test chamber (ETC).

In our previous study, we had reported that high water vapor transmission rates are observed when hydrophilic poly(acrylamide) coatings are used on cotton substrate. These values do not change significantly between lower and higher add-ons. Therefore only one add-on for both poly(acrylamide) and SSP coatings has been considered.

To determine the responsiveness of SSP coated samples, the WVTR values of coated samples at a set of condition (temperature and relative humidity) are plotted as a percentage of the WVTR of the control (uncoated) fabric at the same condition (Fig. 7.15). At 20% relative humidity and 15 °C, the percentage water vapor transmitted through the SSP coated fabric was 58% as compared with the 70% obtained for the poly(acrylamide) coated fabric. While at a temperature higher than the transition temperature, 45 °C, the percentage water vapor transmitted was 94% in SSP coated fabric compared with 96% obtained for the poly(acrylamide) coated fabric. This shows that a significantly higher change in transmission occurs in SSP coated fabrics compared to poly(acrylamide) coated fabrics, when temperature is

![Table 7.12 Water vapor transmission of coated and control samples at different atmospheric conditions](image-url)

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To determine the responsiveness of SSP coated samples, the WVTR values of coated samples at a set of condition (temperature and relative humidity) are plotted as a percentage of the WVTR of the control (uncoated) fabric at the same condition (Fig. 7.15). At 20% relative humidity and 15 °C, the percentage water vapor transmitted through the SSP coated fabric was 58% as compared with the 70% obtained for the poly(acrylamide) coated fabric. While at a temperature higher than the transition temperature, 45 °C, the percentage water vapor transmitted was 94% in SSP coated fabric compared with 96% obtained for the poly(acrylamide) coated fabric. This shows that a significantly higher change in transmission occurs in SSP coated fabrics compared to poly(acrylamide) coated fabrics, when temperature is
changed across the transition temperature and both values tend to reach the control sample values. The results clearly demonstrate that the breathability of the fabric could be automatically altered with stimulus from the environment. Similar results were observed when the samples were compared at higher relative humidity of 30% and 65%. However, the change in water vapor transmission values was smaller as the relative humidity of the ETC was increased. This may be because WVTR values decrease as the relative humidity is increased. At a relative humidity of 95% the WVTR values at low temperature are so small that their relative differences cannot be compared.

The WVTR values of SSP coated fabrics tend to approach those of poly(acrylamide) coated fabrics at temperature higher than the transition temperature. However, they remain a little lower than poly(acrylamide) coated fabrics. There appear to be two mechanisms by which water vapors are transmitted across the SSP and poly(acrylamide) coated fabrics. The first is through micro-cracks present in the coating and second by the diffusion of water molecules through the hydrophilic polymer coating. The lower WVTR values of SSP coated fabrics may be attributed to the presence of hydrophobic moieties in the coating. The diffusion of water molecules largely depends upon their molecular interaction with the polymer chains, which may get adversely affected with the presence of hydrophobic pendant group, N-tert-NTBA, in the stimuli-sensitive copolymer.

The SSP coated fabrics act as a switch to control the transmission of water vapor. At 15°C, the SSP coating exists in a swollen state by absorbing the water from the surroundings. This may result in closure of micro-cracks (Fig. 7.14). At higher temperatures than the transition temperature the SSP coating exists in a collapsed state, due to the predominance of hydrophobic interactions, and results in opening of the micro-cracks. Another factor
which may affect is the change in diffusion flux, which is governed by changes in both the diffusion coefficient and diffusion path of water molecules through the swollen or collapsed coating. As a consequence of these two factors the diffusion flux is likely to decrease at lower temperature compared to higher temperatures.

This study opens up a new area of application in producing smart fabric using stimuli sensitive polymers integrated to textile substrates.

7.5 References


Abstract: As one kind of promising stimuli-responsive materials in recent years, shape memory polymers (SMPs) have found great applications in various fields. In this chapter, SMPs are introduced, followed by a discussion of their coating and laminates, in particular, temperature-sensitive shape memory coating and laminates. In addition, two main applications of SMPs – sportswear and medical hygienic applications – are discussed; finally the future outlook about SMP research and SMP coatings and laminates is assessed.

Key words: shape memory polymer, polyurethane, coating, laminate.

8.1 Introduction to shape memory polymers

8.1.1 Definition of shape memory polymers

In recent years, shape memory polymers (SMPs) have been one kind of promising stimuli-responsive materials because they have the ability to ‘memorize’ a macroscopic (permanent) shape, be manipulated and ‘fixed’ to a temporary and dormant shape under specific conditions of temperature and stress, and then later relax to the original, stress-free condition under thermal, electrical, or environmental command. Compared with the shape memory alloy, SMPs have characteristics such as large recoverability, light weight, superior molding property, and lower cost. Owing to these advantages, the applications of SMPs is developed in various areas of everyday life, such as smart fabrics, heat-shrinkable tubes or film, self-deployable sun sails, self-disassembling mobile phones and intelligent medical devices.

The term ‘shape memory’ was first mentioned in a dental polymeric material made of methacrylic acid ester resin by L. B. Vernon in 1941, ten years earlier than the appearance of the first shape memory alloy in 1951. However, the importance of SMPs was not recognized until the 1960s, when covalently crosslinked polyethylene was included in heat shrinkable tubing and films. Significant efforts began in the late 1980s, accelerated in the 1990s and have kept growing since then. Up to now, lots of other polymers
Shape memory polymers in coatings and laminates for textiles

have been developed to demonstrate shape memory properties for diverse applications, such as polynorbornene, poly(trans-isoprene), styrene–butadiene copolymers, and some polyurethane elastomers.\textsuperscript{10,11}

8.1.2 Mechanism of shape memory polymers

SMPs are dual-shape materials belonging to the group of ‘actively moving polymers’.\textsuperscript{2} They are elastic polymer networks and the driving force for strain recovery of SMPs results from the elastic entropy of polymer chains.\textsuperscript{12} The polymer network of SMP consists of switch units or segments and netpoints or domains (Fig. 8.1). The netpoints determine the permanent shape of the polymer network and can be of a chemical (covalent bond) or physical (non-covalent bond) nature. For example, in the polymer containing at least two segregated domains, crystal domains, glassy domains, or other forms of entangled chains, some non-covalent interaction, e.g. hydrogen bond, physical crosslinking can be formed. However, the switch unit or a segment is responsible for elasticity during deformation and undergoes strain recovery. Thus, the amorphous soft phase with low glass transition temperature, \( T_g \), the crystalline soft phase with low melting temperature, \( T_m \), or even the liquid crystalline phase with low isotropization temperature, \( T_i \), in the liquid crystalline elastomers can be used as the switch segment of thermal-induced SMPs. Phase transition from the glassy state to the rubber state, from the crystalline state to the rubber state, or from the anisotropic phase (liquid crystalline phase) to the isotropic phase will result in strain recovery. For example, in the thermal-induced shape memory block polyurethane, hard domains with higher thermal transition temperature (\( T_{perm} \))
act as the physical netpoints, while soft phases with the second thermal transition, $T_{\text{trans}}$, above room temperature act as molecular switches. When the polymer is put on the temperature above $T_{\text{trans}}$, the soft segment will be flexible, resulting in entropic elastic behaviors of polymer networks. If the sample has been previously manufactured into a second shape with an external stress, the deformed shape snaps back to its initial state once the external stress is released. Similarly, in light-induced SMPs. The switch unit is the reversible photo-reactive molecular switch which is independent of any temperature effects. A typical example is that of cinnamic acid (CA) or cinamylidene acetic acid (CAA) moieties, which work as light-triggered switches, and have been incorporated into the polymer architecture. Upon irradiation with light of suitable wavelength, a [2 + 2] cycloaddition reaction occurs between two of these light-sensitive moieties, forming a cyclobutane ring with reversible covalent crosslinks. Irradiation with a different wavelength results in cleavage of the covalent bond.

In general, the shape memory effect (SME) is not an intrinsic property of SMPs, that is, SMPs do not display SME by themselves; the shape memory results from a combination of polymer morphology and specific processing. This combination process can be described as follows: by conventional processing, e.g. extruding or injection molding, the polymer is formed into its initial, permanent shape B. Afterwards, in a process called programming, the polymer sample is deformed and fixed into the temporary shape A. Upon application of an external stimulus, the polymer recovers its initial permanent shape B. This cycle of programming and recovery can be repeated several times, with different temporary shapes in subsequent cycles. However, if there is no programming process, there is no change in shape, even though SMPs have the necessary morphology. Therefore, to display shape memory functionality, the polymer network has to be temporarily fixed in a deformed state under environmental conditions relevant to the particular application. This requires the deformed chain segments, which are under external stress, to be reversibly prevented from recoiling, and is achieved by the introduction of reversible netpoints as the molecular switches. These additional netpoints can be formed by physical interactions or by covalent bonds. Physical crosslinking is obtained by vitrification or crystallization of domains related to $T_{\text{trans}}$. These switching domains can be formed either by the chain segments driving the entropic elastic behaviour themselves or by side chains, whose aggregation is able temporarily to prevent recoiling of that chain’s side chains or the side chain segments themselves. Reversible covalent crosslinking is obtained by attaching functional groups to the chain segments. Controlled by an external stimulus, these functional groups must be able to form covalent bonds reversibly by reaction with each other or suitable counterpart functional groups.
The phase transformations in the shape memory materials are accompanied by remarkable or even drastic changes in physical and mechanical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, thermal conductivity, thermal expansion coefficient, resistivity, magnetic susceptibility, flexibility, vapour permeability, shape fixity, and dielectric constant, enabling the materials to exhibit some novel functions or making them adaptable to the external changes in temperature, stress, and magnetic or electrical field. This gives materials great potential for application in sensors, actuators, smart devices, media recorders, and smart textiles.

8.1.3 Classification of shape memory polymers

On the basis of the molecular mechanism given above, there are lots of classifications for SMPs. For example, according to the external stimulus, SMPs has been described as thermal-induced SMPs, light-induced SMPs, electro-active SMPs, pH-responsive SMPs and magnetic-sensitive SMPs. On the basis of the nature of crosslinks, SMPs are subdivided into physically crosslinked SMPs and chemically crosslinked SMPs, and biodegradable SMPs have been designated a category. On the basis of the nature of switching segments, SMPs are subdivided into $T_g$-type SMPs with amorphous switching segment and $T_m$-type SMPs with crystalline switching segment. Liquid crystalline elastomers with anisotropic to isotropic phase transition constitute one new class of SMPs because of their two-way shape memory effect. As one application form of SMPs, the function of SMPs in coatings and laminates mainly results from the constituent SMPs.

Traditional SMPs change shape through the application of external stimuli such as temperature. Polymers which can change in dimension by interacting with chemicals such as pH solvents, or through non-contact stimulation, coupled with electrical energy, also show an SME. In this chapter, we introduce SMP coatings and laminates from the widely used temperature-sensitive SMPs.

8.1.4 Thermally induced shape memory polymers

Shape memory is usually a thermally induced process though it can be triggered by electrical, magnetic, or electromagnetic stimulus. Thermally induced SMPs have the capability of sensing and responding to external temperature in a predetermined way. Their thermally induced SME is summarized in Fig. 8.2, which shows how an initial, permanent shape B can be prepared by conventional processing, e.g. extruding or injection molding. Without the process of programming, even though shape B can be fixed through the formation of switch segment and netpoints when it is cooled.
to below \( T_{\text{trans}} \), it cannot change itself when the temperature rises above \( T_{\text{trans}} \) again. However, in the programming process, at a temperature above \( T_{\text{trans}} \), the polymer shape B is deformed with the external force and fixed into the temporary shape A when it is cooled to below \( T_{\text{trans}} \). Afterwards, upon heating to above \( T_{\text{trans}} \), the polymer recovers its initial permanent shape B. This is the shape recovery process induced by temperature.

In order to achieve thermally induced shape memory behavior, heating to above \( T_{\text{trans}} \) is a direct process which also includes another concept to induce shape transition. This is the application of an electric or magnetic stimulus by Joule heating through the incorporation of highly dielectric susceptible components such as carbon nanotubes, liquid crystalline phases to the materials, and even magnetic nanoparticles in an SMP matrix.\(^{16}\)

Decreasing the transition temperature below \( T_{\text{trans}} \) is another route to induce shape recovery by absorbing moisture or water,\(^{17}\) or even some chemical solvent or gas. In general, given the condition of the formation of either physical netpoint or chemical netpoint, polymers having a \( T_g \) or \( T_m \) above ambient temperature can be used as thermally induced SMPs, and the \( T_g \) or \( T_m \) of polymer will act as the switch segment. Thus, a lot of physically crosslinked amorphous or semicrystalline segments, polymers
such as polyurethane, polynorbornene, and polyethylene/nylon-6-graft copolymer, and chemically crosslinked polymers such as cross-linked polyethylene are found to exhibit the SME. In particular, segmented shape memory polyurethane (SMPU) composed of hard and soft segments has been extensively researched since its discovery by Mitsubishi in 1988.\textsuperscript{18–20} SMPU is generally synthesized from diisocyanates such as 4,4-diphenylmethane diisocyanate (MDI) and isophorane diisocyanate (IDI) and polyglycols such as poly(ε-caprolactone) (PCL),\textsuperscript{21,22} poly(hexylene adipate) glycol (PHAG),\textsuperscript{18} poly(tetramethylene glycol) (PTMG)\textsuperscript{23} and poly(butylene adipate) glycol (PBAG),\textsuperscript{24} using 1,4-butanediol as chain extender; and phase-separated structures consisting of hard and soft domains due to thermodynamic immiscibility were observed, under a microscope. Hard segments can bind themselves via hydrogen bonding and crystallization, making the PU very solid below melting temperature. Reversible phase transformation of the soft segment is reported to be responsible for the SME acting as the switch segment. In order to exhibit good shape memory effect in the segmented polyurethanes, in addition to the formation of physical crosslink structure in the hard segments, crystallization in the soft segment and above-ambient temperature glass transition are two necessary conditions.\textsuperscript{25,26} Therefore, much literature has reported the control of the shape memory behavior of PU by varying the content of soft or hard segments, the length of the soft segment, and the preparation process.\textsuperscript{27,28} Furthermore, through the molecular design of polymers by proper selection of polyglycol and content of soft segment, the switch temperature ($T_m$ or $T_g$ of soft segment) of SMPU could be controlled close to the application temperature for breathable textiles. Phase transition results in a great change in thermo-mechanical properties of polymeric materials, e.g. a significant decrease in modulus and an enhanced micro-Brownian motion in molecular chains at $T_{\text{trans}}$ and can be used in the molecular design of SMPs.\textsuperscript{29–31}

8.2 Temperature-sensitive shape memory polymer coatings and laminates

As mentioned above, besides shape changing, some other remarkable or even drastic changes in the physical and mechanical properties enable the materials to exhibit some novel functions or making them adaptable to the external changes in temperature. In particularly, there is usually a significant changing in water vapor permeability (WVP) of the polymeric membrane. By means of appropriate molecular design, the abrupt change in water vapor permeability of thermally induced shape memory polymeric material has a broad application in textile industry, medicine, environmental projects, and so on.
Usually, the water vapor molecules transmit through the nonporous membrane by molecular mechanism (sorption–diffusion–desorption). Therefore, the morphology and microstructure of the polymer play the main role in the breathability of nonporous membrane. Segmented SMPU became one of the best candidates for breathable laminated nonporous fabrics due to its unique properties including high strength and toughness; outstanding resistance to abrasion, chemistry, hydrolysis and fungal growth; and low temperature flexibility. SMPU generally has high water vapor permeability during the rubbery state, and has low permeability during the glassy state. Thus, by molecular design, the $T_g$ or $T_m$ of the soft segment in polyurethane could be set at the application temperature ($T_a$) of textile, e.g. body temperature, or room temperature; then the SMPU nonporous laminated fabric will show quite different WVP properties between above $T_a$ and below $T_a$. That is, this behavior could provide thermal insulation at cold and high permeability at room temperature or above; and fabrics laminated with the SMPU would provide better comfort in both cold and warm climates.\cite{25} Comparing with the conventional polymer coating, SMPU coating which derives the development of smart garments have the advantage of controlling the permeability according to both the surrounding temperature and body temperature.

In the last decades, the controlling of permeability is one of the most attractive topics to scientists, and lots of works has been reported. For example, Yontz \textit{et al.} studied the effect of soft block composition of hydrophilic polyurethane–urea (PUU) on water vapor transporting (WVT) rates with varied PEO contents from 0 to 50 wt\%.\cite{32} It performed at $23^\circ$C and 50\% relative humidity, the relationship between PEO content and WVT followed an increasing S-shaped curve. There was also a significantly increasing WVT with an increase in temperature from 23 to 37°C. Moreover, the plot of WVT and temperature showed an almost perfect fit to the Arrhenius relationship. Besides, Mondal and coworkers reported the influence of hydrophilic segment content and soft segment crystal melting on mass transfer properties of nonporous-segmented polyurethane membranes, which would be applicable to breathable textiles and packaging.\cite{33,34} In this report, a series of polyurethanes of varying hydrophilicity were obtained by varying the content of polyethylene glycol (number average molecular weight 3400 g mol$^{-1}$, PEG 3400). They found that different PEG 3400 content in the polymer not only affects the structural properties of the derived SMPUs, but also aimed to contribute to improve the mass transfer properties. Water vapor permeability of SMPUs was influenced by both hydrophilic group content and soft segment crystal melting. In addition, polyurethanes without PEG show lower water vapor permeability; while the WVP increases with increasing PEG content in the polyurethane with PEG in its backbone. SMPU with higher PEG 3400 content has higher...
permeability due to the increasing number of polar groups in the polymer backbone. Soft segment crystal melting further enhances the water vapor permeability of polyurethane membranes (see Fig. 8.3).

In addition, Ding et al. also synthesized a series of SMPUs with a broader switching temperature range including ambient range, and then investigated the relationships between microstructure and water vapor transport properties of thermally induced SMPUs. Such research enabled the identification of the key parameters governing the water vapor permeability of thermally induced SMPUs membrane and opened the way for new tailor-made polymeric materials with specified properties. The results show that only polyols formed crystallites in the segmented SMPUs, and the crystalline properties of the SMPUs, including degree of crystallinity and crystal melting temperature ($T_m$), depend on the chemical structure of the polyols and hard segment concentration. The water vapor permeability of the PU membranes increased significantly with increasing temperature within the temperature range of crystal melting from 10 to 40 °C, which was triggered by crystal melting of the crystalline soft segment. This property can be applied to the development of smart textiles.

8.3 Applications of shape memory polymer coatings and laminates

8.3.1 Sportswear applications

Smart waterproof and breathable fabric (SWBF) is one famous example for textile applications. Comfort in all its interpretations, physical and psychological, is a well-researched area because it is also the principal requirement of all garments including protection textiles, sports or work
clothes. So far, many publications have been written focusing on the comfort of garments. These properties also drew great attention to SMPs in coating and laminated application. For example, in 1992, Horri et al. claimed in a patent\textsuperscript{37} that they developed a urethane polymer having a $T_g$ of 0–60°C. When the material was applied to the surface of fabrics through the laminating or coating technology, the resulting fabrics had excellent moisture permeability. Moreover, the polyurethane membrane having different $T_g$ could control the dissipation of sweat from the body to the outer atmosphere by varying the moisture permeability. Therefore, this kind of fabric was extremely suitable for clothes. This is the first publication about temperature-sensitive polyurethane found in the literature.

In 1993, some researchers began to report the development of SMPU and introduced its potential applications to the textile industry.\textsuperscript{38–41} They were confident that fabrics coated or laminated with SMP would have the significant transition in moisture permeability at temperatures below and above the $T_g$ respectively. Therefore, the clothing materials would not only be waterproof at any temperature, but also provide more comfort in both cold and warm climates. Later, Diaplex Co., Ltd, represented in the United States by MHI in New York, announced the successful development of ‘smart fabrics’ with SMP for the outerwear industry. According to their report, the resulting Diaplex\textsuperscript{TM} fabrics showed excellent waterproof and breathable features with 20000–40000 mm H$_2$O in water pressure resistance and 8000–12000 g/m$^2$ 24 h in moisture permeability. Such properties provided the resulting garments with high performance, and enabled wearers to be comfortable in the various conditions.

Common polymers such as segmented polyurethane, poly(vinyl chloride) or rubber-coated fabric are waterproof but are not ‘breathable’, i.e. they do not allow perspiration to pass through the fabric to lower body temperature. As a result, the perspiration condenses on the inside of the garment and the wet feeling makes the wearer uncomfortable. During a shower, people may mistake this condensed perspiration as rain leaking into the garment, and they are surprised to find water exuding from their own bodies. In hot weather, or during strenuous activity, it is easy to produce perspiration and the body sweats more. Recently, breathable waterproof fabrics have been successful in dealing with this disadvantage. On the market are two typical polyurethane coatings products, one developed and sold by Union Chimique Belge (UCB) (Belgium) and one invented by the Shirley Institute (later British Textile Technology Group – BTTG) and marketed by Baxenden Chemicals. The waterproofness and breathability of UCB products result from the microporous polyurethane coating; while the BTTG product is solid polyurethane coating without pores. However, the BTTG product contains hydrophilic groups which allow the water molecules to move freely in the molecular chain to the other
side. The driving force for this action in the BTTG product results from the difference of relative humidity which is higher on the inside of the garment than on the outside. Baxenden now has both water-based (Eco Dry) and solvent-based (Witoflex Superdry) resins for the production of breathable waterproof garments by direct coating. Witoflex Superdry can also be used in transfer coatings. Later, Porvair also launched its Porelle microporous polyurethane film for breathable waterproof garments.

Many of the up-market garments now produced are made from films such as Gore-tex and Sympatex (AKZO). They are laminates made from waterproof breathable film joined to the garment face fabric for protection and support. In some cases, a second scrim fabric is joined to the other side of the film to produce a three-component laminate. This is necessary to protect the thin film from damage. However, in recent years, this method tends to have been replaced more and more by another method using loose lining material replacing the central third component in laminated waterproof textiles. Generally, the loose lining material consists of an open mesh knitted fabric and has an open construction which allows the passage of perspiration. Moreover, the lining material can also soak up some of the perspiration and remove it from the surface of the membrane. This structure is beneficial to the overall performance of the microporous membranes. In addition, it is significantly better than the stiff and poor draping trilaminated materials. Care is needed for this lamination process because the wrong process can significantly reduce breathability as well as cause stiffness. In order to get the optimum performance, breathable adhesives could be used in trilaminated materials.

Waterproof and breathable membranes are now used successfully in footwear, gloves and socks. Therefore, by combining the excellent water vapor permeability of SMPs like SMPU with microporous coating and laminated technology of garments, it is expected that SMP coatings and laminates will find a wide application in textiles/garments field, e.g. sportswear, footwear, gloves, and socks.

### 8.3.2 Medical applications

Generally, medical textiles refer to the textiles used in medical, healthcare, and hygiene, including clothing, bedding, and feminine hygiene products such as sanitary napkins, baby and adult diapers, etc. The fibers used in medical textiles are usually biocompatible as well as skin-friendly accompanied with additional functionalities besides of their inherent properties. The functionalities may be imparted to the fibres during the production or applied to the fiber, yarn, fabric or the product through a special post-finishing process. Thus, various techniques are required to finish medical textiles, such as coating, spraying, and padding. An infection-free
environment is usually required in such finishing processes or the finished products must be sterilized before entering into the market. Furthermore, the applied finishing may make the medical textiles with an auxiliary function. Standard coating products for medical applications include the self-adhesive plaster, plaster and bandage materials, wound dressing and compresses, collagen and silicone tissues, and operation or post-operative textiles such as clothing and covers.

Recently, medical textiles have been developed that are capable of reacting to an external stimulus, and are called ‘interactive materials’. For example, an interesting application of shape memory materials has been developed in disposable hygiene products, such as feminine care, diapers, training pants, and incontinence products. It also can be used as a gatherable or elastic part in medical textiles or equipments.

Another attractive application area for SMPs is their use in active medical devices. First examples include a laser-activated device for the mechanical removal of blood clots. The device is inserted by minimally invasive surgery into the blood vessel and, upon laser activation, the shape memory material coils into its permanent shape, enabling the mechanical removal of the thrombus (blood clot). Another example is that thermal-sensitive shape memory foams have been proposed as a measuring device to survey the shape of a human ear canal, so a hearing aid can be fitted properly. The material is commercially available polyurethane foam with a $T_g$ switching transition.

SMPs are also used in stents for the prevention of strokes. Here, coils of a composite consisting of tantal and a polyetherurethane ($T_{\text{trans}} = T_g$, $T_g = 33 ^\circ C$) have been studied. Tantal is needed as radio-opaque filler for diagnostic detection. The filling does not affect the shape-recovery behavior but lowers $T_g$ and the maximum recovery stress.

The investigation of application of SMP in the medical field does not stop; much work is exploring in different area. As an intelligent material, SMP is playing an important role in biomedical devices.

Besides the temperature-sensitive SMPs introduced above, shape change is also responsive to the pH value (pH-sensitive polymers); and interest in electro-active polymers (EAPs) has been growing: there are intelligent polymers because they also respond to electrical stimulation with a significant change in shape or size change. By coupling with coating or laminated technology, these kinds of SMPs have found many interesting applications in coatings and laminates.

### 8.4 Future trends

The research regarding SMPs is divided between enabling technologies (materials, processes, and techniques) and application identification and prototyping. On the enabling front, there are an increasing number of reports discovering novel recovery trigger mechanisms other than external
heating. Examples include photographs, magnetism and humidity. Aside from alternative triggering mechanisms, there is also an emerging interest in SMPs capable of memorizing two or more temporary shapes. Reversible shape recovery, or two-way SMPs is also an attractive research topic. In addition, driven by their utility in the area of self-actuating biomedical devices, there are an increasing number of research studies focused on the development of biodegradable and/or drug-eluting SMPs.\textsuperscript{1}

Polymer nanofibers with oriented polymer chains and diameters in the range of 100 nm or less have drawn great interest in science and technology. Owing to their typical unique properties, e.g. high specific surface area, small fiber diameter, high permeability, and low basis weight, non-woven fabric composed of SMP nanofibers are expected to show some novel properties in WVP, sensitivity and mechanical properties which will make them excellent candidates for use in garments, filtration, and membrane applications. Fabrics or textiles coated with SMP nanofibers are also expected to find wide application in sportswear application and medical applications.\textsuperscript{44}

In addition, layer technique provides an effective method to prepare two-way SMP laminates with the traditional one-way SMPs. Not only can the two-way shape memory effect be achieved, but also the reversible deformation is controllable and a wide range of response temperature can be achieved in the resultant SMP laminates. This technique is expected to promote the research of two-way SMP; and promising applications are being explored in the biomedical device and textiles fields and in other deployable structures.\textsuperscript{45}

\section*{8.5 References}


3. VERNON L B and VERNON H M (1941), ‘Producing Molded Articles such as Dentures from Thermoplastic Synthetic Resins’, US Patent, 2234993.


42. WALTER F (2002), Coated and Laminated Textiles, Cambridge, Woodhead Publishing Ltd.


Abstract: This chapter covers the use of phase change materials in textile coatings and laminates. The chapter reviews the thermal effects obtained by phase change materials and methods to measure these thermal effects. Based on these thermal effects, specific applications of textile coatings and laminates treated with phase change materials in protective garments, active wear, and architectural roofing systems are discussed.

Key words: phase change material, microencapsulation, macroencapsulation, dynamic heat transfer measurements, active thermal insulation effect.

9.1 Introduction

Phase change materials (PCMs) are substances which absorb or release large amounts of so-called ‘latent’ heat when they go through a change in their physical state, i.e. from solid to liquid and vice versa. In a heating or a cooling process, this phase change takes place as soon as the material reaches its specific phase change temperature. During the latent heat absorption or latent heat release, the temperature of the PCM remains constant. The PCM’s property of absorbing and releasing large amounts of heat in a controlled way can be utilized to improve the thermal performance of various end-use products to which the PCMs are applied. The latent heat absorbed by the PCM can be stored therein. Therefore, PCMs are considered to be highly efficient thermal storage means.

The technology for incorporating phase change materials into textile structures was developed in the early 1980s as part of a research program funded by the US National Aeronautics and Space Administration (NASA). The program’s aim was to improve the thermal performance of space suits to provide astronauts with protection against the extreme temperature fluctuations they encounter in outer space. The concept never led to any practically applicable materials for use in the space program, but the basics of the technology were further developed into ‘terrestrial’ applications.

Nowadays, textiles with PCM treatment are widely used in garments and home furnishing products. However, many other textile products utilizing
the PCM technology are under development and will be introduced to the market soon. In order to incorporate PCM in a specific textile product, it is first microencapsulated or macroencapsulated. The microencapsulated PCM is then added to a binder and applied to a textile substrate in the form of a coating. The macroencapsulated PCM is either directly applied to a textile substrate by coating or it is formed into a thin film which could be laminated to a textile substrate.

9.2 Phase change materials

PCMs possess the ability to change their physical state within certain temperature ranges. Outside this so-called ‘phase change temperature range’ the PCM behaves like any other material. Therefore, in a heating process the PCM absorbs a small amount of sensible heat and its temperature rises constantly. However, when the melting temperature is reached in such a heating process, the phase change from the solid state to the liquid state occurs. During this melting process, the PCM absorbs and stores a large amount of latent heat. The temperature of the PCM and its surroundings remains nearly constant throughout this entire phase change process. When the phase change is complete, a continued heating process leads to a further increase of the material’s temperature while a small amount of sensible heat is being absorbed.

The latent heat stored in the PCM is released into the environment in a cooling process when the PCM’s crystallization temperature is reached, and a reverse phase change from the liquid state to the solid state takes place. During this crystallization process, the temperature of the PCM and its surroundings remains also nearly constant.

In order to compare the amount of latent heat absorbed by a PCM during the actual phase change with the amount of sensible heat absorbed in an ordinary heating process, the ice-to-water phase change process will be used for illustration. When ice melts, it absorbs an amount of latent heat of about 335 J/g. When the water is further heated, it absorbs an amount of sensible heat of only 4 J/g while its temperature rises by one degree Celsius. Thus, water needs to be heated from about 1 °C up to about 84 °C in order to absorb the same amount of heat which is absorbed during the melting process of ice.¹

In addition to ice (water), more than 500 natural and synthetic PCMs are known. These PCMs differ from one another in their phase change temperature ranges and their latent heat storage capacities. Commonly used PCMs are paraffins and salt hydrates. Paraffin PCMs suitable for textile applications are summarized in Table 9.1.²

The paraffin PCMs are either used in technical grades with a purity of approximately 95% or they are blended with one another in order to cover...
specific phase change temperature ranges. The paraffin PCMs are nontoxic, noncorrosive, and nonhygroscopic. Their thermal behavior remains stable under permanent use. Paraffin PCMs are by-products of petroleum refining and, therefore, inexpensive.

Salt hydrates are alloys of inorganic salts and water. They are non-combustible and therefore meet the fire-resistant requirements of a variety of products. An attractive property of salt hydrates is the comparatively high latent heat storage capacity. Salt hydrates often show an incongruent melting behavior which results in a lack in reversible melting and freezing, making them unsuitable for permanent use. However, this undesired feature of salt hydrates can be eliminated by adding stabilizing chemicals. Salt hydrates suitable for textile applications are summarized in Table 9.2.

### 9.3 Textile coatings and laminates with phase change material treatment

Before applying a PCM to a textile substrate, it needs to be durably contained in a carrier material in order to prevent dissolution while in its liquid stage. In one part of the PCM technology, paraffin-PCMs are microencapsulated, i.e. enclosed in very small spheres. These PCM microcapsules possess approximate diameters between 1 and 20 μm. The shell of the PCM microcapsules consists of either a melamine resin or an acrylic resin. The shell takes about 20% of the microcapsule’s total weight. The remaining

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<td>Melting temperature (°C)</td>
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<td>Heptadecane</td>
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<tr>
<td>Octadecane</td>
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<tr>
<td>Nonadecane</td>
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<td>Eicosane</td>
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<th>Table 9.2 Salt hydrate PCMs</th>
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<tr>
<td>Melting temperature (°C)</td>
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<tr>
<td>Calcium chloride hexahydrate</td>
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<tr>
<td>Sodium hydrogen phosphate dodecahydrate</td>
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80% comprises the PCM filling of the microcapsule. The microcapsules are resistant to mechanical actions (i.e. abrasion, shear, and pressure), heat, and most types of chemicals. However, the microencapsulation of the PCM reduces its latent heat storage capacity. For instance, encapsulating an octadecane-type paraffin with a latent heat storage capacity of 244 J/g results in an octadecane–PCM microcapsule with a latent heat storage capacity of about 170 J/g.3–5

For coating applications, the microcapsules with paraffin core are embedded in a polymer binder (e.g. acrylic, polyurethane, or rubber latex coating compound) and are topically applied to a woven fabric, a knitted fabric, or a non-woven fabric. Suitable coating procedures are, for instance, knife-over-roll coating, transfer/cast coating, or dip coating.6,7 Figure 9.1 shows an example of microcapsules with paraffin core incorporated in a coating compound. In most applications, where a fabric is coated with a binder containing microencapsulated PCM, the fabric’s surface is completely covered with the coating layer. However, a coating layer which covers the whole surface of the fabric reduces water vapour transfer through the fabric and, thus, also reduces the fabric’s breathability substantially. Therefore, in another technique, the polymer binder with the microencapsulated PCM is applied to the fabric’s surface in the form of discrete dots. This discontinuous coating technique is called screen-printing. The technique allows for a substantially higher water vapour transfer through the fabric and, thus, enhances the breathability of the fabric. In addition, the coated fabric becomes softer and more flexible. However, a disadvantage in utilizing this technique consists of the reduction in latent heat storage capacity due to lower amounts of PCM microcapsules which are applied to the fabric.

In another PCM technology, microencapsulated PCM is integrated in a polymeric binder which is used to bond a fiber web in order to create a non-woven fabric. The non-woven fabric with the PCM microcapsules incorporated therein could be laminated to another fabric, creating a textile composite material.
Finally, applied in a foam dispersion, the PCM microcapsules are mixed into a water-blown polyurethane foam matrix. The foam with PCM microcapsules is then formed in a drying process where the water is taken out of the system. These foams can be topically applied to a fabric in a lamination process.

In contrast to the microencapsulation technology, a macroencapsulation technology has been developed wherein the PCM itself is crosslinked into a polymer matrix and durably contained therein. The polymer matrix with the PCM treatment is either coated onto a textile structure or is formed into a thin film which can be laminated onto a textile. This PCM macroencapsulation procedure possesses some advantages compared with the microencapsulation of PCM. The macroencapsulation technology is comparatively cheaper. Furthermore, using the macroencapsulating technology instead of the microencapsulating technology, a substantially higher latent heat storage capacity is obtained due to the larger amount of PCM which is contained within a comparative volume.

In one of the developed macroencapsulation technologies, salt hydrate PCMs are durably contained in a specific silicone rubber substrate. This PCM technology fulfills the fire-resistant requirements of a multitude of technical product applications.

### 9.4 Thermal effects

In treating fabrics with PCM, the following thermal effects are obtained:

- a cooling effect, caused by heat absorption of the PCM;
- a heating effect, caused by heat release of the PCM;
- a thermoregulating effect, resulting from an alternating heat absorption and heat release of the PCM.

The efficiency of each of these effects and their duration are mainly dependent on the latent heat storage capacity of the PCM itself. However, the heat storage capacity and, thus, the duration of the thermal effects can be further controlled by the quantity of the applied PCM.

Furthermore, the phase change temperature range and the application temperature range need to correspond in order to realize the desired thermal benefits. Figure 9.2 shows temperature gradients through the different layers of a ski clothing ensemble consisting of underwear, sweater, and ski suit for two ambient temperatures. The figure indicates that there is a steady decrease in the temperature from the skin through the garment layers into the environment and the temperatures in the different garment layers themselves vary widely. This must be considered when selecting a
PCM to be used in a certain application. For instance, if a PCM should be applied to the underwear fabric, the phase change of the selected PCM would have to take place in a temperature range which corresponds with the skin temperature. On the other hand, a PCM applied to the liner material of the ski suit needs to exhibit a phase change which takes place at much lower temperatures.\(^8\)

In addition, the structure of the carrier system also influences the efficiency of the phase change effect. For instance, dense and thin carrier systems readily support the cooling process (latent heat absorption) of the PCM. In contrast, the latent heat release of the PCM is delayed in a loft and thick textile structure such as a batting. The latent heat released by the PCM remains longer in such a configuration.\(^9\)

It has to be considered that the thermoregulation effect obtained by alternating latent heat absorption and latent heat release lasts much longer than a continuous latent heat absorption or latent heat release. In the case that solely a cooling effect is desired in a specific PCM application, the cooling effect provided by a continuous latent heat absorption will only last as long as the PCM is melting. After the melting process is complete, the PCM needs to be recharged (crystallized) in order to perform a cooling procedure (latent heat absorption) again.
9.5 Determination of the thermal effects

In order to determine the thermal effects of the PCM applied to a textile structure, a measuring and evaluation system was created which includes the following measuring procedures:

- differential scanning calorimetry (DSC);
- dynamic heat transfer measurements;
- temperature and heat input variation measurements.

9.5.1 Differential scanning calorimetry

DSC measurements are used to determine latent heat absorption during the melting process, latent heat release during the crystallization process, and latent heat storage capacity of the PCM solely or embedded in a textile substrate.

Furthermore, the phase change temperature ranges in which the latent heat absorption and latent heat release of the PCM take place are measured by this procedure. The test method involves the heating or cooling of a sample of the test material (PCM itself or textile substrate with PCM inside) at a controlled rate through the temperature ranges in which the melting or the crystallization of the PCM takes place. A transition, for instance, from solid to liquid is marked by absorption of energy by the test sample resulting in a corresponding endothermic peak in the heating curve. The latent heat absorption and the phase change temperature range in which the latent heat absorption takes place are determined from this peak in the heating curve shown in a DSC diagram. On the other hand, a transition from liquid to solid is marked by release of energy by the test sample, resulting in a corresponding exothermic peak in the cooling curve. The latent heat release and the phase change temperature range in which the latent heat release takes place are determined from this peak in the cooling curve. The latent heat storage capacity of the PCM is then calculated by averaging the values received for the latent heat absorption and the latent heat release.

9.5.2 Dynamic heat transfer measurements

The transfer of the PCM’s latent heat storage capacity into thermal insulation terms is accomplished using a measuring procedure referred to as ‘dynamic heat transfer measurements’. In these measurements, the dynamic thermal insulation effect of the PCM is determined and clearly separated from the basic thermal insulation effect provided by the textile substrate. Consequently, a thermal performance comparison of textiles with and without PCM is possible.
This measuring method can be used to test the cooling effect resulting from the PCM absorbing latent heat as well as the heating effect resulting from the latent heat release of the PCM. Based on these measurements, the active thermal insulation effect as well as the thermo-regulating effect can be determined. Furthermore, the test results can be used to evaluate textile structures which best support the desired thermal effects of the PCM.

In a first step of the measuring procedure, the basic thermal resistance of the textile substrate is determined without initiating a phase change effect within the PCM. In order to accomplish this requirement, only a short heat impulse is transmitted into the test sample, which increases the sample temperature by only one to two degrees. In order to prevent the phase change from taking place, the temperature of the sample must remain outside the phase change temperature range. The basic thermal resistance is determined from the supplied heat flux, as well as the sample thickness and temperatures taken at different locations and various times during the measurement.

In a second step of the measuring procedure, the dynamic thermal resistance of the PCM resulting from its heat absorption is determined. The test sample is pre-cooled to a temperature below the phase change temperature range, and at the same time, a metal plate is preheated to a temperature above the phase change temperature range. To start the measurement, the test sample is brought into contact with the preheated metal plate. The heat emitted from the plate then penetrates the sample. The temperature increase on the back side of the sample is recorded over time. The measurement process is finished when the temperature on the back side of the sample exceeds the phase change temperature range. This indicates that the phase change is complete.

The test is repeated with a control sample of the same substrate without PCM. The time necessary to exceed the phase change range in the two tests is then determined. For the sample without PCM, the duration of this temperature increase is directly related to its basic thermal resistance. But for the sample with PCM, the measuring time recorded for the temperature increase is found in the basic thermal resistance of the substrate as well as the dynamic thermal resistance of the PCM. The dynamic thermal resistance by heat absorption of the PCM is then calculated from the comparison of the measuring times recorded for the temperature increase on the back side of the samples with and without PCM, with reference to their basic thermal resistance values.

A similar procedure is carried out to determine the dynamic thermal resistance of the PCM due to its heat release. The only difference between this and the procedure described above is that the latter involves the samples being preheated before being brought into contact with a pre-cooled plate.
The total thermal resistance of a textile treated with PCM is then the sum of the basic thermal resistance of its substrate and the dynamic thermal resistance achieved by the PCM. The total thermal resistance of a textile without PCM is equal to its basic thermal resistance.\textsuperscript{10}

9.5.3 Temperature and heat input variation measurements

The duration of the PCM’s thermal effects obtained under different application conditions are studied by means of a temperature and heat input variation testing device. These tests are carried out on single fabrics as well as textile composites with a PCM treatment under different ambient temperature and variable radiant and convective heat incidences. The measuring times are used to evaluate the efficiency of the PCM treatment for certain applications.

9.6 Applications of textile coatings and laminates with phase change materials

Textile coatings and laminates with PCM treatment can be used, for instance, to improve the thermal protective function of heat-protective gloves, to create an active thermal insulation effect in a skiwear ensemble, or to provide an active heat and moisture management function to a chemical protective garment system.

Beside garments, there are numerous technical applications whose thermal performance can be improved by the application of PCM. For instance, the PCM applied to a roofing system of a building structure can control the heat flux into and out of the enclosure, enhancing the building’s thermal comfort and its energy efficiency.

9.6.1 Increased thermal protection by the phase change material application in heat-protective gloves

The latent heat absorption of the PCM can be used to improve the thermal protective function of heat-protective gloves. If in contact with a hot object, the heat released by the hot object penetrates through the glove, resulting in a temperature rise inside the glove and hence a rise in the skin temperature. After the skin temperature reaches 45°C the wearer experiences a pain sensation. An increase of the skin temperature above 55°C results in burn injuries. Applying a PCM to the gloves which absorbs latent heat at a temperature of approximately 35°C, the temperature inside the glove will not rise above 35°C as long as the melting process of the PCM is not complete. Thus, for a limited time, the glove possesses an additional thermal
protective function which can help to prevent burn injuries and can lead to extended wearing times.

The PCM applied to heat-protective gloves should be a non-combustible salt hydrate which is macro-encapsulated in a silicone rubber substrate and is arranged inside the glove’s textile structure.\textsuperscript{11}

9.6.2 Enhanced thermo-physiological wearing comfort of skiwear through an active thermal insulation effect provided by the phase change material

The active thermal insulation effect is obtained by the PCM’s thermo-regulating feature due to the alternating latent heat absorption and latent heat release of the PCM. The active thermal insulation effect provided by the PCM can be described by the example of a skiwear ensemble equipped with PCM.

In an ordinary skiwear ensemble, the thermal resistance values of the textile layers (i.e. underwear, sweater, ski suit) and the air layers in between limit the heat flux from the human body to the environment. This passive thermal insulation effect can only be adjusted to the often changing thermal wearing conditions during skiing activities by adding or removing garment layers. But in reality this is not always possible. Thus, strenuous body activities during downhill skiing or cross-country skiing often lead to thermal stress situations and to an increase in the body’s sweat production. The reason for these thermal stress situations is that the heat production of the body exceeds the possible heat release through the garment layers into the environment during such activities. In contrast, sitting in the lift or standing and waiting at the lift at low ambient temperatures often results in a decrease in the body temperature. A heat loss through the garment layers, which exceeds the body heat production, is responsible for the decrease in body temperature.

The application of PCM to a skiwear ensemble provides an active thermal insulation effect acting in addition to the passive thermal insulation effect of the garment system itself. The active thermal insulation of the PCM controls the heat flux through the garment layers and adjusts the heat flux to the thermal circumstances, i.e. the prevailing activity level and the ambient temperature. If the heat generation of the body exceeds the possible heat release through the garment layers into the environment, the PCM will absorb and store this excess heat. Alternatively, if the heat release through the garment layers exceeds the body’s heat generation during lighter activities, the heat flux through the garment layers is reduced by heat release of the PCM.

In a skiwear ensemble, the applied fabrics should be as lightweight as possible and should possess a sufficient breathability. Therefore, textile
substrates with a dotted coating with a compound utilizing PCM microcapsules or a non-woven substrate containing PCM microcapsules should be preferably used in such a garment system. The fabric treated with PCM microcapsules should be arranged close to the body in order to interact directly with the wearer’s body. Applied to the skisuit, the most suitable arrangement of the textile with PCM microcapsule treatment is between the suit’s inner liner and its insulation layer.12

9.6.3 Active thermal and moisture management by the phase change material application in chemical protective garments

The active thermal and moisture management feature added to a chemical protective garment system by the PCM application is based on the PCM’s cooling effect by a continuous latent heat absorption. Chemical protective garments are used in a variety of applications such as the transportation of hazardous chemical goods and the cleaning of chemical facilities and contaminated soil areas. They provide a high barrier function against the penetration by dust, liquids, or gases. However, in the same way the fabric system prevents the transfer of hazardous materials into the garment, it also limits the outward passage of body heat and moisture. Under these strenuous activities, the wearer’s body produces a substantial amount of heat which cannot be released through the garment system in a sufficient manner. As a result, the core temperature of the wearer’s body may rise quickly above the comfort level into the heat stress zone. The body reacts to its overheating with the production of a substantial amount of sweat by the skin’s sweat glands. The sweat cannot be released through the moisture-impermeable structure of the chemical protective equipment and, therefore, remains in the microclimate and does not fulfill its cooling function. This will lead to a further rise in the skin temperature and the body temperature, leading to a heat stress situation which creates a substantial health risk.

In its application in chemical protective garments, the main function of the PCM will be the absorption of excessive heat generated by the body while performing strenuous activities. The latent heat absorption by the PCM will keep the microclimate temperature in the comfort range over an extended period of time, preventing a higher amount of sweat from being produced by the skin. Figure 9.3 shows the development of the mean skin temperature during a 60 minute wearing time of chemical protective garments with and without PCM. The respective moisture development in the microclimate is shown in Figure 9.4.

The thermal and moisture management feature received by the PCM application provides a substantial improvement in the thermo-physiological
wearing comfort of chemical protective garments. In this way, heat stress situations are avoided. Furthermore, wearing times of the chemical protective garments can be extended without the potential health risk, which will in turn result in increased productivity. In its chemical protective garment application, the PCM is directly incorporated into a polymer film which is part of the laminate the chemical protective garment consists of.\textsuperscript{13}

9.6.4 Improved thermal comfort and enhanced energy efficiency of buildings by the phase change material application in architectural membranes

Membrane materials used for roof structures of buildings provide a relatively low thermal insulation capacity compared with the classic building materials. Therefore, a large amount of heat penetrates daily through such roof structures into the building especially during the summer months,
leading to an overheating of the building’s interior. On the other hand, the nightly heat loss through these roof constructions, specifically during the winter months, is significant. The low thermal insulation capacity of conventional architectural membranes can be vastly improved by using a membrane material with thermoregulating properties. The thermoregulating properties of the membrane material are provided by the application of PCM.

In its roof application, the PCM starts to absorb the heat provided by solar radiation during the day in the form of latent heat as soon as the membrane material’s temperature exceeds a given value. During the latent heat absorption by the PCM, its temperature and the temperature of the surrounding membrane material remain nearly constant. Therefore, the heat absorption by the PCM limits the heat flux into the building during the day. Especially on hot days, the thermal comfort inside the building will be enhanced significantly as a result of the PCM’s latent heat absorption feature. The PCM releases the stored latent heat overnight in a reverse, cooling process, which also limits the heat flux out of the building and, therefore, results in a significant reduction of the nightly heat loss through the membrane roof.

The thermoregulating properties of architectural membranes achieved by the PCM application allow for a substantial improvement of the thermal management of buildings with membrane enclosures. The enhanced thermal management reduces the building’s air-conditioning and heating demands, and, therefore, makes the building more energy efficient. The reduced temperature fluctuations that the membrane material is provides during the day may influence the material’s aging behavior in a positive manner which will lead to a longer service life.

Architectural membranes with PCM treatment are made by macro-encapsulating a non-combustible salt hydrate in a silicone rubber binder. The binder with the incorporated salt hydrate is then applied to a fiberglass fabric by knife-over-roll coating.

The architectural membrane material with PCM treatment also shows an interesting feature regarding its light transmission. The translucency of the membrane material equipped with PCM changes in the course of the day. The silicone rubber layer with the PCM becomes transparent as soon as the PCM is completely melted. However, when the PCM crystallizes, the silicone rubber layer with the PCM becomes opaque. The difference in the light transmission between the two states of the PCM incorporated into the silicone rubber which is coated onto the fiber glass fabric totals about 15%.

### 9.7 Sources of further information and advice

The following companies are suitable sources for information pertaining to textiles with microencapsulated PCM:
• Outlast Technologies, Inc., The Valmont Building, 5480 Valmont Street Suite 200, Boulder, CO 80301, USA.
• Freudenberg Vliesstoffe KG, D-69456 Weinheim, Germany.
• Schoeller Textil AG, Bahnhofstr., CH-9475 Sevelen, Switzerland.

Research regarding the microencapsulated PCM technology is also carried out at:
• Yonsei University, Department of Clothings and Textiles, Shinchon-Dong, Sudaemun-Gu, Seoul, 120-749, South Korea.

Information regarding the macroencapsulated PCM technology can be obtained from:
• Textile Testing & Innovation, LLC, 7161 Christopher Court, Longmont, CO 80503, USA.

The company Textile Testing & Innovation, LLC is specialized further in the development of end-use products with microencapsulated and macroencapsulated PCM and in the test of such products.

9.8 References

1 Pause B (1995), ‘Phase change materials – the technology and incorporation into textiles’, 5th International Conference on Textile Coating and Laminating, Williamsburg, USA.
9 Pause B (2001), ‘Textiles with improved thermal capabilities through the application of phase change material (PCM) microcapsules’, Mellians Textilberichte, 9, 753–754.


Nanotechnology-based advanced coatings and functional finishes for textiles

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Abstract: In this chapter, concepts and techniques to develop successful applications of nanotechnology in textile coatings and structures are discussed. The new products development comes from maintaining the stability of interfaces and the integration of these ‘nanostructures’ at micron-length and macroscopic scales in a form of new and improved functional nanocomposite fiber and film, coating or laminate.

Key words: nanotechnology, functional nanocoating, nanocomposites, nanofibers, nanostructures.

10.1 Introduction

The National Science and Technology Council’s Subcommittee on Nanoscale Science, Engineering and Technology defines (NNCO, 2004) nanotechnology as follows:

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. A nanometer is one-billionth of a meter; a sheet of paper is about 100,000 nanometers thick. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

At this level, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology R&D is directed towards understanding and creating improved materials, devices, and systems that exploit these new properties.

US government agencies are involved in research and developments efforts expected to provide cleaner/less wasteful manufacturing techniques, stronger/lighter materials and smaller/faster/energy-efficient computers, powerful biosensors, and more effective treatments for disease.

Nanotechnology is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes due to their nanoscale size. Industrial applications can be developed not only by
exploiting these properties and gaining control of structures and devices at atomic, molecular, and supramolecular levels but also by learning how to efficiently manufacture and use these devices.

New products can be developed by learning from principles to mimic specific functions occurring in nature. For example, a self-cleaning superhydrophobic surface can be found on natural surfaces of plants and animals. The nanostructured self-cleaning surfaces on lotus leaves were studied by botanists with scanning electron microscope (SEM) and they found that the self-cleaning effect comes from low surface energy and minimization of adhesion area available to attaching agents by nano- and/or micro-scaled surface structures (Barthlott and Neinhuis, 2001). For example, Percenta AG, Germany, developed ‘Percenta Nano Textile & Leather Sealant’, which is a water- and oil-resistant impregnator for textiles and paper. The product develops an almost invisible film on the surface around the fibers in treated fabrics.

In this chapter, concepts and techniques to develop successful applications of nanotechnology in textile coatings and structures are discussed. The new products development comes from maintaining the stability of interfaces and the integration of these ‘nanostructures’ at micron-length and macroscopic scales in a form of new and improved functional nanocomposite fiber and film, coating or laminate.

10.2 Principles of nanotechnologies for nanocoating, surface finishing and laminates

Polymer nanomaterials are classified into nanostructured materials and nanophase/nanoparticle materials. The former usually refers to condensed bulk materials that are made of grains (agglomerates), with grain sizes in the 1–200 nm range, whereas the latter are usually dispersive nanoparticles (Koo, 2006). Nanomaterials demonstrate unique and novel properties different from their corresponding bulk materials due to the fact that quantum mechanical properties of electrons and atomic interactions inside of the matter are influenced by nanometer-scale material variations. Thus, nanoscale structures have unique fundamental properties such as melting temperature, electrical and magnetic properties, and even their color, without changing their chemical composition.

The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNs) exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. For example, mechanical properties of low loading (<1%) carbon nanotubes/nylon composites are dramatically improved over high loading (~30%) carbon black/nylon (Kim and Patra, 2007).
Multifunctional polymer nanocomposites may improve their thermal resistance and/or flame resistance (Razdan et al., 2004), moisture resistance, decreased permeability, charge dissipation, chemical resistance, and other material properties. The selected polymer systems’ property can be enhanced to meet or exceed the requirements of current military, aerospace, and commercial applications with control/alteration of the nanoscale additives. The technical approach involves the incorporation of nanoparticles into selected polymer matrix systems whereby nanoparticles may be surface-treated to provide hydrophobic characteristics and enhanced inclusion into the hydrophobic polymer matrix.

Uniform dispersion of these nanosized fillers (nanoparticles) produces ultra-large interfacial area per volume between the nanoparticles and the host polymer: at low volume fraction the entire matrix is essentially part of the interfacial region. Schadler (2003) demonstrated that interparticle spacing is only 10 nm for 15 nm particles at a filler loading of 10 vol%. If the interfacial region is more extended with smaller size nanofillers, the entire polymer matrix behaves differently from the bulk at much smaller loading. Thus, by controlling the degree of interfacial interaction, the entire properties of PNs can be controlled: particle size and distribution, dispersion and interfacial interaction.

Nanomaterials used in textile structures, finishes, and coatings are nanofibers, polymer nanocomposites (PNs), and nanostructured surfaces. The nanotechnologies to produce these materials are briefly discussed in the following sections.

10.2.1 Nanofibers

The diameter of a typical textile fiber is 10 μm (10000 nm) or larger, while the diameter of typical nanofibers is in the order of 10 nm or larger. Since the specific surface area of fibrous material is inversely proportional to the fiber diameter, nanoscale fibers have 1000 times of specific surface area increase from the micro-scale textile fiber materials.

Nanofiber webs are used for filtration media to capture nanosize particles or microbes by exploiting nanosize pores together with the large surface area of nanowebs. Nanosize fibers (>100 nm) can be manufactured by traditional sea-island conjugate extrusion techniques together with splitting and laser-beam drawing.

Electrospinning of nanofibers from polymer solutions is based on the electrohydrodynamic atomization principle. In the common implementation, a conductive spinning liquid is delivered to the tip of a metal capillary, which is connected to a high DC potential power source. The hemispherical droplet on the tip is unstable and deformed into a conical shape by accumulated surface charge. This cone is referred to as a Taylor cone, and a jet
of liquid is ejected continuously at high surface charge density. This jet experiences a bending/whipping instability. The whipping motion causes the jet diameter to rapidly diminish down to the order of 10 to 100 nm. The nanofiber structures formed are collected on a counter electrode.

Formhals (1934) patented electrospinning techniques for spinning solutions from cellulose and cellulose derivatives. He claimed this method is applicable for dry spinning or wet spinning. Recently, electrospun nanofibers have been investigated intensively by many research groups from many countries around the world (Reneker and Chun, 1997; Kalayci et al., 2005; Brown and Stevens, 2007). By arranging the collecting counter-electrode and electric field distribution, one can make many types of nanofibrous structures with different fiber orientation: yarns, and nonwoven webs (Smit et al., 2007). Spinning solution may contain nanoparticles (e.g. carbon nanotubes (CNTs), ZnO) to impart special functional properties.

Electrospinning suffers from drawbacks of very low throughput and lack of fiber structure development (amorphous polymer mass). Among the applications, electrospun nanofiber membranes with functional finishes can be used for neutralizing chemical biological agents or scaffolds for tissue engineering.

10.2.2 Nanocomposites

Polymer nanocomposites for coating and finishing can be engineered to meet multifunctional requirements by selecting a nanoparticle/polymer system. The most commonly used nanoparticles in literature are: montmorillonite organoclays (MMT), carbon nanofibers (CNFs), polyhedral oligomeric silsesquioxane (POSS®), carbon nanotubes (multiwall nanotubes (MWNTs) and single wall nanotubes (SWNTs)), nanosilica (N-silica), and nanometaloxides (ZnO, TiO2, Al2O3, etc.).

Two major findings in the field of polymer nanocomposites pioneered the research of these materials (Ugbolue, 2009). First, Kurauchi et al. (1991) at Toyota Research reported nylon nanocomposite, where moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Second, Giannelis (1996) demonstrated the possibility of melt mixing polymers and clays without using organic solvents. Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements of many materials’ properties by the nano-dispersion of inorganic silicate layers.

Mani et al. (2005) characterized fine structures of montmorillonite nanoclay and polypropylene (PP)/MMT nanocomposites with wide-angle X-ray scattering (WAXS) at ambient temperature on a Rigaku rotating
anode diffractometer with Cu Kα radiation of wavelength 1.54 Å and an accelerating voltage of 60 kV. MMT nanoclay particles were studied as powders, and the PP/MMT nanocomposites were studied as 400 μm thin films. The characterization of the nanocomposite films prepared with a melt mixer running at 70 rpm for 2 hours at 170 °C showed increased d-spacing and a large number of single layered exfoliated platelets compared with the films prepared at 35 rpm for 30 minutes.

Toshniwal et al. (2007) have shown that after the addition of clay into the polymer matrix, a slight reduction in percentage crystallinity is observed. The percentage crystallinity of fibers is shown to be related to their dyeability, as low crystallinity implies that more polymer chains in the PP matrix would be accessible to the dye molecules. The reduction in percentage crystallinity of nanocomposite fibers as compared with neat PP ranges from 2% to 4%. With increasing clay add-on, a diminishing improvement in the K/S (absorption/scattering) values of dyed nanocomposite fibers was observed. Thus, a slight reduction in crystallinity may result in improved dyeing properties of nanocomposite fibers as compared with neat PP fibers; but this cannot be considered the only factor for improving the dyeability of nanocomposite fibers.

The increase in dyeability of the PP nanocomposite is also due to the formation of interphase high energy surfaces and existence of van der Waals forces between the disperse dye molecules and the clay particles (Toshniwal et al., 2007). Addition of clay, in general, did not cause any significant changes in the melt-onset temperature and peak melting temperature of the polymer. The improvement in properties of polymer nanocomposites is attributed to the higher contact area offered by nanoparticles for polymer–filler interaction. So, a uniform dispersion of the nanoparticles and their compatibility with the polymer matrix are desired to enhance functionality of the PNs.

Toshniwal et al. (2007) also examined the effect of dye structure on the color yield of the nanocomposite fibers. For dyeing of the fibers with Disperse Red 65, a monoazo type of dye, values of K/S for the nanocomposite fibers were as high as for the polyester fibers. For Disperse Yellow 42, a nitrodiphenylamine type of dye, there was an improvement in the K/S values for nanocomposite fibers as compared with the neat PP fibers but the color yields for nanocomposite were not comparable to those for polyester fibers. While with Disperse Blue 56, E-type anthraquinone dyes, moderate improvement in the K/S values for nanocomposite fibers was observed; at higher depth of shade, i.e. 6% for higher clay loading (6% on the weight of polymer) the values of K/S close to those for polyester fibers can be obtained. Thus, by properly selecting the dye structure, higher color yield can be obtained for nanocomposite fibers.
Thus, these nanoparticle additives can improve properties of resulting composites, but the additives may cause processing difficulties and unacceptable color and optical properties as shown in Table 10.1.

A significant improvement in mechanical properties of MWNT/nylon-6 nanocomposite fibers was reported by Kim and Patra (2007). To overcome the difficulties in dispersing MWNT in a nylon-6 matrix, they employed \textit{in situ} polymerization with MWNT additives in a \(\varepsilon\)-caprolactam monomer solution. By adding 0.5\% MWNTs, it was found that the nanocomposite fiber drawn 400\% showed a 46\% increase in tensile strength and 41\% stiffer modulus, while the strain at break was reduced 7\%.

Razdan \textit{et al.} (2004) found that the nanocomposites prepared from maleic anhydride grafted PP and methylated zinc oxide nanoparticles showed significant changes in crystallization temperature, decomposition temperature, and residue formed upon decomposition, as compared with the rest of the nanocomposites or control PP samples. This was attributed to a higher degree of interaction existing at the interphase between the organic and inorganic phases for these nanocomposites. The results showed that zinc oxide induced changes in the morphology and thermal stability of PP, though by varying amounts depending on the type of nanocomposite prepared.

Hybrid Plastics (2009) manufactures POSS\textsuperscript{\textregistered} materials that are a type of inorganic–organic hybrid nanostructured material in the form of \((\text{RSiO}_{1.5})_n\) as shown in Fig. 10.1, where \(R\) is methacrylate. By adding POSS particles, one can create hybrid materials which are tough, lightweight, and temperature resistant, while processing is as easy as regular polymers. Thermal resistance of POSS/epoxy composites is demonstrated in Fig. 10.2. POSS-modified epoxy maintains more or less the same level of storage modulus over the temperature range from 25 to 300\(^\circ\)C, while the loss tangent shows no peak.

<table>
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<tr>
<th>Properties improved</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical (tensile strength, modulus, toughness)</td>
<td>Increased viscosity (processing difficulties)</td>
</tr>
<tr>
<td>Gas diffusion barrier</td>
<td>Dispersion difficulties</td>
</tr>
<tr>
<td>Flame retardancy</td>
<td>Optical problem</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>Black color from carbon nanoparticles</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>Ablation resistance</td>
<td></td>
</tr>
<tr>
<td>Chemical resistance</td>
<td></td>
</tr>
<tr>
<td>Reinforcement</td>
<td></td>
</tr>
</tbody>
</table>
10.1 Methacryl POSS® cage mixture, (C\textsubscript{7}H\textsubscript{11}O\textsubscript{2})\textsubscript{n}(SiO\textsubscript{1.5})\textsubscript{n}, \(n = 8, 10, 12\) (MA 735 from Hybrid Plastics, Inc., Hattiesburg, MS, USA).

10.2 Dynamic mechanical properties of POSS modified epoxy (after Hybrid Plastics, 2009).
The flame retardancy of nylon-6/laponite and nylon-6/montmorillonite nanocomposites was investigated by Inan et al. (2004). The pronounced effect of layered silicates on heat release and mass loss rates of nylon-6 were examined. They found that nylon 6/laponite had 46% and nylon 6/montmorillonite had 52.5% lower peak heat release rates than that of neat nylon 6 as shown in Table 10.2. The 6.5% difference between the peak heat release rates of laponite- and montmorillonite-based nanocomposites was attributed to differences in aspect ratio and surface charge density of the nanoparticles (Fig. 10.3). For traditional flame proofing treatment of synthetic fibers, very high loading (up to 30% owf (on the weight of fiber) of
flame retardant is applied, but nanocomposite fibers with low loading (≈5 wt%) of nanoclays such as MMT are found to be as effective.

10.2.3 Nanocoating

Nanocoating is a surface engineering process by atomistic or molecular deposition of less than 100 nm thin films. Thus, the thickness nanocoating films from these processes are quite different from bulk coating methods such as dipping and roll-over-knife etc. There are many techniques to accomplish the atomistic/molecular deposition on a given substrate: physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, electroless plating, laser vaporization, plasma enhanced chemical vapor deposition (PECVD), etc. (Mattox, 1998). According to the operating environment, PVD processes are further divided into vacuum evaporation, sputter deposition, ion plating and ion beam-assisted deposition. The typical PVD deposition rate is 1 to 10 nm/s. The quasi-reactive sputter deposition of indium tin oxide (ITO) conductive films can be obtained from an ITO sputtering target using a partial pressure of oxygen in the plasma. The thermal CVD is the deposition of atoms or molecules by the high temperature reduction or decomposition of a chemical vapor precursor species which contains the material to be deposited. For polymer film deposition, plasma-based CVD can be used (plasma polymerization).

10.2.4 Nanofinishing

Nanofinishing is loosely defined as forming a functional molecular layer on fiber substrates. Soane and Offord (2003) formed nanolayer of many functional molecules by covalently bonding to preactivated complementary functional group on the cotton fibers. The functional polymeric nanolayers for ‘nanofinishing’ are formed by electrostatic self-assembly (Hyde and Hinestroza, 2007), ‘grafted from’ polymer brush nanolayers being formed by initiator groups attached covalently to the substrate, and ‘grafted to’ polymer brush nanolayers being formed by reacting end-functionalized polymer molecules with complementary functional group located on the substrate (Luzinov, 2007). This approach can be used to produce self-cleaning superhydrophobic nanolayers on individual fiber surfaces similar to the Lotus-effect®.

On the other hand, nanofinishing is enabled by the hybrid polymer nanolayer responding differently to environmental changes. Minko and Motornov (2007) considered many types of hybrid polymer brushes for nanofinishing: mixed polymer brushes, block copolymer brushes, and polymer–particle hybrid layers. The advantage of surface finishing/coating with various nanolayers is that the finished fabric has excellent drape
characteristic and soft touch because of the lack of inter-fiber adhesion in the yarn structures.

10.2.5 Nanoparticles

Nanoscale fillers can be grouped into three categories: fiber, plate-like, and three-dimensional (3D) fillers. Fiber or tube fillers have a diameter <100 nm and an aspect ratio of at least 100. The aspect ratio of some carbon nanotubes can be as high as 10⁶. Plate-like nanofillers are layered materials with a typical thickness on the order of 1 nm, but an aspect ratio in the other two dimensions of at least 25. The 3D nanofillers are relatively spherical particles <10 nm in their largest dimension (Schadler, 2003).

In this section only 3D inorganic nanoparticles for functional finishes and coatings are considered, since tube-like and plate-like nanofillers were discussed in Section 10.2.2. Nanoparticles in this category can improve electrical conductivity, antimicrobial properties, refractive index, UV absorption behavior, strength, transparency, and odor-neutralization characteristics of fibers, coated or finished fabric surfaces. Nanoparticles are dispersed in finishing or coating media, and then finish or coating films are formed by a suitable sol/gel technique.

The nanoparticles can be made by two methods: a ‘top-down’ and a ‘bottom-up’ approach. For the former approach, nanosize particles are formed by breaking down microparticles of the same composition mechanically. The nanosize fillers are also assembled from the molecular vapor of the particle material in the latter approach. Inorganic nanoparticles are manufactured by the latter technique with aerosol processes: flame hydrolysis (nanosilica, titania, alumina, zirconium oxide), pyrolysis (carbon black, 20–300 nm), gas condensation (TiO₂, Al₂O₃, CuO, CeO₂, ZnO, ZrO₂, Fe₂O₃, and Y₂O₃), laser ablation, etc. Silver nanoparticles used in antimicrobial and odor control finishes are manufactured either from ion beam sputtering of a silver target or from precipitation of a silver salt solution. This method has a lower production rate, but particle size is on the order of 10–100 nm and high purity nanoparticles are obtained from the aerosol processes.

10.3 Nanotechnology applications in textile structures and functional coatings and finishes

To survey the recent trends in nanotechnology applications in functional coating and finishing, the SciFinder Scholar® database was accessed (ACS, 2008). The search result listed 30 references, where the two concepts ‘nano surface finishing’ and ‘fabrics’ were present anywhere in the reference. The references are broken down into nanotechnology classes as shown in
Table 10.3. In this survey nanofibers and nanostructures were not surveyed, which are discussed elsewhere (Brown and Stevens, 2007).

The most commonly used techniques are nanocomposites and/or nanoparticles (57%). To accomplish the desired finishing effects, a coating formulation with various nanoparticles or an encapsulated nanoparticle with a suitable polymeric emulsion system is applied on the fabric surfaces. For example, silver nanoparticles were used in Agfresh® product (Nisshinbo, Japan) for antibacterial and odor neutralizing finishes. Thermoplastics (nylon, polyester, polypropylene, etc.) with intercalated and or exfoliated nanoclay (MMT) particles can be extruded in fiber form or thin film for coating. These nanocomposite fibers or coating materials exhibit excellent flame resistance and thermal stability at very low loading.

Commercial products based on ‘nanofinishing’ techniques defined in Section 10.2.4 include Resist Spill®, Release Stains® (Nano-Tex, USA), NanoMatrix® (Toray, Japan), and Perma-Freshy® (Teijin, Japan). A series of easy-care finishing from Nano-Tex is based on the principle that functional finishing molecules are covalently bonded to reactive groups pre-activated on the hydroxyl groups of cotton fiber cellulose chains. The ‘grafted’ functional molecules were selected to deliver the desired finishing effects (Soane and Offord, 2003).

Toray’s NanoMatrix is a nanofinishing platform, which is basically a 3–20 nm thick nanolayer formed on individual fiber surfaces of knitted or woven fabrics. This technique can be applied to various functional finishes such as soil release and antistatic by selecting material with targeted functionality. ‘Percenta Nano Textile & Leather Sealant’ (Percenta AG, Germany) is a water- and oil-resistant impregnator for textiles and paper, which works very similar manner to Nanomatrix. The product develops an almost invisible nano-film on the surface around the fiber.

Perma-Freshy from Teijin is a sweat deodorizing treatment. This is a nanolayer (50–200 nm thick) applied on individual fiber surfaces of woven or knitted fabrics, into which sweat odor absorbing particles of 0.5–1 μm are embedded. This mode of nanofinishing on individual fiber surfaces does
not induce fiber–fiber adhesion, and the fabric treated with this manner shows good drape and hand characteristics.

It is important to notice that in any successful textile coating and finishing applications, nanoscale features should be formed on individual fiber surfaces of fabric substrates. This will ensure that breathability, drape, and hand characteristics of the nanofinished fabric are comparable to those of the untreated fabric. The nanofinishes are more durable than traditional finishes due to the fact that nanofeatures are covalently bonded or complete nanocoating on individual fiber surface.

10.4 Sources of further information and advice

Textile coating and surface finishing technologies are well-established practices in industry. It is conceivable that we can reinvigorate the practices and develop new products by infusing the concepts and techniques of emerging nanotechnologies into these well-established technologies.

By efficient nano-manufacturing with reduced material and energy usage, the new products from these efforts will have superior performance, safety, and low environmental impact over traditionally manufactured products in the twenty-first century. Production of nanoparticles and structures by a top-down approach is inherently low rate to meet the scale-up of production. This problem may be overcome exploiting self-assembly techniques and controlling self-assembled supramolecular structures.

The following web links are helpful. The links are current at the time of going to press.

- http://www.nano.gov

10.5 References


Abstract: Conventional flame retarded coatings for textiles are chosen not only because of their flame resistance but also because they have minimal effects on the physical properties of the final products. Flame retardants present may also act as plasticisers if in liquid form. Typical retardants include phosphorus-containing, halogen-containing and inorganic retardants including magnesium and aluminium hydroxides, zinc stannates and borates. Intumescent systems are particularly useful since their normal water solubility is offset by the encapsulating matrix polymer and their expanding chars yield greater levels of fire protection. Smart flame resistant coatings may (i) use conventional flame retardants in an unusual or smart way in order to create a novel effect; (ii) introduce a flame retardant property into a coated textile or laminate in a novel or smart way; and (iii) react to a fire and/or heat hazard in a measured and proportionate way. Each of these areas is discussed and the chapter concludes with those technologies most likely to see success.

Key words: smart, flame resistance, flame retardant, textile, fibres, coating, lamination, halogen replacement, intumescent, nanoparticles, plasma.

11.1 Introduction: general requirements and properties of fire retardant coatings

The established and lamination coating technologies for textiles have been recently reviewed by Woodruff although those specifically relevant to flame retardant applications have not been highlighted. However, most types of coating and lamination systems processes incorporate flame retardancy if required by the application performance requirements. For example, automotive seatings and linings are often laminated structures comprising at least two different textile substrates, a face and backing fabric, in combination with polymer coatings on the reverse face to create mouldability and adherence to the underlying automotive component surface. For European and US markets, the whole composite must pass the internationally accepted US Federal Motor Vehicle Safety Standard FMVSS 302 horizontal burning test in which a clamped 356 mm (14 inches) × 102 mm (4 in.) specimen not exceeding 12.7 mm (0.5 in.) thickness is horizontally mounted and one edge subjected to a burner flame for 15 s. The specimen passes the test if the burning rate is less than 102 mm/s (4 in./min). While this is only a moderate
test of flame retardancy, other coated textiles may have to pass far more stringent test conditions. Examples here are simulated leather, coated textile contract furnishing fabrics, which in the UK must pass the ignition criteria defined in BS7176 in which the specimen, mounted around a filling such as polyurethane foam in both seat and back geometries is subjected to a wooden crib (BS 5852: 1990: Source 5). After the crib has been ignited, it burns with an energy output equivalent to two burning sheets of newspaper (∼300 J). The sample must self-extinguish after the crib has burnt out and no evidence of continuing afterflame or smoulder should occur within the total test period of 10 minutes.

While these two examples do not represent extremes, since even higher levels of fire resistance may be required in aerospace and military applications, they do represent a fair spread of flame retardancy levels required in many of the non-specialist or consumer-oriented application areas. In generating respective levels of flame resistance, coated fabrics may comprise a balance of normal non-flame retardant components (e.g. normal polyester yarns and fabrics) in combination with less flammable or inherently flame retardant fibres or fabrics and/or flame retardant coatings. These latter may comprise an inherently flame retardant resin such as poly(vinyl chloride), PVC, or a flammable one such as an acrylic copolymer or a synthetic rubber in which a flame retardant additive chemical is included. In other words, there is a significant armoury of flame retardant fibres, polymers and additives available in order to ensure that a given coated textile or laminate can achieve a desired level of flame resistance.

However, none of these flame retardant products may be designated as ‘smart’ since in each case a formulation has been designed and produced to generate a specified level of performance defined by a specific performance standard. A truly smart or intelligent flame retardant or resistant coating should be able to respond to a variety of fire hazards in a proportionate manner by being able to ‘switch on’ or activate varying levels of resistance. At the present time, no such smart coated or laminated textile structures exist but it is true to say that they are becoming ‘smarter’ in their ability to have increased versatility, be processed using more efficient processes and be generally more environmentally acceptable than hitherto. This chapter will review such recent developments as well as attempt to point the way to the means of developing truly smart and intelligent coatings and laminations.

### 11.2 Main types of fire retardant/resistant coatings and laminates

Normally flame retardant coatings are expected to confer a defined level of flame retardancy to the overall coated textile of laminate and their
effectiveness is often determined by the flammability of the underlying substrate fibres. In many cases these may be conventional unretarded fibres and blends, e.g. pure cotton, cotton/polyester, 100% polyester, 100% polyamide, or be already flame retarded fibres and blends, e.g. flame retardant cotton and flame retardant cotton-rich/synthetic fibre blends. However, in the latter case, antagonisms may arise between flame retardant species present in the coating and those present in the underlying fibres/textile and so care must be taken when developing such formulations. The simplest situation is probably one where the coating contains the flame retardant species and the underlying substrate has no such presence. In the case of inherently flame resistant fibres, antagonisms may still exist if the flame retardant property is conferred by an additive or comonomer since the underlying chemistries are similar to those present in the flame retardant present in the coating. Thus, for instance, the phosphorus-containing species present in the inherently flame retardant polyester Trevira CS® (Trevira GmbH) is similar to phosphorus-containing additives that could be present in a coating formulation. While it is possible that antagonisms might occur in such a situation, it is more likely that both flame retardant systems will function with a degree of additivity. However, if a halogen-based flame retardant is present in either fibre or coating, it is possible that some antagonistic interactions might occur. Anecdotal evidence suggests that some flame retarded PVC coating formulations when applied to cotton flame retarded with some phosphorus-containing agencies are inferior to the same coating applied to unretarded cotton. Unfortunately, flame retardancy is not an exact science and predicting antagonisms and indeed synergisms is often impossible; empirical formulation is usually the preferred means of achieving a flame retardant, coated textile or laminate having a defined performance in terms of both flammability and other required properties.2

Typical coating polymers include the following:1

- Natural and synthetic rubbers of which the latter include polyisobutylene (or ‘butyl’), styrene butadiene (SBR), poly(butadiene-acrylonitrile) (or ‘nitrile’), poly(chloroprene) (or neoprene), chlorosulphonated polyethylene, poly(fluorocarbon) and silicone elastomers.
- PVC plastisols and emulsions are widely used to confer the most cost-effective balance of both water resistance and flame retardancy because of the high polymer chlorine content. However, environmental concerns regarding their high chlorine and plasticiser contents have encouraged their replacement by alternatives, although at a higher cost.
- Poly(vinyl alcohols) or PVAs have varying degrees of water solubility depending on the degree of saponification of the parent poly(vinyl acetate). They find application in end uses where wash durability is not

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greatly significant and because of this, flame retardant inclusion not only has to render the very flammable base polymer flame retardant but also possess a similar level of durability.

- Formaldehyde-based resins, including phenol-, urea- and melamine-formaldehydes offer a relatively cheap range of durable, coating polymers in which flame retardants may be introduced. The phenolics have the advantage of relatively high inherent flame resistance.
- Acrylic copolymers (or more simply, ‘acrylics’) offer a combination of high levels of flexibility and softness as well as some degree of moisture permeability and so find preferred applications in many textile areas where aesthetics are important. Typical applications include curtains and linings, roller and pleated blinds, mattress tickings and bedding to confer dust and microbe impermeability and textile back-coatings as carriers for flame retardants. It is in this last area where significant interest in flame retardancy has lain since the UK furnishing regulations of 1988.3
- Vinyl acetate copolymers (including crosslinkable varieties) with vinyl chloride and/or ethylene. These are flexible coatings ideal for upholstered furnishings and behave in a manner similar to the acrylics; presence of vinyl chloride will add to the overall flame retardant formulation property.
- Polyurethanes (or PURs) may be applied to textiles by solvents and more recently by hot melt coating and as direct powders. Addition of flame retardants is effective but has to be selected to suit the application method.
- Silicones offer water repellency and an inherent flame resistance because of their tendency to promote the formation of a siliceous char and eventually silica. However, when present on synthetic textiles they may prevent melt dripping and so prevent energy being removed from the burning textile as flaming drips. Thus the silicone-coated textile may appear to be quite flammable relative to the textile and resin alone.
- Fluorocarbons are typified by poly(tetrafluoroethylene) (PTFE) although others exist such as fluorinated ethylene polymers (or FEPs) and poly(vinyl fluoride) (PVF) and poly(vinylidene difluoride) (PVDF). All have varying levels of inherent flame resistance which when applied to flame retardant substrates will enhance performance although their presence is often insufficient to fully flame retard a flammable substrate.
- A number of fusible polymers that may be applied in powder or hot melt form such as low and high density polyethylenes, polyamides (e.g. PA6 and PA66), polyesters, copolyesters and ethylene-vinyl acetate (or EVA) copolymers. Whilst being inherently flammable, they offer the opportunity of incorporation of flame retardant additives during the resin compounding stages.
Table 11.1 lists these generic polymer types and gives approximate measures of their flammability in terms of limiting oxygen index (LOI) values noting that for acceptable levels of flame retardancy LOI > 26–27 vol% is required. It should be noted that actual LOI values depend on sample dimensions, polymer processing history, presence of fillers, etc. Notwithstanding this, it is evident that certain polymer coating and laminating matrices will have varying levels of inherent flame retardancy (e.g. PVC and chlorine- and fluorine-containing polymers), although the more commonly used polymers and copolymers are quite flammable and so the
presence of flame retardants is necessary to flame retard both the coating matrix polymer and the underlying textile substrate.

11.2.1 Use of additives

Most flame retardant additives are selected from the range offered across the flame retardant additive field and the reader should consult standard texts and Horrocks,2 Horrocks and Price5 and Lewin.6 Selecting those for coating and lamination applications is largely dependent upon the following factors apart from flame retardant efficiency:

• compatibility with matrix polymer; e.g. the flame retardant should mix and disperse well and even dissolve in the polymer if possible;
• have minimal effect on coating/lamination processing efficiency; e.g. the additive should be stable during processing and have minimal effect on rheological properties;
• have minimal effect on overall product properties including aesthetics; e.g. presence of large diameter solid particulate flame retardants will reduce surface lustre and cause unacceptable roughness.

Specific examples presented below are flame retardants with particular benefits to coating and laminating applications.

**Phosphorus-containing agents**

Ideally, liquid flame retardants are preferred providing they do not unduly plasticise the polymer film although in many cases some level of plasticisation is required. Table 11.2 lists typical examples of acceptable flame retardants, including the long chain alkyl/aryl-substituted phosphate examples where plasticisation is also required. While Table 11.2 concentrates on single chemical entities, many commercial proprietary flame retardants are formulated mixtures or blends of more than one species which are especially achievable when component FRs are liquids. Such blends enable balances of flame retardancy to be achieved while offering acceptable processing and end-product performance. Where coating or resin layer thicknesses are significant, then solid, particulate agents based on ammonium polyphosphate chemistry may be used. These may be part of an overall intumescent system and so are considered in the next section.

On a final point, P-containing agents have efficiencies which depend on the polymer type and chemistry. Since they act primarily in the condensed phase by promoting the formation of carbonaceous char, this depends on the polymer matrix structure. Polymers rich in hydroxyl or pendant ester groups favour dehydration and carbonisation under the Lewis acid-driven activity of phosphorus-containing species when heated.7,8 Consequently, in
Table 11.2 Selected phosphorus-containing flame retardants for use in coating and lamination

<table>
<thead>
<tr>
<th>Chemical formula/name</th>
<th>Commercial examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triaryl phosphates</td>
<td>Reofos 35–95; Chemtura Phosflex 71B; Supresta*</td>
<td>Proprietary formulations with 7.6–8.5% P</td>
</tr>
<tr>
<td>Cresyl diphenyl phosphate</td>
<td>Kronitex CDP; Chemtura</td>
<td>9.1% P</td>
</tr>
<tr>
<td>Tricresyl phosphate</td>
<td>Kronitex TCP; Chemtura</td>
<td>8.4% P</td>
</tr>
<tr>
<td>Trixylyl phosphate</td>
<td>Kronitex TXP; Chemtura Phosflex 179; Supresta*</td>
<td>7.8% P</td>
</tr>
<tr>
<td>Triethyl phosphate</td>
<td>Fyrol TPE; DSBG</td>
<td>17% P</td>
</tr>
<tr>
<td>Isodecyl diphenyl phosphate</td>
<td>Phosflex 390; Supresta*</td>
<td>Functions as plasticiser in PVC; 7.9% P</td>
</tr>
<tr>
<td>Oligomeric phosphate-phosphonate</td>
<td>Fyrol 51; Supresta*</td>
<td>Textile back-coatings; 20.5% P</td>
</tr>
<tr>
<td>Cyclic organophosphates and phosphonates</td>
<td>Antiblaze CU; Rhodia Pekoflam PES; Clariant Aflammit PE; Thor</td>
<td>Substantive to PES fibres but may be incorporated in most coating resins; 17% P</td>
</tr>
<tr>
<td>Nitrogen-containing polyol phosphate</td>
<td>Exolit OP 920; Clariant</td>
<td>Non-halogen FR for lattices with plasticising effects; 16% P, 9% N</td>
</tr>
</tbody>
</table>

*Formerly Akzo and now ICL.

Poor char-formers like poly(ethylene) and polyesters, P-containing agents are not very efficient unless part of an intumescent system.

Halogen-containing flame retardants

Unlike the phosphorus-containing flame retardants, halogen-containing flame retardants are not polymer-specific in that they act primarily in the vapour phase by suppressing the flame chemistry.9 Bromine-containing agents predominate because not only are they more efficient than similar chlorine-containing species, but also the high atomic weight of bromine ensures that it is present in a high mass fraction within most organobromine compounds. Typically for many polymers acceptable levels of flame retardancy are achieved if about 5% (w/w) bromine is present in the final formulation. In flame retardants such as the very commonly used decabromodiphenyl ether (decaBDE; see Table 11.3) where bromine contents are as high as 83% w/w, flame retardant presence is often less than 10% w/w, which is quite low compared with most flame retardant polymers containing other flame retardants. However, antimony III oxide (ATO) is
usually present as synergist.\textsuperscript{9} For greatest effectiveness the molar ratio Br:Sb = 3 (reflecting the possible formation of SbBr\textsubscript{3} as an intermediate\textsuperscript{8,10}) is commonly used and this equates in the case of decaBDE to a mass ratio Sb\textsubscript{2}O\textsubscript{3}:decaBDE = 1:2, thereby ensuring that the total flame retardant concentration present in the polymer may be as high as 15% w/w or so. Recently, a number of tin compounds including zinc stannate (ZS) and zinc hydroxystannate (ZHS) have been shown to be synergistic with halogen-containing flame retardants, but unlike ATO, bromine-containing FR/ZS or ZHS combinations have to be selected for maximum efficiency.\textsuperscript{11} Table 11.3 lists the more commonly used halogen-containing flame retardants which have applications in textile coatings and laminates.

Phosphorus and halogen together in the same molecule often produce additivity and even synergy in terms of flame performance with respect to the contributions of each element present.\textsuperscript{12} A number of phosphorus and chlorine-containing flame retardants have been developed and commercially used in applications often requiring a degree of flexibility such as foams, films, coatings and laminates. Table 11.4 presents a selection of these.

### Table 11.3 Halogen-containing flame retardants for coatings and laminates

<table>
<thead>
<tr>
<th>Chemical formula/name</th>
<th>Commercial examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibromostryene</td>
<td>Great Lakes DBS; Chemtura</td>
<td>59% Br</td>
</tr>
<tr>
<td>Decabromodiphenyl ether</td>
<td>Great Lakes DE-83R; Chemtura</td>
<td>Principal FR for textile back-coatings; 83% Br</td>
</tr>
<tr>
<td></td>
<td>FR-1210; DSBG</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saytex 102E; Albemarle</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Myflam and Performax; Noveon</td>
<td></td>
</tr>
<tr>
<td>Hexabromocyclododecane (HBCD)</td>
<td>Great Lakes CD-75; Chemtura</td>
<td>Competes with decaBDE in textile back-coatings; 73% Br</td>
</tr>
<tr>
<td></td>
<td>Flacavon H14; Schill &amp; Seilacher</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FR-1206; ICL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saytex HP-900; Albemarle</td>
<td></td>
</tr>
<tr>
<td>Tetrabromophthalic anhydride and diol</td>
<td>Great Lakes PHT4 and PHT4-DIOL; Chemtura</td>
<td>68% Br</td>
</tr>
<tr>
<td></td>
<td>Saytex RB-49; Albemarle</td>
<td>46% Br</td>
</tr>
<tr>
<td></td>
<td></td>
<td>68% Br</td>
</tr>
<tr>
<td>Tetrabromobisphenol A (TBBA)</td>
<td>Great Lakes BA-59; Chemtura</td>
<td>59% Br</td>
</tr>
<tr>
<td></td>
<td>FR-720; ICL</td>
<td></td>
</tr>
<tr>
<td>Dedecachloropenta-cyclooctadecadiene</td>
<td>Dechlorane; Occidental</td>
<td>Used in elastomeric coatings (synthetic and silicone); 65% Cl</td>
</tr>
</tbody>
</table>
Table 11.4 Selected phosphorus- and chlorine-containing flame retardants

<table>
<thead>
<tr>
<th>Chemical formula/name</th>
<th>Commercial examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris (1,3-dichloroisopropyl) phosphate (TCDP)</td>
<td>Fyrol 38 &amp; FR-2; ICL</td>
<td>7.1% P, 49% Cl</td>
</tr>
<tr>
<td>Oligomeric chloroalkyl phosphate ester</td>
<td>Fyrol 99; ICL</td>
<td>14% P; 26% Cl</td>
</tr>
<tr>
<td>Chlorinated phosphate ester</td>
<td>Antiblaze 78; Albemarle</td>
<td></td>
</tr>
<tr>
<td>Tris (2-chloroisopropyl) phosphate (TCPP)</td>
<td>Fyrol PCF; ICL</td>
<td>9.5% P; 32.5% Cl</td>
</tr>
</tbody>
</table>

11.2.2 Intumescent systems that form a carbonaceous/vitreous protective layer over the polymer matrix

For coated and laminated textiles requiring high levels of flame barrier properties then it is more usual to incorporate an intumescent system\textsuperscript{13,14} within the polymer. Such formulations may be intumescent in their own right and generate carbonaceous chars independently of the surrounding polymer matrix or they may interact with the matrix so that the flame retardant polymer together give rise to an expanded, intumescent char when exposed to heat and flame. The majority of these are based on ammonium phosphate (APP) and melamine chemistries and selected examples are presented in Table 11.5. All are particulate solids, of which one or more components may be water soluble, and so for water durability they may only be used in hydrophobic polymer matrices which may create dispersion problems during processing. Hence, many commercial particulate examples are coated or microencapsulated either to reduce water solubility and/or to improve polymer matrix compatibility. Furthermore, manufacturers are attempting to reduce particle sizes as shown for APP in particular. While APP is not an intumescent in its own right, it is a powerful char-former when in the presence of oxygen-containing polymers and copolymers. However, to ensure intumescent action, it used in combination with other agents such as pentaerythritol and melamine.\textsuperscript{13} The melamine phosphates shown in Table 11.5 do have a greater degree of inherent intumescent activity since the acid-forming component phosphate is chemically combined with the gas-forming melamine. They also have superior water insolubilities often <1 g/100 cm\textsuperscript{3} before any subsequent coating or microencapsulation. Particle sizes are often less than normal APP samples and may have particle diameter values of $D_{50} \leq 8 \ \mu$m.

Of all flame retardant coating innovations of the last few years, it is probably true to say that those incorporating intumescent flame retardant agents have been the most commonly reported.\textsuperscript{2,13–15} Indeed the recent demand for...
Table 11.5 Selected intumescent and intumescent component flame retardants

<table>
<thead>
<tr>
<th>Chemical formula/name</th>
<th>Commercial examples</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Ammonium polyphosphate | *Phase I types:*  
Antiblaze MC; Albemarle  
Exolit AP 412; Clariant  
FR CROS 480–485; Budenheim | Water solubility ∼4 g/100 cm³ |
|                       | *Phase II types:*  
Exolit AP 422; Clariant  
FR CROS 484; Budenheim | Water solubility ∼4 g/100 cm³ |
|                       | *Coated Phase II types:*  
Exolit AP 462 & 463  
FR CROS 486; Budenheim  
FR CROS 487; Budenheim  
FR CROS C30/C40/C60/  
C70/489; Budenheim | Micro-encapsulated version of AP 422; water solubility <0.5 g/100 cm³  
Silane coated: melamine-formaldehyde (MF) coated: water solubility <0.1 g/100 cm³  
Surface reacted MF, varying particle sizes $D_{50} = 7–18$ μm; water solubility ≤0.1 g/100 cm³ |
| Melamine phosphates   | BUDIT 310; Budenheim  
Antiblaze ND; Albemarle  
BUDIT 311; Budenheim  
BUDIT 312; Budenheim  
Antiblaze NH; Albemarle  
Melapur MP; Ciba  
Antiblaze NJ; Albemarle  
Melapur 200; Ciba  
BUDIT 3141; Budenheim | Dimelamine orthophosphate  
Dimelamine orthophosphate  
Dimelamine pyrophosphate  
Melamine phosphate  
Melamine phosphate  
Melamine phosphate  
Melamine pyrophosphate  
Melamine polyphosphate  
Melamine polyphosphate |
| Other melamine salts  | BUDIT 313; Budenheim  
BUDIT 314/315  
Melapur MC; Ciba | Melamine borate  
Melamine cyanurate  
Melamine cyanurate |
| Other pentaerythritol derivatives | Great Lakes NH 1197; Chembura  
Great Lakes NH 1511; Chembura | Phosphorylated pentaerythritol  
Phosphorylated pentaerythritol/melamine salt |
| Intumescent blends    | BUDIT 3077 and related products; Budenheim  
Antiblaze NW; Albemarle | Melamine phosphate and dipentaerythritol |

open flame-resistant barrier fabrics in US markets driven by Californian regulations for furnishings (TB 133) and mattresses (TB 129 and 630) and federally by the US Consumer Product Safety Commission (CPSC 16 CFR 1633) for mattresses has encouraged the development of intumescent
coatings applied to inherently fire resistant fibre-containing fabrics including glass which are exemplified by the Springs Industries-patented products (now Springs Global)\textsuperscript{17} and fabrics from Sandel International Inc.

### 11.3 Increasing flame retardant coating smartness

At the present time, most flame retardant formulations used in coatings and laminated textiles are based on the need to achieve a defined flammability performance measured in terms of a standard test performance pass/fail or graduated criterion. This will define a maximum level that any given product will be expected to achieve and the flame retardant present cannot in any way be defined as being ‘smart’.

Introducing ‘smartness’ into flame retarded coatings and materials may be undertaken in three ways:

- the use of conventional flame retardants in an unusual or smart way in order to create a novel effect;
- the introduction of a flame retardant property into a coated textile or laminate in a novel or smart way; and
- the development of a flame retardant formulation that reacts to a fire and/or heat hazard in a measured and proportionate way. In this case, the flame retardant property may be passive in that the maximum level is fixed, but the product may react in a number of different ways to a fire stress below this maximum. Alternatively, the FR property may be reactive in that it responds to a fire hazard in a proportionate and reversible manner. In this latter case, such a formulation would be truly smart in that, for example, it might offer an acceptable level of ignition resistance to low heat flux ignition and heat sources while changing its overall properties very little. However, at higher heat fluxes, the formulation may offer a barrier property which, unlike intumescent treatments via transformation to a voided char, offers protection for only so long as the fire threat is present. If the hazard is removed, the product should then recover and revert to its initial form. It must be emphasised that this is a goal which at the present time has not been achieved (see Section 11.3.3).

#### 11.3.1 Use of conventional flame retardants in a smarter way

One of the major issues that has faced the flame retardant industry for the past 15 years or so, has been the desire to remove flame retardant chemicals from use that have been shown to have an unacceptable level of environmental risk. This whole issue is too complex for this present discussion but
an outline has been presented elsewhere. An extensive risk analysis of 16 commonly used flame retardants was undertaken by the US National Academy of Sciences in 2000 and current debate continues as shown by following web-sites belonging to organisations such as the US Consumer Product Safety Commission (CPSC), the European Flame Retardants Association (EFRA) and the Bromine Science and Environmental Forum (BSEF). In summary, all halogen and, more specifically, bromine-containing flame retardants have come under scrutiny, and while some like penta- and octabromodiphenyl ether have been banned, others like deca-bromodiphenyl ether (decaBDE) and tetrabromobisphenol A (see Table 11.3) have been subjected to risk assessments and have been found to be safe. However, in spite of the scientific evidence, the pressures to replace bromine-containing FRs and, in the case of textile back-coatings and other coated textiles, the replacement of decaBDE in particular has been and continues to be intense.

This author has reviewed the challenges posed by the desire to reduce the use of brominated flame retardants in textile back-coatings which includes previously reported results of a number of initial attempts to replace brominated flame retardants in formulations with varying degrees of success. For instance, gradual replacement of the decaBDE-antimony III oxide content in a conventional formulation with a number of bromine-free alternatives including APP, a cyclic oligomeric phosphonate (Amgard CU; Rhodia), alumina trihydrate and ZHS, shows that when applied as back-coatings to cotton, fabrics may pass a simulated version of the small flame ignition source (source 1) method defined in BS 5852: 1979: Part 1 when total add-ons are 30% (w/w) or less with respect to substrate. However, while all non-bromine-containing formulations examined pass if present as 100% replacements for the decaBDE-based component, in formulations containing both brominated and non-brominated retardants, only those containing either APP or the cyclic oligomeric agent passed at commercially acceptable add-on levels. In the latter case, however, because it is a liquid, the back-coating formulation was plasticised to the extent of yielding a tacky and unacceptable handle when present at greater than 50% (w/w) with respect to the original decaBDE-antimony III oxide component concentration. The UK regulations require that flame retarded upholstered fabrics pass the small flame, simulated match test as defined in BS 3651. After application of the 30 min 40 °C water soak, however, both formulations failed to pass the small flame ignition source requirement. It is worth noting that the revised BS 5852: 2006 includes the automatic requirement to submit all samples to be tested to Source 1 after this prior 40 °C water soak.

In a later paper, the performance of selected, less soluble as well as intumescent phosphorus-based flame retardants was studied in which a
number were applied in a standard back-coating formulation to 100% cotton and 35% cotton–65% polyester blend fabrics of typical area densities for furnishing fabrics. Only APP-based formulations could yield passes on both cotton and cotton–polyester substrates and this appeared to be associated with their relatively low temperatures of thermal decomposition behaviour as determined by thermogravimetric analysis. However, the associated poor water durability caused all APP-containing samples to fail after the required 40 °C water soak treatment. A major conclusion from these results was that any phosphorus-based candidate for replacing conventional bromine-containing back-coating formulations would have to decompose and preferably transform to a liquefied state at temperatures well below the ignition temperature of the most flammable fibres present in the supporting fabric. This would enable the now-fluid flame retardant to wet substrate fibre surfaces and diffuse from the back-coating through the fabric and to the front face and prevent ignition by the igniting flame. In the case of cotton fibres which ignite at about 350 °C, this would require the flame retardant component to decompose at about 300 °C or less, a condition shown only by APP. To the authors’ knowledge, no single phosphorus-based flame retardant fulfils both the low decomposition temperature and high water insolubility criteria at the present time.

Thus in developing a phosphorus flame retardant strategy for the replacement of decaBDE and similar bromine-based formulations, it is evident that the vapour-phase activity of the latter is a key factor in determining their efficiency apart from their excellent insolubility and general intractability. Notwithstanding these prime issues, the outcomes of our previous research10,23 have led to three strategies that may be proposed to achieve these requirements:

1. the sensitisation of decomposition or flame retarding efficiency of phosphorus-based systems;24
2. the reduction in solubility of successful but soluble systems; and
3. the introduction of a volatile and possible vapour phase-active, phosphorus-based flame retardant component.21

With regard to the first, we have demonstrated that the inclusion of small amounts of certain transition metal salts, notably those of zinc II and manganese II can reduce the onset of decomposition of APP from 304 °C to as low as 283 °C in the case of 2% (w/w) manganese II sulphate addition.24 When applied in a back-coating formulation with APP, the presence of metal ions increases LOI values slightly (of the order of 1–1.5 LOI unit for manganese and zinc salts) from 25.1 for APP-only coated cotton to 26.6 vol% in the presence of 2% manganese acetate. However, all coated fabrics still failed the simulated small flame ignition version of BS 5852, which is not perhaps surprising since our earlier research indicated that an LOI
value for a coated cotton fabric above 26 and closer to 29 vol% was required for a pass. Furthermore, it was noted that the presence of the transition metal salt reduced the width of the charring area subjected to the flame source when compared with the APP-only sample. It should be pointed out, however, that even if passes had been obtained, the problem of durability to water soaking would still remain.

Recent work by Bourbigot and coworkers has shown that micro-encapsulation of otherwise soluble flame retardants like ammonium phosphate with polyurethane shells can improve the durability of coatings containing them. However, the preparation of these micro-encapsulated agents is not an easy process with different techniques being developed in order to improve yields.

**Role of nanoparticles**

An extension of the first strategy above is, perhaps, the possible sensitisation using nanoparticulate additives. The inclusion of nanoparticles in coating formulations has been investigated by Bourbigot and coworkers. Both nanoclay and polyhedral oligomeric silsesquioxanes (POSS) when present alone in polyurethane coatings applied to polyester and cotton fabrics, were found to reduce peak heat release values of back-coated fabrics determined by cone calorimetry, although neither increase ignition times not reduce extinction times. In fact the converse tends to be the case. Subsequent work by us has shown that the introduction of nanoparticulate clays by themselves has no beneficial effect to a back-coating polymeric film in terms of enhancing its thermal resistance and the introduction of fumed silica to a flame retarded back-coating formulation reduces its effectiveness when a conventional flame retardant such as APP is present. Figure 11.1 shows the effect of adding nanoparticulate fumed silica to a back-coating formulation containing increasing levels of APP. While it must be noted that silica particle dispersion was poor, the presence of higher amounts of silica do not relate to increasing values of limiting oxygen index of a coated fabric.

In other polymers, the incorporation of nanoparticles along with conventional flame retardants indicates that possible synergies may occur, enabling considerably lower amounts of the latter to be used to provide the same level of flame retardant performance. This has been demonstrated by Bourbigot and Duquesne for selected intumescent–montmorillonite clay and –nanosilica polypropylene/polyamide blend formulations such as EVA-APP/PA6-clay and EVA-APP/PA6-nanosilica and EVA–clay–alumina trihydrate blends for cable applications by Beyer. We have also demonstrated that the inclusion of nanoclays and APP and similar flame retardants in polyamide 6 and 6.6 films promote synergistic interactions and
the opportunity to reduce APP levels by up to 50% while maintaining an acceptable performance (measured as LOI). However, to the author’s knowledge there appears to be no published evidence of this potential synergy having been introduced into flame retardant coating formulations for textiles and laminates.

**Introduction of volatile phosphorus-containing species**

In addressing the need for such vapour phase activity (strategy (3) above), it must be remembered that the generally poor performance of all APP-containing coated fabrics is associated with our earlier observation that enhanced char formation alone at the rear of a fabric is insufficient to prevent burning of the front face. The obvious way of overcoming this situation is to introduce phosphorus-containing species that may be rendered volatile and so enter the flame chemical reactions in a manner similar to bromine-containing retardants. However, if this were to be effected, there remains the question of the flame retarding efficiency of such volatile species and here the literature is not very helpful, with usually only indirect evidence of vapour phase activity being cited. For instance Rohringer et al. have proposed that the relatively superior flame retarding efficiency of flame retardants based on tetrakis(hydroxymethyl) phosphonium chloride (THPC) applied to polyester–cotton blends may be associated with the evolution of volatile phosphine oxides, which then act in the vapour phase and retard the burning polyester component. Day et al. have also provided evidence that the flame retarding efficiency of now-banned tris...
(2,3-dibromopropyl) phosphate or ‘tris’, when applied to polyester, is also a consequence of vapour phase activity of phosphorus species. Hastie and Bonnel\textsuperscript{35} used spectroscopic and high pressure sampling mass spectrometry to study possible flame inhibition effects of a number of phosphorus-containing compounds including trimethyl phosphate, phosphoryl chloride and triphenylphosphine oxide. When mixed with methane and propane fuels, flame inhibition was noted in diffusion flames burning in air, although in premixed flames (with air), some P-containing additives could increase flame strength. These same experiments suggested that previous considerations that the PO\textsuperscript{+} radical was the predominant species in flames would have to be revisited since now it appeared that the HPO\textsubscript{2}\textsuperscript{+} radical was more significant. It was then suggested that this then interacts with H\textsuperscript{+} and OH\textsuperscript{+} radicals in manner similar to halogen radicals, thus interfering with the main flame propagation reactions as follows:

\[
\begin{align*}
\text{HPO}_2^+ + \text{H}^+ & \rightarrow \text{PO}^+ + \text{H}_2\text{O} \\
\text{HPO}_2^+ + \text{H}^+ & \rightarrow \text{PO}_2^+ + \text{H}_2 \\
\text{HPO}_2^+ + \text{OH}^- & \rightarrow \text{PO}_2^- + \text{H}_2\text{O}
\end{align*}
\]

Work by Babushok and Tsang\textsuperscript{36} concerning the inhibition of alkane combustion in premixed flames suggests that in the vapour phase, phosphorus may be more effective than halogen. In accordance with these findings, our recent work\textsuperscript{21,22} initially considered four potentially volatile phosphorus flame retardants selected from their reported boiling or decomposition data and these were the monomeric cyclic phosphate Antiblaze CU (mass loss occurs above 197 °C\textsuperscript{23}), tributyl phosphate (TBP) (melting point (MP) = −80 °C, boiling point (BP) = 289 °C with decomposition), triphenyl phosphate (TPP) (MP = 48–52 °C, BP = 244 °C at 10 mm Hg, 5% weight loss at 208 °C) and triphenylphosphine oxide (TPPO) (MP = 156–158 °C), this last being one studied by Hastie and Bonnel.\textsuperscript{35} Because interest lay in generating new back-coatings for both polypropylene and cotton fabrics, thermogravimetric studies suggested that TBP would be most suitable because it starts to lose mass (i.e. produces volatiles) at about 150 °C, well below the melting temperature of polypropylene (~165 °C) and the ignition temperature of cotton (~350 °C), although tackiness was anticipated to be a problem. TPP was also selected as the next most volatile agent with volatilisation starting at about 200 °C. Each was combined with an intumescent char-forming agent, Great Lakes NH 1197 (Chemtura) comprising phosphorylated pentaerythritol\textsuperscript{23} (see also Table 11.5) in formulations that maintained constant overall flame retardant contents, although in varying volatile:non-volatile phosphorus ratios, namely:

- 250 dry mass units NH1197/100 dry mass units resin;
- 200 dry units NH1197, 50 dry units TBP or TPP/100 dry mass units resin;
Formulating novel flame retardant combinations is often fraught with problems which impede or prevent facile sample preparation. Here the liquid TBP produced a very tacky coating at dry unit contents beyond 100 parts while TPP, although a solid thereby removing the tackiness problem, tended to agglomerate, thus producing a very granular back-coating formulation, which prevented even coating. Nevertheless, formulations were back-coated on to 220 g m\(^{-2}\) cotton and 260 g m\(^{-2}\) polypropylene fabrics respectively to achieve nominal dry add-ons in the 40–70\% w/w range.

Table 11.6 shows the LOI and small-scale simulation test of BS5852 results after 40 °C water-soaking test for 30 minutes.

Table 11.6 Flammability testing results of back-coated cotton and polypropylene fabrics after 40 °C water soak treatment\(^ {22} \)

<table>
<thead>
<tr>
<th>Formulation (dry units FR with 100 dry units resin)</th>
<th>Fabric</th>
<th>Dry add-on (%)</th>
<th>Simulated BS 5852</th>
<th>LOI (vol%)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH-1197 (250) Cotton 41 – 26.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH-1197 (250) PP 64 – 22.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH-1197 (200) Cotton 37 Pass 26.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBP (50) PP 57 Fail 21.5</td>
<td></td>
<td></td>
<td></td>
<td>Visual observation suggests near to pass</td>
<td></td>
</tr>
<tr>
<td>NH-1197 (200) TBP (50) Cotton 52 Pass 26.3</td>
<td></td>
<td></td>
<td></td>
<td>Char length greater than 200:50 analogue</td>
<td></td>
</tr>
<tr>
<td>NH-1197 (150) TBP (100) Cotton 52 Pass 26.3</td>
<td></td>
<td></td>
<td></td>
<td>Char length greater than 200:50 analogue</td>
<td></td>
</tr>
<tr>
<td>NH-1197 (150) TBP (100) Cotton 49 – 26.7</td>
<td></td>
<td></td>
<td></td>
<td>High add-on is a consequence of agglomeration of solids</td>
<td></td>
</tr>
<tr>
<td>NH-1197 (200) TBP (50) Cotton 104 – 26.4</td>
<td></td>
<td></td>
<td></td>
<td>High add-on is a consequence of agglomeration of solids</td>
<td></td>
</tr>
</tbody>
</table>

- 150 dry units NH1197, 100 dry units TBP or TPP/100 dry mass units resin.

Formulating novel flame retardant combinations is often fraught with problems which impede or prevent facile sample preparation. Here the liquid TBP produced a very tacky coating at dry unit contents beyond 100 parts while TPP, although a solid thereby removing the tackiness problem, tended to agglomerate, thus producing a very granular back-coating formulation, which prevented even coating. Nevertheless, formulations were back-coated on to 220 g m\(^{-2}\) cotton and 260 g m\(^{-2}\) polypropylene fabrics respectively to achieve nominal dry add-ons in the 40–70\% w/w range. Table 11.6 shows the LOI and small-scale simulation test of BS5852 results after 40 °C water-soaking test for 30 minutes.

These show that the partial replacement of the char-forming retardant NH 1197 by the volatile TBP and less volatile TPP gave back-coated cotton samples that showed improved performance with the dry mass ratio formulation of 200:50 giving the highest LOI values. It is interesting to note that while the agglomerating effect of TPP at 100 parts presence resulted...
in a high add-on of 104%, this almost double the total flame retardant presence with respect to fabric, has minimal effect on LOI. This suggests that once the flame retardant presence in the back-coating is sufficient to raise the fabric LOI to just above 26 vol% and this represents an asymptotic maximum value. A similar position may exist for the back-coated polypropylene samples except that this maximum value is just above an LOI value of 22 vol%.

The significance of the simulated match test pass of the NH 1197/TBP-containing coated cotton sample suggests that the presence of the volatile phosphorus-containing component improves flame extinction during front face ignition. This same effect is not obviously seen in the polypropylene fabrics which have relatively low LOI values and excessive thermoplasticity with melting, which is not overcome or supported by the char-promoting elements within the back-coating. In fact the additions of TBP or TPP have little effect on the overall LOI with respect to back-coated PP fabrics containing only NH 1197; however, the 200:50 NH 1197:TBP only just failed the simulated BS 5852 test in spite of an LOI of only 21.5 vol%.

Further evidence of the volatile phosphorus activity was gained by determining the retention of phosphorus in charred samples comprising the following back-coating flame retardants:

- ammonium polyphosphate (Antiblaze MCM, Albemarle),
- melamine phosphate (Antiblaze NH, Albemarle),
- cyclic phosphonate (Amgard CU, Rhodia),
- oligomeric phosphate-phosphonate (Fyrol 51, ICL),

where the liquid Amgard CU and Fyrol CU species (see Table 11.2) were selected as potentially vapour-phase active flame retardants. In order to produce chars having different thermal histories, back-coated samples of known weight were then placed in a furnace at 300, 400, and 500 and 600°C for 5 minutes in an air atmosphere. These experiments were not intended to simulate actual combustion conditions but were designed to create chars having residual phosphorus contents that would be dependent on the volatility of the phosphorus-containing moieties present and Table 11.7 summarizes the results of char phosphorus content analyses expressed as ΔP%, the respective phosphorus loss from each char, where ΔP equals the theoretical phosphorus content assuming 100% retention in the char minus the experimental value.21,22

It is evident that phosphorus loss is lowest for the fabrics containing the char-promoting Antiblaze MCM (APP) and NH (melamine phosphate) retardants and highest for the Amgard CU and Fyrol 51 liquid components. These two also exhibit the highest coated fabric LOI values suggesting that not only is the phosphorus present volatile but, when released into the flame, it reduces flammability.
Table 11.7 Back-coated fabric LOI values and loss of phosphorus ($\Delta P$) from chars

<table>
<thead>
<tr>
<th>Flame retardant/dry parts by weight</th>
<th>Initial add-on, %</th>
<th>LOI (vol%)</th>
<th>$\Delta P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300°C</td>
<td>400°C</td>
</tr>
<tr>
<td>Antiblaze MCM/250</td>
<td>13.9</td>
<td>23.2</td>
<td>0.41</td>
</tr>
<tr>
<td>Antiblaze NH/250</td>
<td>11.0</td>
<td>20.8</td>
<td>−0.16</td>
</tr>
<tr>
<td>Amgard CU/250</td>
<td>11.9</td>
<td>26.3</td>
<td>1.91</td>
</tr>
<tr>
<td>Fyrol 51/250</td>
<td>16.6</td>
<td>26.1</td>
<td>1.62</td>
</tr>
</tbody>
</table>

11.3.2 Novel or smart ways of introducing flame retardant coatings to textiles and laminates

Coating levels versus nanotechnological challenges

Before considering potential for and present evidence of novel means of introducing flame retardant coatings, it is pertinent to address a number of factors which will influence their success or failure. Unlike some surface treatments such as those that confer extreme hydrophobicity and/or soiling resistance and which may be effective if only a single molecular layer of an appropriate chemical species is deposited on fibre surfaces, there needs to be a critical minimal presence of a flame retardant treatment if it is to be effective. For a typical retardant to prevent ignition of a typical fibre-containing textile, concentrations of between 5 and 20% w/w with respect to the textile are usual. This is because for a phosphorus-containing flame retardant, phosphorus levels typically between 1 and 3% w/w are required. Most commercial flame retardants contain only 8–20% P (see Table 11.2) which results in actual chemical levels present on the fabric ranging from as low as 5% up to as high as 25% w/w. With brominated flame retardants in which bromine contents are much higher (see Table 11.3), the levels of flame retardant may be less but then once the additional antimony III oxide synergist is taken into account, total flame retardant concentrations approach similarly high levels as discussed in Section 11.2.1 above. In the particular case of coated textiles, the flame retardant present must not only act on the textile fibres present, but also on the coating resin, which, unless it has an inherent flame retardant property (see Table 11.1), will be similarly flammable. Thus levels of flame retardant present in many coatings are often higher than is necessary to be effective on the fabric alone.

Once the level of effective flame retardant has been established to achieve the required flame retardancy, the application requirement may also influence the final concentration and physical form required. In free-standing
textiles such as curtains, linings and drapes, ignition resistance and self-extinction are the sole flame retardant requirements. However, if the flame retardant textile must act as a barrier to an underlying surface, such as the filling in upholstered furnishings or as an underlying clothing layer in protective clothing, then the flame retardant treatment should maintain or even enhance the insulative property of the outer fabric layer, usually by char promotion. For char-forming fibres such as the cellulosics and wool, this is quite easily achieved and in back-coated furnishing fabrics made from these fibres, total dry coating levels of 20–30% w/w of a formulation containing about two-thirds by weight of flame retardant and one-third by weight of resin are typical. However, if the fibres are thermoplastic and possibly fusible, e.g. polyester, polyamide and polypropylene, then the coating formulation must be char-promoting in its own right and be able to support the melting/shrinking substrate fibres in order to maintain an effective flame barrier. This is why back-coatings for polyester and polypropylene furnishing fabrics, for example, are applied at levels typically in the 50–100% w/w range.

Thus any novel or smart means of applying flame retardant coatings must be able to achieve such high levels of application. Recent reviews highlight the possibilities of conferring films and coatings at nanodimensions on to fibre and textile surfaces in order to achieve high level novel effects such as hydrophobicity, soil release, self-cleaning, bioactivity, etc. Methods cited include:

- self-assembly of nanolayer films
- surface grafting of polymer nanofilms, and
- synthesis of smart switchable hybrid polymer nanolayers.

Even assuming that the conferred nanofilms possessed the required flame retarding functions and efficiencies of conventional coatings, it is likely that none of these will be relevant to the present argument because of the need to achieve high loadings. The possibility does exist, however, of reducing coating thickness while retaining overall constant levels, if the coating, instead of being applied on textile surfaces, is applied only to component fibre surfaces. In the case of the application of fluorocarbons at about 0.6% w/w to a typical polyester fibre of 10 dtex (~30 μm diameter), the surface layer thickness is calculated to be above 50 nm. At microfibre dimensions (<10 μm diameter), the surface layer thickness on the increased fibre surface area reduces to about 10 nm and at sub-microfibre dimensions, even thinner films are theoretically possible. However, flame retardant coatings will be required to be present at 10–20 times these fluorocarbon concentrations yielding much thicker theoretical film thicknesses as well as problems associated with interfibre adhesion and occlusion of fibre interstices.
Generation of heat reflective finishes at the nanolevel

Notwithstanding the above discussion, there are the possibilities of gaining some degree of heat and fire protection using coatings or films applied at the nanolevel if they are not seen to be simple replacements for conventional flame retardant coatings. Coated textiles and laminates are physically quite thin materials when compared with more conventional ones such as bulk polymers. In fire science terms, they are also more often to be defined as thermally thin materials in which the temperature of the surface is assumed to equal the temperature of the interior during heat exposure. In thermally thick materials, such as bulk polymer extrusions and mouldings, a thermal gradient exists in a fire-exposed sample with the surface temperature being close to that of the igniting source and the interior much cooler. This enables the material surface to offer insulative properties to underlying structures and, if the heated surface forms an intumescent char, the overall insulative character of the whole sample may actually increase. In normal flame retardant textiles and coated fabrics and laminates, unless they are quite thick (>3–5 mm), the ability to form a thick, surface insulating char is limited and the underlying fibres soon reach temperatures approaching that of the igniting source (>500 °C) when they degrade and may ignite. Even the most inherently flame resistant fibres such as the poly(meta- and para-aramids), poly(benzimidazole), semicarbons, etc., are only able to offer a thermal barrier during sustained high heat exposures for limited periods.

If, however, we are able to convert a thermally thin textile into one showing so-called thermally thick behaviour, its overall fire protective character will increase and many conventional coatings, especially those comprising intumescent additives, attempt to do this. It is highly unlikely that nanocoatings could promote a similar effect unless they could offer a heat shield property of unusual efficiency.

In the area of heat protective textiles, use is made of the deposition of reflective metal films on to fabric surfaces to reduce the effects of heat radiation from a fire source and it is in this area that nanofilm and nanocoating deposition may have opportunities.

Plasma technology offers a means of achieving the means of developing novel nanocoatings having the desired thermal shielding effects, although the literature is sparse with regard to reported examples. Shi has demonstrated that low pressure, radio frequency discharge plasma treatment of a number of polymer surfaces including poly(ethylene terephthalate) in the presence of gaseous (CF₄/CH₄) leads to flame retardation. Later studies in which ethylene-vinyl acetate copolymers were plasma-exposed for times up to 15 minutes followed by immersion into acrylamide, gave very high yields of surface grafted poly(acrylamide) and LOI values approaching...
24 vol% at 47 w/w% grafting levels. The more recent studies of low pressure argon plasma graft polymerization by Tsafack and coworkers have reported the successful grafting of phosphorus-containing acrylate monomers (diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl) phosphonate (DEAMP) and dimethyl(acryloyloxymethyl)phosphonate (DMAMP)) to polyacrylonitrile (PAN) fabrics (290–300 g/m²). In the presence of a grafting agent, ethyleneglycoldiacrylate (EGDA), graft yields were optimized (as high as 28% w/w) resulting in limiting oxygen index values as high as 26.5 vol%, although after accelerated laundering this reduced to 21 vol%. Fabric samples were first immersed in a solution of monomer in ethanol followed by plasma exposure. This and Shi’s techniques would not be expected to provide nanofilms since this type of grafting may be perhaps best considered as a variation of established polymer surface and textile-grafting procedures and the high yields (28% w/w in the case of grafted DMAMP, CH₂ = CH–CO–O–CH₂–P(CH₃)₂) would explain both the level of flame retardancy but poor launderability achieved. When extended to cotton (120 and 210 g/m²), low pressure argon plasma graft polymerisation of these same acrylate monomers, again yielded grafted fabrics having elevated LOI values as high as 26.0 vol% in the case of DMAMP. However, even higher and more acceptable levels of flame retardancy were achieved only if synergistic nitrogen was also present in grafts which they demonstrated following the grafting of the phosphoramidate monomers, diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) and acryloyloxy-1,3-bis(diethylphosphoramidate)propan (BisDEAEPN). These yielded LOI values of 28.5 and 29.5 vol% respectively at levels of 38.6 (≈ 3.36%P) and 29.7 (≈ 3.29%P) w/w%. Launderability was improved when the crosslinking agent, EGDA, was present at high concentration and, in the case of BisDEAEPN, after a simulated laundering, graft level reduced to 26.7 w/w% and LOI reduced to 25.0 vol%. The improved durability achieved here is probably associated with the greater reactivity of the plasma-activated cellulose chains compared with those generated on PAN fibre surfaces. In this work, the challenge of achieving the high flame retardant agent levels has been reached and, while no grafted film thicknesses have been reported, they are probably within the micron range and not the nanometer range.

Marosi and coworkers have used plasma treatment of a polyethylene substrate surface-treated by vinyltriethoxysilane and by organoboroxosiloxane (OBSi), and an OBSi-containing intumescent flame-retarded compound (IFR-OBSi) based on polypropylene, ammonium polyphosphate and pentaerythritol in attempts to improve the oxygen barrier properties of the intumescent coating. Plasma treatment did in fact reduce the oxygen permeability of the coating by one order of magnitude although the effects
that this has on the fire barrier properties are not reported. The possibility that plasma deposition of silicon-based films might improve the flame retardancy of underlying polymer surfaces has been reported by Jama et al. Here normal and nanocomposite polyamide 6 films were activated by a cold nitrogen plasma and then transferred to a reactor containing 1,1,3,3-tetramethyldisiloxane (TMDS) vapour in an oxygen carrier gas for 20 minutes. This remote plasma-assisted polymerization is similar to that used by Tsafack et al. above except that the monomer is in the vapour phase prior to polymeric deposition. Thermogravimetry shows that increasing the oxygen flow rate considerably increases the thermal stability in air of deposited coatings (see Fig. 11.2) as the increasingly oxygenated polysiloxane coating transforms to a silica-based structure at about 800°C. This gives the opportunity for a thermal barrier effect coupled with a moderate increase in flame retardancy of a coated polyamide 6 film and a surprising increase in the flame resistance of the nanocomposite polyamide 6 films, as determined by LOI (see Figure 11.3) with LOI values exceeding 45 vol% for the latter. Char residues mirror respective LOI trends and analysis shows that those from the coated nanocomposite films are largely silica-based while those for coated normal polyamide 6 films are essentially polysiloxane-like. The presence of the nanoclay at 2% w/w appears to have synergized the formation of silica from the plasma-generated coating.

The thermal barrier efficiency of the coated nanocomposite films is demonstrated by cone calorimetric analysis under an incident heat flux of 35 kW/m². Here the peak heat release rates (PHRR) of plasma-coated nanocomposite films are reduced in intensity by 25% compared with the
uncoated films. A subsequent paper\textsuperscript{52} demonstrates that on scaling up the experiments using a larger low pressure plasma source and reactor, thereby enabling larger and more consistently coated samples to be produced. Of particular interest to the present discussion is that the film thicknesses obtained in the earlier and smaller reactor were about 48 μm whereas those from the larger reactor reduced to only 1.5 μm and coated nanocomposite polyamide 6 films continued to yield LOI values as high as 48 vol%. Furthermore if film thickness was increased above 1.5 μm, LOI reduced to a constant value of about 42 vol%. Once again, cone calorimetry showed that PHRR values were advantageously reduced compared with uncoated nanocomposite films (PHRR = 1972 kW/m\textsuperscript{2}) showing an expected reduction of 44% with respect to normal polyamide films (PHRR = 1102 kW/m\textsuperscript{2}) and the additional coating reduced PHRR by a further 59% to a value of 807 kW/m\textsuperscript{2}. Once again, analysis of residues after cone calorimetric exposure shows that the coated nanocomposite film transforms to a silica-like structure and it is this that creates the thermal shielding effect.

Very recent work in our own laboratories has led to a patented process\textsuperscript{53} in which using atmospheric plasma we have demonstrated that the flash fire resistance of a conventionally flame retarded fabric may be improved by surface treatment in the presence of nanoparticulates and a silicon-containing monomer. Table 11.8 shows the changes in cone calorimetric behaviour of a 200 g/m\textsuperscript{2} woven meta-aramid fabric subjected to an argon plasma alone and the plasma in the presence of a silicon-containing monomer, a nanoclay alone and a combination of silicon-containing monomer

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Limiting oxygen index (LOI) versus oxygen flow rate of remote plasma polymerised TDMS coated on (a) polyamide 6 and (b) nanocomposite polyamide 6 films.\textsuperscript{51}}
\end{figure}
Table 11.8 The cone calorimetric behaviour of m-aramid-containing fibres exposed to 60 kW/m² heat flux after subjecting them to various atmospheric plasma treatments

<table>
<thead>
<tr>
<th>Sample and treatment</th>
<th>Mass change (%)</th>
<th>Time-to-ignition, TTI (s)</th>
<th>Time-to-peak heat release, TTP (s)</th>
<th>Peak heat release rate, PHRR (kW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meta-aramid alone</td>
<td>−</td>
<td>13</td>
<td>16</td>
<td>83</td>
</tr>
<tr>
<td>Argon plasma only</td>
<td>−2.8</td>
<td>16</td>
<td>20</td>
<td>73</td>
</tr>
<tr>
<td>Argon plasma with silicon-containing monomer</td>
<td>−0.6</td>
<td>NI*</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Argon plasma with nanoclay</td>
<td>1.6</td>
<td>NI*</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Argon plasma with silicon-containing monomer and nanoclay</td>
<td>3.5</td>
<td>NI*</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Sample did not ignite.

and nanoclay. The fabric alone failed to ignite when exposed at the more typical heat flux of 50 kW/m² but did ignite when exposed at 60 kW/m². Flash fire testing is usually associated with heat fluxes of 80 kW/m² or more and this level was not achievable by our equipment. The results show that even after argon plasma treatment alone, slight increases in both the time-to-ignite (TTI) and time-to-peak (TTP) heat release are observed with a similarly slight reduction in PHRR. The loss of mass is associated with the effect of surface ablation following plasma treatment. When any of the combinations of silicon-containing monomer and nanoclay are introduced, the fabric becomes non-ignitable under a 60 kW/m² heat flux. The effect of additional components gives rise to either reduced mass loss or an actual increase in sample mass as would be expected if a surface layer were being deposited. Clearly the already high heat flux ignition resistance of the meta-aramid fabric is being significantly improved following plasma treatment. The advantage of this method is that in principle it may be applied to any textile substrate retrospectively and so offers great opportunity for enhancing the heat and fire resistance of a range of textile substrates.

In conclusion, it should be noted that plasma technological modification of fibre and textile surface has a history spanning about 40 years and although it has gained commercial significance within industrial sectors such as microelectronics and more recently in improving paint/coating adhesion to plastics for automotive and other applications, its adoption by
the textile industry has been slow. One of the main reasons for this is that the majority of successful plasma applications occurred using low pressure plasma and it is only recently that atmospheric pressure plasma technologies have been developed which are considered to be more appropriate to continuous processing of textile fabrics. The desire to use atmospheric pressure plasma increases further the challenge of achieving high levels of surface deposition since plasma polymerization can be best controlled in low pressure plasmas which have more well-defined plasma zones. Hegemann and Balazs, also state the preference for low pressure plasma systems, at least at the research level, because the greater mean free paths of ions within such plasma enable greater penetration depths within textile materials, hence the potential for more cohesive nanocoatings. Furthermore, plasma metallisation sputtering techniques, currently used to confer conductive nanolayers on textile surfaces, but with the potential for thermally reflective coating deposition, favour the use of low pressure plasmas.

However and notwithstanding these arguments, it is most likely that any commercial plasma process acceptable for the textile industry will have to be based on atmospheric pressure technologies and so future research efforts should be cognisant of this requirement, especially given that the established non-thermal plasma processes previously feasible at low pressures have been successfully transferred to atmospheric pressure conditions as evidenced by the current (2007) range of Dielectric Barrier Discharge, arc-jet, microwave and hybrid sources available.

11.4 Truly smart flame retardant coatings and laminates and future trends

At the beginning of Section 11.3, three ways of introducing smartness were defined and discussions in Sections 11.3.1 and 11.3.2 focused on the first two. The third, namely the development of a flame retardant formulation that reacts to and responds to a fire and/or heat hazard in a measured and proportionate way, is an ideal yet to be achieved especially if a degree of reversibility is also required. Given the technological economic challenges of replacing many of the currently useful coating and surface treatments available, successful development of such smart coatings would be in a niche area where the price of the effect and product can justify the cost. Alternatively, the new process will partly replace or be a component within a more conventional process. Potential areas of opportunity may lie within novel hot melt laminating/coating (all dry) where absence of the need for solvents is a prime advantage as well as ease of addition of modifying additives, use of multi-melting ceramics which offer a spectrum of thermal protection, hybrid polymer brushes which not only act as durable surface grafts to substrate polymers and fibres but also may offer novel
functionalities and nanofilm deposition using a range of technologies including chemical vapour deposition and plasma. Finally it might be commented that while the research literature abounds with interesting novel surface-modifying processes and effects, scaling these up to fully commercial process within a correct economic model and which meet repeatable performance demands commensurate with today’s requirements of high performance textiles and materials pose greater challenges in most cases than the original research required to prove the respective concept in the first instance.

11.5 References


16. CONSUMER PRODUCT SAFETY COMMISSION. Final Rule for the Flammability (Open Flame) of Mattress Sets (4010); http://www cpsc.gov/LIBRARY/FOIA/foia06/brief/briefing.html Jan. 13, 2006


19. EUROPEAN UNION RISK ASSESSMENT REPORT FOR BIS(PENTABROMODIPHENYL) ETHER, European Chemicals Bureau, 2003 (closed 26 May 2004); www.bsef.com


54. NFPA 2112; Standard on flame resistant garments for protection of industrial personnel against flash fire, 2007 edition, National Fire Protection Association, MA
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WVP. see water vapour permeability
WVTR. see water vapour transmission
  rate

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