# 7 Coated and laminated fabrics

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## 7.1 Introduction

Coated and laminated textiles usually consist of a textile substrate, which will typically be a woven, knitted or non-woven textile fabric, which has been combined with a thin, flexible film of a natural or synthetic polymeric substance.

A *coated* fabric (Figure 7.1a) usually consists of a textile substrate on to which the polymer is applied *directly as a viscous liquid*. The thickness of the film is controlled by applying it via a blade or similar aperture.

A *laminated* fabric (Figure 7.1b) usually consists of *one or more* textile substrates which are combined with a *pre-prepared polymer film or membrane* by adhesives or heat and pressure.

### 7.1.1 History

Textile coated fabrics have been used for over a thousand years. The earliest coated fabrics originated in Central and South America where the natives collected natural rubber latex which exuded from the trunks of certain trees.
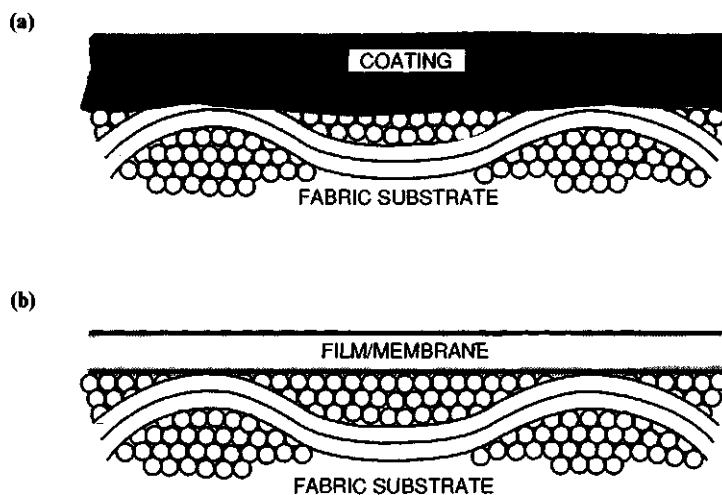
(a)

(b)

Figure 7.1   Cross-sections of: (a) coated fabric; (b) laminated fabric.

They could spread this milky latex on to fabrics which then coagulated in sunlight to form a flexible, elastic, liquid-proof fabric. This could be used for waterproof bags, covers and containers.

During the 16th and 18th centuries, the discovery of America made this knowledge widespread in Europe. By the late 18th century a rubber industry had been established. Natural rubber could be dissolved in benzene to produce a viscous spreading solution.

Other substances based upon waxes and setting oils, such as linseed oil and tars, were also used to impregnate textile fabrics to render them liquid-proof.

The vulcanisation process for crosslinking rubbers using sulphur was invented in 1840 by Goodyear but patented by Hancock. This led to a large period of growth in the uses of rubber, and plantations were started in Malaysia, Africa and Sri Lanka. Synthetic rubbers and plastic polymers were developed in the 1930s and 1940s. This work became particularly important during the Second World War, when supplies of natural rubber from the Far East were cut off by the Japanese invasion. This led to the abundant and versatile supply of products for a wide range of purposes.

### 7.1.2 General usage

Coated and laminated fabrics have certain advantages over unsupported films or sheets. They have much higher tensile and tear strengths, better puncture resistance and better handle. Coated and laminated fabrics are used for the following purposes.

(a)   To confer liquid- and gas-resistant properties on flexible textile fabrics. The most common liquid is rainwater, and the most common gas is air.
(b)   To provide a soil-resistant, easily cleaned surface.
(c)   To provide materials having the appearance and wearing qualities of leather, or other animal skins, at a much lower cost, and to satisfy the ethical conscience of those who dislike the exploitation of animals.

## 7.2   Textile substrates

### 7.2.1   Synthetic continuous filament fabrics

Modern high-performance coated fabrics tend to be based upon continuous filament woven nylon 6 and 6.6 or polyester fabrics (polycaprolactam, poly(hexamethylene adipamide), and poly(ethylene terephthalate), respectively). These provide high tear strength, high dimensional stability and resistance to microbiological and chemical attack. Flat multifilament fabrics provide a thin hairless surface to which the continuous coatings can be applied. Where the filament fabric is used as the outer layer of the coated fabric, it prevents

abrasion of the coating and sheds liquids and soil readily. In rainwear, the water-shedding facility is enhanced by applying a water-repellent treatment based upon silicones or fluorocarbon finishes.

Filament fabrics can be texturised (Taslan air jet process) to improve coating or film adhesion, to improve handle, and to reduce noise and gloss. This gives the aesthetic appearance of staple fibre fabrics.

*Warp- or weft-knitted fabrics* tend to have too low a cover factor to be used as the substrate for coated fabrics. They are used as the basis of lightweight laminates for linings or as the second substrate in three-layer sandwich-laminated fabrics.

*Non-woven spun-bonded fabrics* form the basis of laminates used for disposable items such as disposable clothing, covers and linens. Those utilising polyolefins (Tyvek®) or polyamide are widely used.

### 7.2.2   Staple fibre fabrics

Early coated and laminated fabrics were predominantly based upon woven or knitted cotton fabrics. Heavier coated fabrics may have used wool, flax, jute or hemp fabrics, although these were not so common. Some modern coated fabrics or laminates utilise blends of polyester and cotton or polyester and viscose.

Staple fibre substrates tend to preclude lightweight coatings due to the difficulty in maintaining a continuous film over a 'hairy' fabric. Thus, they tend to produce heavy coated fabrics for tarpaulins, covers, furniture, synthetic leathers, etc. Such fabrics tend to have a softer, quieter handle than their filament-fibre fabric analogues, although strength and puncture resistance tend to suffer.

### 7.2.3   Special substrates

*Glass filament fibres* in woven fabric are used for heavy coated laminated fabrics where flame retardance, heat resistance, resistance to chemicals and good weathering properties are required. Glass fibre has low resistance to flexing fatigue, due to its brittle nature, and can only be applied where flexing, crumpling and folding are kept to a minimum. Semipermanent covers for sports stadia, tensioned structures, thermal insulation and endless conveyor belts are typical examples.

*Aromatic polyamide* (Aramid) fabrics, both woven and knitted, are used where flame retardance and non-melting behaviour are required. Blends of poly(*meta*-phenylene isophthalamide) and poly(*para*-phenylene terephthalamide) (Nomex® and Kevlar®) provide fabrics of great strength and abrasion resistance. Other Aramid fibres used include Conex®, Apyeuil®, Kermel® and Twaron®.

## 7.3    Techniques for coating fabrics

### 7.3.1    Basic techniques

There is a wide range of techniques in industrial use, but they all require similar basic approaches.

(a)    The textile fabric to be coated or laminated is supplied full width on a roll.

(b)    The fabric is fed under careful tension control to a coating or laminating head or zone.

(c)    After application, the coated fabric is passed through an oven to cure the composite and remove volatile solvents before cooling and rolling up.

(d)    The film or coating can range in weight from about $10 \, g/m^2$ up to several hundred $g/m^2$, according to usage.

### 7.3.2    Application systems (Smith, 1971)

(a)    *Knife over roller.*    This is one of the most common coating techniques in use. The diagram (Figure 7.2) shows a metal Doctor blade which is suspended above a steel or rubber-covered roller. The gap between the roller and blade can be set very accurately to about 0.01 mm to control the thickness of the coating. The polymer to be applied is in the form of a viscous solution or gel which rolls against the Doctor blade as the fabric passes underneath and leaves a layer of polymer on the fabric.

(b)    *Floating knife.*    In this system the Doctor blade is fixed above the fabric, as shown in Figure 7.3. The coating weight and thickness are controlled by the tension in the fabric and the depression of the knife. This process tends to be used for impregnating fabrics with small amounts of coating.
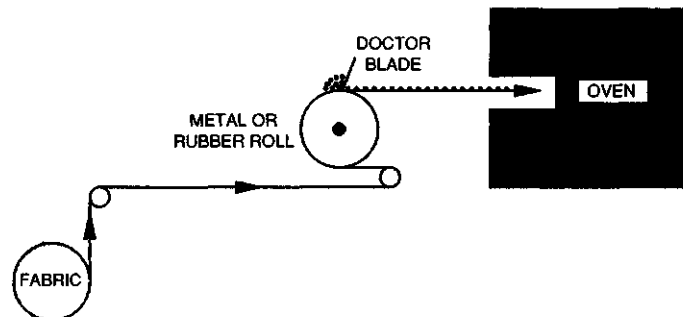


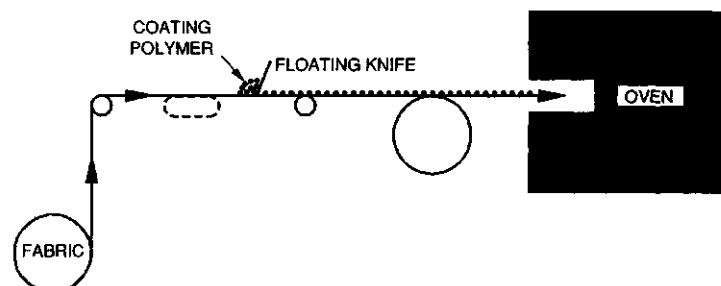Figure 7.2    'Knife over roll' system.

**Figure 7.3**  Spreading by 'floating knife' system.

(c)  *Back coating.*  In this system the coating polymer is contained in a trough where it is picked up by a revolving gravure roller and transferred to the underside of the fabric, as shown in Figure 7.4.

(d)  *Reverse roll.*  In this process, one slow-moving precision roll is used to meter the thickness of the coating composition on to another precision roll, by accurately adjusting the distance between the two. The second roll is allowed to contact the moving substrate which is supported from below by the main rubber roll. The coating applied is such that its linear weight remains constant however uneven the surface of the substrate may be. This is thus a precision process (see Figure 7.5).

(e)  *Transfer coating.*  This is a sequential process in which the coating composition is metered by Doctor blade on to a silicone release paper, in a process similar to process (a), above. The prepared non-tacky and smooth film is then coated with a layer of an adhesive polymer (which may be the same as the original coating formulation) known as a tie-coat. Immediately
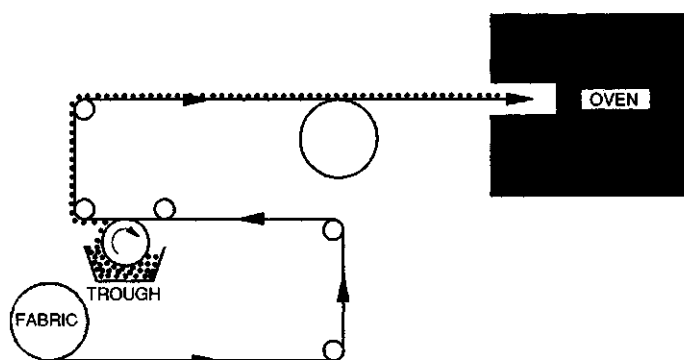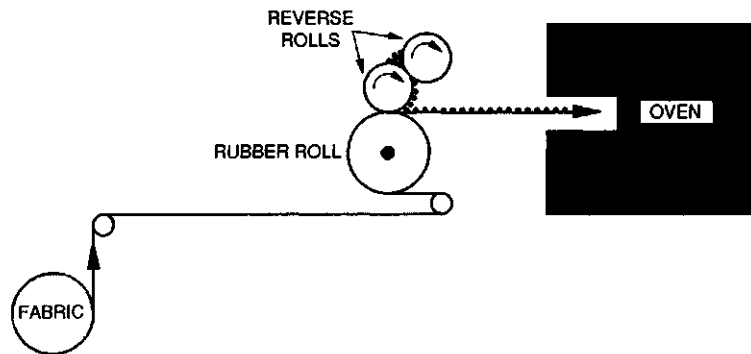


**Figure 7.4**  Back coating.

Figure 7.5 'Reverse roll' system.

after this a suitable textile substrate is combined with the tacky adhesive by passage through laminating rolls (see Figure 7.6a). After drying and curing in an oven, the release paper is peeled away, leaving a smooth compact coated surface (see Figure 7.6b).

(*f*) *Lamination.* This is a process similar to transfer coating, in that a pre-prepared film (without release paper) is coated with adhesive prior to combination with one or more textile fabrics under pressure between laminating rolls (see Figure 7.6b).

(*g*) *Flame lamination of foams.* This process is similar to adhesive lamination (f), except that a pre-prepared thin, thermoplastic foam sheet is exposed to a wide slot flame burner situated before the laminating rolls. A thin layer of foam is melted and adheres to the fabric during laminating and cooling. No drying or curing oven is required in this process.

(*h*) *Screen printing.* This is an ideal process for applying even coatings to fabrics with uneven surfaces. Rotary screens dispense the coating composition on to the fabric. The composition may be a stable foam or paste or even an unstable foam. A Doctor blade then controls the coating thickness precisely (Matthews, 1993).

### 7.3.3 Control parameters in coating

The coating process requires a delicate balance between adhesion efficiency and parameters such as tear-strength performance and handle of the finished fabric. It is important that:

(a) Specially formulated tie-coats may need to be applied on certain substrates to prepare the fabric surface for subsequent coating layers.
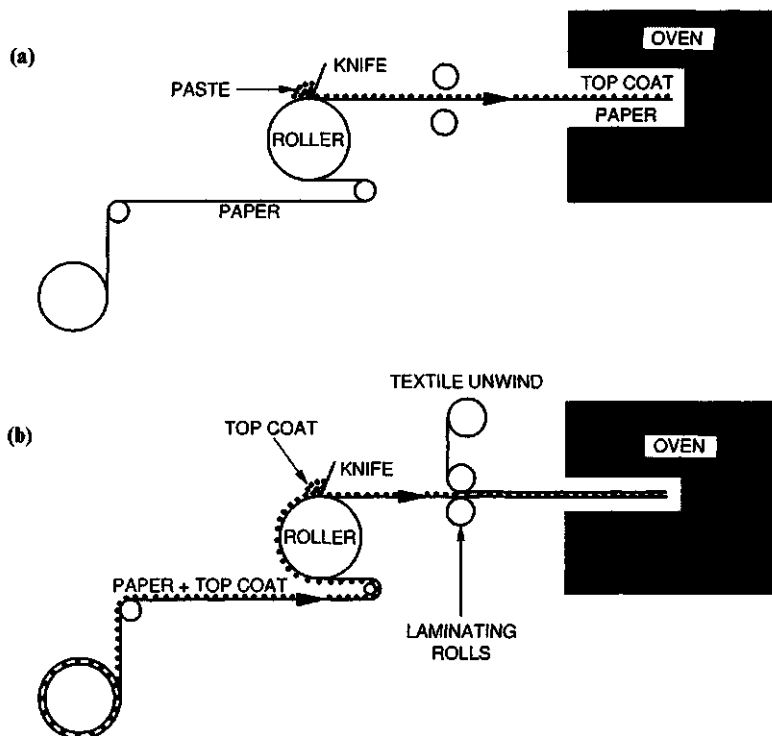
**Figure 7.6**   Transfer coating: (a) stage 1: film preparation; (b) stage 2: lamination of the textile to the film.

(b)   If the coating is applied in several passes or stages, the barrier properties are improved, as imperfections such as pin-holes are covered.

(c)   The polymer coating should not penetrate through the fabric warp and weft yarns as this locks the structure, leading to loss of tear strength, poor handle and drape, and increased noisiness.

(d)   The coating should be of such a consistency that it sits on the surface of the fabric substrate, but is adequately bonded to it to prevent delamination or coating loss in use.

(e)   Many waterproof coated and laminated fabrics are treated with a water-repellent finish (silicone, fluorocarbon or wax) which is applied to the side of the fabric exposed to the rain. These finishes can also improve abrasion resistance and tear strength. This finish is applied after coating/laminating and curing, otherwise it interferes with the bonding process.

(f)   Some heavy rubber-coated fabrics are cured by pressure contact with a heated metal calender, to produce a compact surface.

## 7.4 Chemistry of coating polymers

### 7.4.1 Polyurethanes

The polyurethanes are a wide class of polymers ranging from rubbers and elastomeric fibres to surface coatings, adhesives and flexible or rigid foams. They are not direct polymers of urethanes, but are derived from the reaction of polyesters or polyethers with di- or poly-isocyanates, to produce complex structures containing urethane linkages (Roff and Scott, 1971b).

The fundamental unit is based upon the urethane group

$$-N-C-O-$$
$$\quad | \quad ||$$
$$\quad H \quad O$$
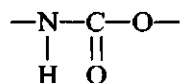
*Polymer structure.* Polyurethanes for coating are complex polymers. The major component of these is a segmented prepolymer, composed of a linear polyester or polyether that has been extended severalfold in chain length by coupling through urethane linkages. The prepolymer molecule (—PP—) can be further extended and crosslinked with a multifunctional isocyanate (—IC—) to produce the following structure:

$$
\begin{array}{c}
-(PP1)-IC-(PP2)-IC- \\
| \\
(PP3) \\
| \\
IC \\
|
\end{array}
$$
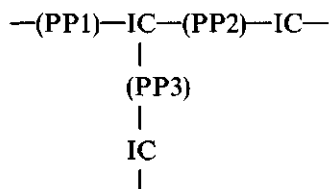
### 7.4.2 Preparation of polyurethanes

The isocyanate (R—NCO) compound is prepared by the condensation of primary amines with phosgene.

$$R-NH_2 + COCl_2 \rightarrow R-NCO + 2HCl$$

Primary amine     Phosgene        Urethane
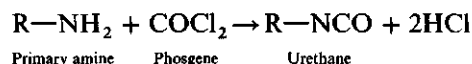
The isocyanate group readily reacts with amino (—$NH_2$) or hydroxyl (—OH) groups.

$$R-NCO + -OH \rightarrow R-NHCO \cdot O- \quad \text{(urethane linkage)}$$

$$R-NCO + -NH_2 \rightarrow R-NHCO \cdot NH- \quad \text{(urea linkage)}$$

When excess isocyanate is present, the above products undergo further reaction, yielding branched structures that lead to crosslinkages of two main types.

$$
\begin{array}{ccc}
 & & \text{R—NHCO·O—} \\
 & & | \\
\text{R—NHCO·O—} + \text{—NCO} \rightarrow & & \text{CONH—} \\
\text{Urethane} \qquad\qquad \text{Isocyanate} & & \text{Allophanate linkage}
\end{array}
$$

$$
\begin{array}{ccc}
\text{R—NHCO·NH} + \text{—NCO} \rightarrow & \text{R—NCO·NH—} \\
 & | \\
 & \text{CONH—} \\
\text{Urea} \qquad\qquad \text{Isocyanate} & \text{Biuret linkage}
\end{array}
$$
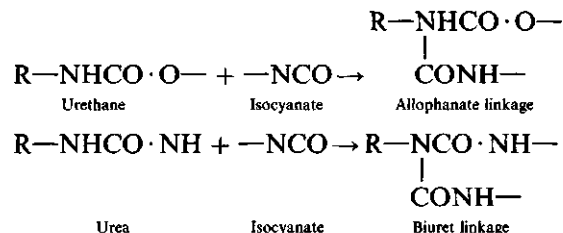
The urethane linkage (—NHCO·O—) is unstable in the presence of water (—OH groups) or carboxylic acid and breaks down to form amines or amides, with evolution of carbon dioxide.
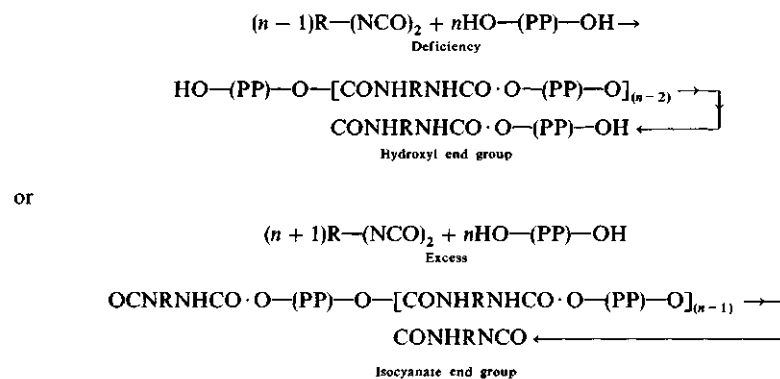
### 7.4.3  Production of complex polymers

The first production step is to prepare segmented prepolymers by coupling a hydroxyl-terminated polyester or polyether with a polyfunctional isocyanate. This extends the molecular size through the urethane linkages.

A typical polyester could be poly(diethyleneglycol adipate) having a molecular weight between 2000 and 3000. A typical polyether is obtained by polymerisation of propylene oxide, usually in the presence of a small proportion of glycerol or sorbitol to provide branched structures. Two of the most commonly used isocyanates are 2,4- and 2,6-tolylene di-isocyanate (TDI). These are chosen because of their reactivity, cheapness and relative low toxicity.

The resulting prepolymer has —OH terminal groups when a deficiency of isocyanate is used, but —NCO terminal groups if an excess of isocyanate is employed (Scheme 7.1).

$$(n - 1)\text{R—(NCO)}_2 + n\text{HO—(PP)—OH} \rightarrow$$
Deficiency

$$\text{HO—(PP)—O—[CONHRNHCO·O—(PP)—O]}_{(n-2)} \rightarrow$$
$$\text{CONHRNHCO·O—(PP)—OH} \leftarrow \underline{\qquad}$$
Hydroxyl end group

or

$$(n + 1)\text{R—(NCO)}_2 + n\text{HO—(PP)—OH}$$
Excess

$$\text{OCNRNHCO·O—(PP)—O—[CONHRNHCO·O—(PP)—O]}_{(n-1)} \rightarrow$$
$$\text{CONHRNCO} \leftarrow \underline{\qquad\qquad}$$
Isocyanate end group

**Scheme 7.1**

### 7.4.4.  Isocyanates

Table 7.1 lists some common di-isocyanates used.

**Table 7.1** Common di-isocyanates

| Abbreviation | Chemical name |
|---|---|
| DADI | Dianisidine di-isocyanate |
| HDI | 1,6-Hexamethylene di-isocyanate |
| MDI | 4,4-Diphenyl methane di-isocyanate |
| NDI | 1,5-Naphthalene di-isocyanate |
| PDI | Phenylene di-isocyanate |
| TODI | Tolidine di-isocyanate |
| XDI | Xenylene di-isocyanate |
| TDI | 2,4- and 2,6-Tolylene di-isocyanate |

### 7.4.5 Coating formulations

(i) *Two-component systems.* Insoluble films can be prepared by mixing a solution of a hydroxyl-terminated polyester with a non-volatile di-isocyanate just before application to the fabric. The hardness of the film depends on the complexity of their composition and the degree of branching. Rubbery prepolymers, solvent-based and curable with di-isocyanates at room temperatures or by heat, adhere well to metals and textiles. Alternatively, isocyanate-ended polymers can be cured by intermediates of epoxy resins containing hydroxyl groups or fatty acid polyamides.

(ii) *One-component systems.* A branched isocyanate-ended polymer, applied from solution, will cure to a hard coating by reaction with atmospheric moisture. The adhesion of rubbers and polyurethanes to textile surfaces can be enhanced by simple treatment with 4,4,4-triphenylmethane di-isocyanate, which probably reacts with surface layers of hydroxide or moisture.

Another type of coating medium, known as a urethane oil or urethane alkoyd, is made by treating a drying oil such as linseed oil (a polyunsaturated glyceride) with glycerol, to yield a mixture of mono- and di-glycerides. An excess of these is then reacted with a di-isocyanate. This gives a product which is highly unsaturated, and which can dry rapidly by atmospheric oxidation.

(iii) *Thermoplastic polyurethane rubbers.* There are two types of product which are processible on plastics processing equipment. These materials undergo allophanate-type crosslinkages during processing. One is based upon adipic acid, 1,4-butanediol and MDI, with the trade name Estane. This is thermoplastic but is virtually crosslinked, and has good extensibility and elasticity. The other is a heat-cured rubber prepared from hydroxyl-terminated polyesters, MDI, and a diol which has the trade name Texin. Thermoplastic polyurethanes can be applied from the melt, and avoid the use of solvents.

(iv) *Polyurethane foams.* Flexible foams for coating fabrics can be made by reacting a polyfunctional isocyanate with a prepolymer and water. This

yields a rubber and carbon dioxide gas sufficient to effect the expansion of a cellular structure.

Flexible foams are usually made from a branched polyether of molecular weight 2000 to 5000 crosslinked with TDI. Polymerisation is catalysed by an organometallic compound (e.g. stannous 2-ethylhexoate) and a tertiary amine catalyst (e.g. triethylene diamine). These act at room temperature and also promote the evolution of the blowing agent, carbon dioxide. A surface-active agent can be included to promote a uniformly textured foam. Flexible foams contain open, interconnected cells, whereas rigid foams have predominantly closed cells.

(v)  *Water-based polyurethanes (Goldsmith, 1988).*   Conventional polyurethanes tend to be applied from organic solvents such as di-methylformamide (DMF), methyl ethyl ketone (MEK) and mixtures containing toluene, xylene and chloro solvents. The solutions can contain up to 40% by weight of solvents. Large quantities of these expensive solvents are discharged into the atmosphere during drying. The economic aspects of this waste have caused concern in the past, but it is the environmental impact of the pollution caused by these organic solvents which is paramount, and is forcing governments to legislate against atmospheric pollution. This forces the manufacturers either to reclaim the solvent, or to move to polymer systems which limit or avoid their use. Solvent reclamation plants are extremely expensive systems which need to be built into the coating plant at the drying oven stage. They are, however, justified when solvent prices are high and local legislation is strict.

Aqueous polymer dispersion systems were introduced in the 1970s and 1980s. They contain up to 50% solids suspended in water, and although they avoid the problem of solvents, they require larger amounts of heat energy to drive off the water to dry and fix the polyurethane film which results. Polyurethane dispersions tend to have inadequate resistance to water. It is probable that surface-active interfaces remain in the solidified and dried polyurethane. These may provide routes for the diffusion of water into the film in moist conditions, leading to structural weaknesses which show when the polymer is strained. Bayer AG have attempted to overcome this by creating chemical crosslinks between the agglomerated microscopic polyurethane particles. An isocyanate has been developed which is stable in water for up to 2 h.

A typical aqueous polyurethane polymer would be prepared by the conventional first stages by reaction of a polyester or polyether diol with an isocyanate. This would be followed by the addition of an ionic functional group into the backbone, before neutralisation of the ionic groups, and finally dispersion in water. The neutralised ionic groups are hydrophilic, thereby eliminating the use of external surfactants to facilitate dispersion and stabilisation.

The advantages of water-based coating polymers are listed in Table 7.2.

**Table 7.2**   Advantages of water-based coating polymers

Low environmental impact
Low odour during application
Low toxicity of discharged vapours
Surfactant-free — no adhesion problems
Easy to use — no reactants or catalysts needed
Can be thermoplastic or thermosetting
Heat-resistant coating
Low-temperature flexibility
Water-vapour permeable

### 7.4.6   Polyurethane properties

The advantages and disadvantages of different types of polyurethanes are listed in Table 7.3.

## 7.5   Natural and synthetic rubbers

Rubbers are widely used in coated fabrics for a variety of purposes. For the purposes of this chapter, the types are:

| | |
|---|---|
| Natural rubber | cis-Polyisoprene |
| Neoprene | Polychloroprene |
| Butyl | Polyisobutylene |
| SBR | Styrene–butadiene rubber |
| Nitrile | Acrylonitrile–butadiene rubber |

**Table 7.3**   Advantages and disadvantages of different types of polyurethanes

| Polyurethane type | Advantages | Disadvantages |
|---|---|---|
| Polyether | Good hydrolytic stability<br>Good microbiological stability<br>Excellent softness and flexibility<br>Cheaper than polyesters<br>Good solvent resistance<br>Range of molecular weights available | Reduced adhesion to low-energy surfaces<br>UV and weathering resistance not good<br>Not as tough as polyester<br>Lower physical properties |
| Polyester | Excellent adhesion to low-energy surfaces<br>Excellent toughness and abrasion resistance<br>Excellent flexibility and softness<br>Range of molecular weights available | Lower solvent resistance<br><br>Lower hydrolytic stability<br><br>Lower microbiological stability<br><br>Higher raw material costs |

### 7.5.1   Natural rubber

The simplest fundamental unit is 1,4-isoprene:

$$
\underset{\begin{array}{c}|\\ -CH_2-C=CH-CH_2-\end{array}}{\overset{CH_3}{}}
$$
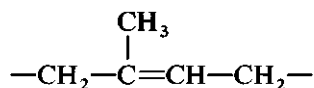
Formula $= C_5H_8$; molecular weight $= 68$; degree of polymerisation $=$ 1500–5000; specific gravity $= 0.93$.

There are two distinct isomeric configurations of 1,4-polyisoprene (Roff and Scott, 1971a):

cis — where the chains substituent to the double bond lie on the same side, as in structure (1). This is natural elastomeric rubber used in coating formulations.

trans — where the chains substituent to the double bond lie on opposite sides as in structure (2). This form is the harder gutta percha, chicle and balata.

As rotation about a double bond is not possible, the two forms are not readily interconvertible. The chains occupy three-dimensional space, which cannot be represented fully in structures (1) and (2). The trans-form permits highly regular zig-zag chains which fit together well, whereas the cis-form does not (Morrison and Boyd, 1987). Both exhibit the long chain structures which typify rubbers.

(1)  cis - polyisoprene
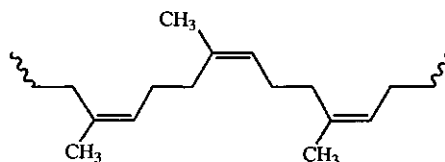


(2)  trans - polyisoprene
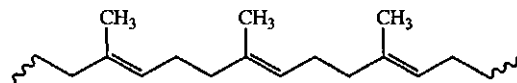


### 7.5.1.1   Preparation.

Natural rubber is obtained by cutting (tapping) the bark of *Hevea braziliensis*, a wild tree occurring originally in South America. The rubber is in a milky form which contains about 35% of latex. The latex rubber can be separated by coagulation with an acid such as acetic acid. When washed and dried in air it becomes 'crepe', or if dried in wood smoke it becomes 'smoked sheet'.

Rubber is soluble in a range of solvents, including hydrocarbons, chlorinated hydrocarbons, certain ketones, esters and carbon disulphide. Raw rubber is mechanically weak, deficient in elastic recovery, stiff when cold and soft when hot. It is necessary to blend it with other constituents and to vulcanise it to improve strength, elasticity and resistance to liquids, and to reduce the temperature sensitivity.
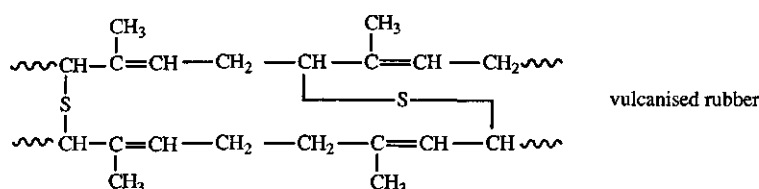
7.5.1.2 *Vulcanisation of rubbers.* Milling and masticating rubbers with sulphur, followed by heating, causes the formation of sulphur bridges between the chain molecules. This reaction involves reactive allylic positions, and thus depends on the double bond in the polymer:

$$\text{vulcanised rubber}$$

7.5.1.3 *Mixing and blending constituents.* Practical rubbers are a complex mixture of organic and inorganic substances which must be mixed carefully to obtain uniformly high strength properties.

Curing system
- Rubber
- {Vulcanising agent
- Activator
- Accelerator}
- Diluting fillers
- Reinforcing fillers
- Plasticisers
- Anti-oxidants
- Colour/pigments

(a) The *vulcanising agent* is usually sulphur.

(b) The *accelerating agents* are usually metal oxides (MgO, PbO) or organic substances such as thiazoles, mercaptobenzthiazoles (MBT) or sulphenamides. The latter have a delayed action, in that they have no activity below a certain temperature.

(c) The *activators* are required to make the organic accelerators function effectively. They can be substances like zinc oxide and stearic acid. Stearic acid is also a lubricant, softener and plasticiser.

(d) *Diluting fillers* such as clays, talc and barytes act as diluents.

(e) *Reinforcing fillers* such as finely divided carbon black increase the tensile and tear strength of the mix.

(f)   *Anti-oxidants* such as ketone–amine condensation products or phenols are used to prevent natural ageing and atmospheric (ozone) cracking.

(g)   *Colours* in the form of pigments are added to colour the mix.

### 7.5.2   Polychloroprene rubbers (neoprene)

The simplest fundamental unit is:

$$-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-$$

Formula is $C_4H_5Cl$; molecular weight $= 88.5$; degree of polymerisation $= 1000-3500$; specific gravity $= 1.20-1.25$.

Polychloroprene consists of about 85% *trans*-1,4 units and about 10% *cis*-1,4 units. The rest is composed of two other isomers.



*cis*-Polychloroprene                                    *trans*-Polychloroprene

#### 7.5.2.1   *Preparation.*   Polychloroprene is normally prepared by dimerisation of acetylene, followed by addition of hydrogen chloride:



A more recent process involves the chlorination of C4 petroleum fractions to obtain 3,4-dichlorobut-1-ene. Dehydrochlorination of this gives the required monomer.

The forms of polychloroprene vulcanised using sulphur are known as 'neoprene' rubber. Vulcanisates resemble those of natural rubber, but have superior resistance to heat and flame, are self-extinguishing, and resistant to oils and ozone. These properties make neoprene a versatile and valuable rubber in coated fabric form.

Copolymers have been prepared commercially. One such is neoprene ILA, which is a copolymer of chloroprene and acrylonitrile, which has exceptional oil resistance. A carboxylated type of latex is manufactured in Germany (Baypren).

### 7.5.3 Polyisobutylene rubbers (butyl)

The simplest fundamental unit is:

$$\left[-\text{CH}_2-\overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}}-\right]_n \text{CH}_2-\overset{\overset{\displaystyle \text{CH}_3}{|}}{\text{C}}=\text{CH}-\text{CH}_2-$$
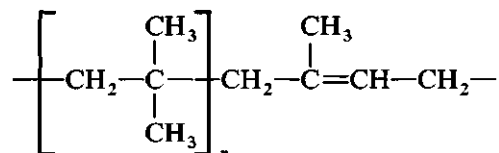
Isobutylene formula $= \text{C}_4\text{H}_8$; molecular weight $= 56$; 1,4-Isoprene formula $= \text{C}_5\text{H}_8$; molecular weight $= 68$; the value of $n$ varies from 20 to 200; specific gravity $= 0.91-0.98$.

The isoprene units are randomly distributed and provide unsaturated bonds which allow the copolymer to be vulcanised. The small number of double bonds remaining in the vulcanisate means that it is resistive to oxidation and chemical attack.

**7.5.3.1 Preparation.** Can be prepared from $\text{C}_4$ petroleum fractions such as butane or butylene. If the starting point is butane, this is dehydrogenated to form butylene. A small amount of isoprene is mixed with isobutylene in an inert solvent (methylene chloride or liquified ethylene). This is made to undergo a Friedel–Crafts reaction using catalysts such as $\text{AlCl}_3$ or $\text{BF}_3$, together with a trace of a cocatalyst such as water. Polymerisation occurs at a very high rate, and cooling of the monomers is required to control a continuous process.

$$\underset{\text{Butane}}{\text{C}_4\text{H}_{10}} \overset{-\text{H}_2}{\underset{\text{Heat}}{\longrightarrow}} \underset{(n\text{- and iso-butylene})}{\text{C}_4\text{H}_8} \overset{\text{Separate}}{\underset{\text{In H}_2\text{SO}_4}{\longrightarrow}} \underset{\text{isobutylene}}{\text{C}_4\text{H}_8}$$

$$\underset{\text{Polyisobutylene}}{[\text{C}_4\text{H}_8]_n} + \underset{\text{Isoprene}}{\text{C}_5\text{H}_8} \overset{\text{Friedel–Crafts}}{\underset{\text{AlCl}_3+\text{H}_2\text{O}}{\longrightarrow}} \underset{\text{Butyl rubber}}{-[\text{C}_4\text{H}_8]_n-\text{C}_5\text{H}_8-}$$
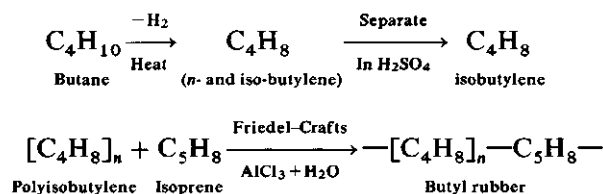
**7.5.3.2 Properties.** Butyl rubber is unaffected by oxygen, alkalis, hydrogen peroxide, alcohols, phenols, animal and vegetable oils, and some ketones, ethers, esters and fatty acids. Its compact structure gives it excellent resistance to gas and liquid permeation. Hence its use in tyres, balloons, tank and pool linings. It has specialist military uses in chemical warfare agent protective clothing, covers and shelters.

Butyl rubbers can be rendered heat-resistant and flame-retardant by combining small proportions of chlorine or bromine in the milling process.
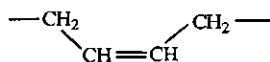
### 7.5.4 Styrene–butadiene rubbers (SBR)

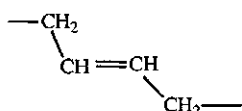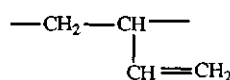The simplest fundamental units are shown in structures 3 to 6.
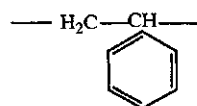
styrene

(3)

$cis$-1,4 ,butadiene

(4)

$trans$-1,4,butadiene

(5)

1,2 or vinyl butadiene

(6)

Styrene formula $= C_8H_8$; molecular weight $= 104$; butadiene formula $= C_4H_6$; molecular weight $= 54$; specific gravity $= 0.91-1.00$.

SBR is a mixture of styrene (3) with various molar proportions of the isomers 4, 5 or 6. The proportions depend on the method and temperature of polymerisation. Table 7.4 shows the proportions resulting from different processes.

Units 3 to 6 are randomly arranged in emulsion copolymers, but in solution polymers may occur in uniform blocks of varying length. Such block copolymers of Sty–Buta–Sty type have reversible thermoplastic–elastomeric properties. They are resilient and rubber-like at room temperature, but are thermoplastic at higher temperatures.

### 7.5.4.1 Preparation

*Emulsion polymerisation route.* Styrene and 1,3-butadiene are emulsified in water containing soap or other surface-active agent. They are polymerised in two different ways:

Table 7.4 Proportions of butadiene isomers in SBR from different processes

| Type of polymerisation process | Percentage of the butadiene units | | |
|---|---|---|---|
| | (4) | (5) | (6) |
| 'Hot' emulsion polymerisation | 18.3 | 65.3 | 16.3 |
| 'Cold' emulsion polymerisation | 12 | 72 | 16 |
| Solution polymerisation | 40 | 54 | 6 |

(a) 'Hot' rubber is produced at about 50°C using an initiator such as potassium persulphate or an organic peroxide.

(b) 'Cold' rubber is produced at about 5°C using a redox initiating system such as ferrous sulphate plus a peroxy compound, sometimes with sodium formaldehyde sulphoxylate. Polymerisation is terminated at about 70% conversion by adding a 'short stopper' such as quinol.

*Solution polymerisation.* The two monomers, diluted with a hydrocarbon solvent, are polymerised using a stereospecific catalyst such as a lithium alkyl.

7.5.4.2 *Properties.* SBRs are similar to natural rubber in that they are susceptible to atmospheric oxidation and ozone cracking when stretched in air. They are swollen and weakened by hydrocarbons and halogenated hydrocarbons. Their abrasion resistance and ageing resistance are superior to those of natural rubber.

### 7.5.5 Nitrile rubbers

The simplest fundamental units are structures (4) to (6) (see section 7.5.4) and structure (7).

$$-CH_2-CH-$$
$$|$$
$$CN$$
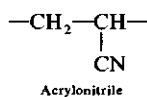
Acrylonitrile

(7)

Acrylonitrile formula $= C_3H_3N$; molecular weight $= 53$; butadiene formula $= C_4H_6$; molecular weight $= 54$; specific gravity $= 0.95-1.02$.

Nitrile rubbers are classified according to the content of acrylonitrile: low acrylonitrile = approximately 20%; high acrylonitrile = approximately 40%; very high acrylonitrile = approximately 45%. The butadiene units are predominantly in the *trans*-1,4 form (5).

7.5.5.1 *Preparation.* Acrylonitrile and freshly distilled 1,3-butadiene are copolymerised in emulsions by methods analogous to those used to prepare styrene-butadiene rubbers detailed earlier in section 7.5.4.1. Both 'hot' and 'cold' rubber processes can be used. The initiator in the hot process can be potassium persulphate. A redox type of hydroperoxide-dextrose sequestering agent is used for the 'cold' process.

7.5.5.2 *Properties.* Nitrile rubbers have low tensile strength unless filled with reinforcing carbon blacks. Resilience is low, and low temperature flex-cracking is worse than that of natural rubber, especially with rubbers containing large proportions of acrylonitrile. They do, however, have better resistance to heat ageing and light than natural or SBR rubbers.

Nitrile rubbers have good resistance to oils, greases and other hydrocarbon liquids, and are thus used for products where this property is of primary importance.

## 7.6 Coating polymers and elastomers

### 7.6.1 Poly(vinyl chloride) (PVC)
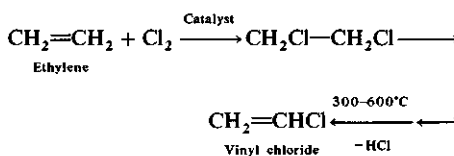
The fundamental unit is:

$$-CH_2-\underset{\underset{Cl}{|}}{CH}-$$
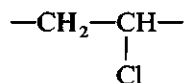
Formula is $C_2H_3Cl$; molecular weight = 62.5; degree of polymerisation = 800–2000; specific gravity (plasticised) = 1.1–1.7.

**7.6.1.1 Preparation.** PVC is an additive polymer made from the monomer vinyl chloride ($CH_2$—CHCl). It can be formed by the following methods.

(a)  The addition of hydrogen chloride to acetylene:

$$CH\equiv CH + HCl \xrightarrow{\text{HgCl}_2 + \text{BaCl}_2} CH_2=CHCl$$

Acetylene                                      Vinyl chloride
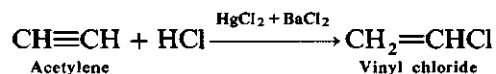
(b)  Chlorination of ethylene, followed by dehydrochlorination by treatment with alkali or by cracking at 300–600°C (Woolfe process):

$$CH_2=CH_2 + Cl_2 \xrightarrow{\text{Catalyst}} CH_2Cl—CH_2Cl$$

Ethylene

$$CH_2=CHCl \xleftarrow[\text{—HCl}]{\text{300–600°C}}$$

Vinyl chloride

(c)  Another process is oxyhydrochlorination of ethylene:

$$CH_2=CH_2 \xrightarrow[\text{500°C}]{\text{Air} + \text{CuCl}_2 + \text{KCl}} CH_2=CHCl$$
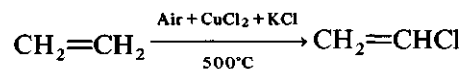
The vinyl chloride monomer can be polymerised by high-energy radiation or free-radical initiators. The most common polymerisation techniques are emulsion and suspension processes (Roff and Scott, 1971b).

*Emulsion polymerisation* is carried out in aqueous emulsions using surface-active agents. The initiator is contained in the aqueous phase.

**Table 7.5** Properties conferred by different plasticisers for PVC

| Plasticiser types | Properties conferred |
| --- | --- |
| Di-octyl phthalate | General purpose plasticisers |
| Trixylyl phosphate | Offers some flame-retardance |
| Di-octyl sebacate, polypropylene sebacate | Low-temperature plasticisers |

*Suspension polymerisation* utilises water-soluble suspension agents such as poly(vinyl alcohol) or methyl cellulose. The initiators used can be benzoyl or lauroyl peroxides.

**7.6.1.2** *Plasticisers for PVC.* Coating formulations are plasticised by using high boiling point esters of $C_8$ to $C_{10}$ alcohols (phthalates, phosphates, sebacates), as shown in Table 7.5.

**7.6.1.3** *Properties.* PVC is dissolved by tetrahydrofuran (THF), dimethyl formamide (DMF), ketones, carbon tetrachloride, and other chloro-solvents. It will not resist petrols and light oils. All PVC polymers are degraded by heat and light, although PVC is flame-retardant. The degradation is thought to proceed as a chain reaction, initiated and propagated by activated chlorine. The polymer decomposes by an unzipping mechanism. Stabilisers such as lead carbonate, lead silicate, salicylates or stearates interfere with the chain reaction.

PVC-coated fabrics stiffen and can crack if flexed at low temperatures (colder than $-10°C$), although choice of plasticisers can extend the utility range downwards to lower temperatures.

**7.6.1.4** *Application in coated fabrics.* PVC can be applied from mixed solvents, or more recently as plastisols, which are creamy pastes. The plastisols consist of very finely divided PVC dispersed in a plasticiser. This method was mainly used for heavy coatings such as artificial leathercloth and heavy-duty industrial clothing, but it is now used for a wider range of products. It has the advantage that no solvents are used, and thus avoids the pollution or recycling problems that solvent can cause.

**7.6.2** *Polyacrylate elastomers*

The simplest fundamental unit is:
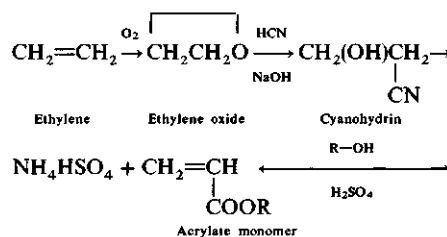
$$-CH_2-\underset{\underset{COOR}{|}}{CH}-$$
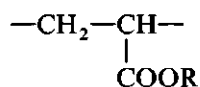
Acrylate polymer

where R can be an alkyl ($C_1$ to $C_{12}$) or an aryl group, or, in the case of water-soluble polymers, a monovalent cation. The formula is $C_3H_3O_2$—(R); molecular weight = 71 + (R); degree of polymerisation = 5000–10 000; specific gravity = 1.05–1.11.
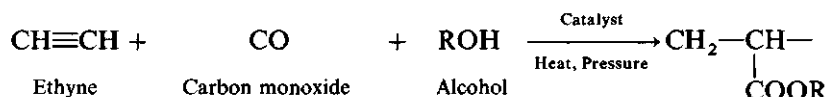
### 7.6.2.1 Preparation. There are two main methods of preparation.

(a) By the oxidation in air of ethylene, followed by conversion to ethylene cyanohydrin. This intermediate is then dehydrated and hydrolysed in the presence of alcohol, as shown in Scheme 7.2.

$$CH_2{=}CH_2 \xrightarrow{O_2} CH_2CH_2O \xrightarrow[NaOH]{HCN} CH_2(OH)CH_2{-}$$

$$\underset{\text{Ethylene}}{\quad} \underset{\text{Ethylene oxide}}{\quad} \underset{\text{Cyanohydrin}}{\quad} \overset{|}{CN}$$

$$NH_4HSO_4 + CH_2{=}\underset{\underset{COOR}{|}}{CH} \xleftarrow[H_2SO_4]{R{-}OH}$$

Acrylate monomer

**Scheme 7.2**

(b) By the Reppe synthesis from ethyne, carbon monoxide, and the appropriate alcohol:

$$\underset{\text{Ethyne}}{CH{\equiv}CH} + \underset{\text{Carbon monoxide}}{CO} + \underset{\text{Alcohol}}{ROH} \xrightarrow[\text{Heat, Pressure}]{\text{Catalyst}} CH_2{-}\underset{\underset{COOR}{|}}{CH}{-}$$

The monomer is polymerised as an emulsion to give latexes for the impregnation and coating of leather, paper and textiles. Molecular weight and reaction rate are controlled by initiators such as peroxides, or a redox system such as persulphate–bisulphite. Polyacrylates can be cross-linked by diamines and peroxides to produce acrylic rubbers.

### 7.6.2.2 Properties. Acrylates are soluble in most chlorinated hydrocarbons, esters, ketones, and aromatic hydrocarbons. They can be plasticised by esters similar to those used for PVC. As the length of the alkyl chain (R) increases, the acrylate polymers increase in softness.

Acrylate polymers used for coatings possess excellent fastness to light, weathering, and microbiological attack. The rubbers have good resistance to flex-cracking, oxidation, ozone, ultraviolet radiation and lubricating oils. They retain light colours, including white, in sunlight. They tend to be used for items such as sun blinds, white hat covers, and snow camouflage for these reasons.

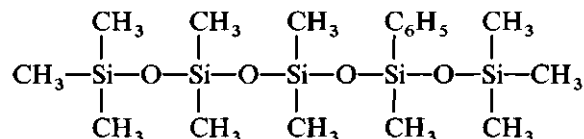### 7.6.3 Silicone elastomers

The simplest fundamental units of silicone are elastomers:

$$
\underset{\text{Monofunctinal}}{R-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-O-} \qquad
\underset{\text{Difunctional}}{-O-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-O-} \qquad
\underset{\text{Trifunctional}}{-O-\overset{\displaystyle R}{\underset{\displaystyle O}{Si}}-O-}
$$
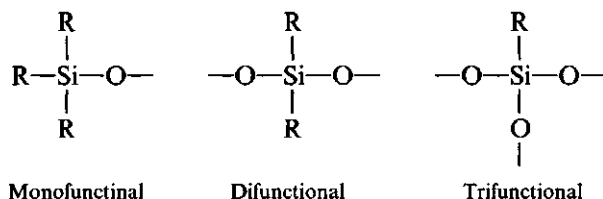
These are polysiloxane units, where R is an organic substituent, usually an alkyl group, and often $CH_3$—.

Silicone rubbers are primarily linear chains of the difunctional units with monofunctional end-groups. General-purpose rubbers use methyl radicals, where low-temperature rubbers utilise about 5–15% molecular percentage of phenyl groups:

$$
CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_3
$$

**7.6.3.1 Preparation.** Silicone monomers can be prepared by the 'direct' process whereas silicon is reacted with methyl chloride at high temperature in the presence of copper. This produces a large proportion of dimethyl dichlorosilane. Hydrolysis in dilute HCl first replaces Cl with OH, which is followed by condensation polymerisation at 175°C to give a mixture of mono- and di-functional units.
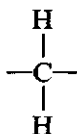
The monofunctional units in small quantities control the molecular weight of the polymer chains by termination. The trifunctional units need to be absent, since they produce chain branching and crosslinking (Roff and Scott, 1971b).

**7.6.3.2 Properties.** Silicones are soluble in hydrocarbons, ketones, esters and ethers. They are unaffected by water, some mineral oils, petrol, cold acids and alkalis.

Silicone rubbers and resins remain flexible at lower temperatures than organic rubbers (down to − 70°C) and resist heat-ageing well. When used as thin coatings on lightweight fabrics they maintain high fabric tear strengths with soft handle. When vulcanised (with organic peroxides) they resist microbiological attack. They are odourless, tasteless, physiologically inert, and water-repellent.

They are used for outdoor purposes such as tents and covers, and in the food, engineering and medical-product industries. Their inertness makes them suitable for surgical implants.

### 7.6.4 Poly(tetrafluoroethylene) (PTFE)

The simplest unit is:

$$\begin{array}{cc} F & F \\ | & | \\ -C-C- \\ | & | \\ F & F \end{array}$$

Formula is $C_2F_4$; molecuclar weight $= 100$; degree of polymerisation $= 10\,000$; specific gravity $= 2.1-2.3$.

**7.6.4.1 Preparation.** An industrial synthesis involves the reaction between chloroform and anhydrous hydrogen fluoride to produce a mixture of chlorofluoromethanes. Chlorodifluoromethane is then cracked thermally to produce the monomer, as shown in Scheme 7.3. The monomer is then polymerised in the presence of a radical initiator (Roff and Scott, 1971b).

$$2CHCl_3 + 3HF \xrightarrow[SbCl_3]{70°C} CHClF_2 + CHCl_2F + 3HCl$$

recycle       Catalyst

Heat and pressure

$$2CHCl_2F \xrightarrow[600-800°C]{AlCl_3} CHClF_2 + CHCl_3$$

$$2CHClF_2 \longrightarrow -CF_2-CF_2- + 2HCl$$

**Scheme 7.3**

**7.6.4.2 Properties.** PTFE is extremely stable and inert. It is not soluble in any known liquids, and is unaffected by concentrated acids and alkalis.

It will not burn in air, and melts only slowly in a flame. It is flexible down to $-80°C$ and dimensionally stable up to $+250°C$. PTFE has an unusually low coefficient of friction and its abrasive resistance is good. Its remarkable non-adhesive properties mean that it sheds or repels liquids, especially water, readily. Processed thin, light films can be laminated to textiles (see section 7.7 on waterproof (breathable) fabrics).

### 7.6.5 Polyethylene

Polyethyelene has one of the simplest fundamental units in organic chemistry:

$$\begin{array}{c} H \\ | \\ -C- \\ | \\ H \end{array}$$

Formula $= CH_2$; molecular weight $= 14$; degree of polymerisation $=$ 200 000; specific gravity $= 0.915$ to $0.94$ (low density), $0.94$ to $0.97$ (high density).

7.6.5.1 *Preparation.* Both low- and high-density polyethylenes are prepared from ethylene ($CH_2=CH_2$) which is obtained by catalytic cracking of natural gases, such as propane, or light oil fractions. The monomer has to be free from impurities such as other hydrocarbons, water, oxygen, etc.

(*a*) *Low-density polyethylenes.* Ethylene is passed over heated copper to remove oxygen. It is then compressed to 2000 to 3000 atmospheres, and a catalyst such as a peroxide compound, and a chain modifier, such as an aldehyde or ketone, are added in controlled amounts. Polymerisation is exothermic, and has to be controlled at temperatures up to $200°C$. Propagation of the polymer radical can be terminated by combination, chain transfer, or disproportionation. Both solution and emission polymerisation processes have been used.

(*b*) *High-density polyethylenes.*
(i) *The Ziegler process* involves feeding ethylene into an inert hydrocarbon solvent containing a Ziegler–Natta catalyst (i.e. triethyl aluminium and titanium tetrachloride). Polymerisation takes place at atmospheric pressure and at about $75°C$. Chain terminators such as oxygen or hydrogen are added to control molecular weight.
(ii) *The Phillips process* involves feeding ethylene into cyclohexane solvent which contains a catalyst of partially-reduced chromium oxide on activated silica or alumina. Polymerisation occurs at 25–35 atmospheres and at up to $175°C$.
(iii) *The Du Pont process* is another high pressure process (over 7000 atmospheres) which uses a catalyst of $\alpha,\alpha'$-azobisisobutyronitrile. Polymerisation occurs in solutions or emulsions, similar to the low-density polyethylene process above.

7.6.5.2 *Properties.* Both low- and high-density polyethylenes are generally insoluble in hydrocarbons and chlorinated hydrocarbons below $50–70°C$. They are relatively unaffected by polar solvents, such as alcohols, phenols, esters and ketones. They will resist attack by alkalis, most concentrated acids, vegetable oils and ozone. Generally, chemical resistance is highest in linear high-density polyethylenes.

Polyethylenes are thermoplastic and melt at around 130–140°C. They burn, melt and drip when exposed to flame. They are susceptible to photo-oxidation by ultraviolet light, which limits their outdoor use, unless protective agents are used.

Polyethylenes are resistant to microbiological attack, water and gas penetration. They are utilised as thin abrasion-resistant films on textiles, predominantly on flash-spun polyolefin non-woven fabrics for use as cheap disposable materials for packaging, protective clothing and linings (e.g. Tyvek).

### 7.6.6 Chlorinated and chlorosulphonated polyethylenes

Chlorinated polyethylenes are prepared by passing gaseous chlorine through a hot suspension or emulsion of polyethylene in carbon tetrachloride, in the presence of a catalyst. Useful polymers contain 25–30% of chlorine.

Chlorosulphonated polyethylenes are prepared by a process similar to that above, except that gaseous sulphur dioxide and chlorine are introduced simultaneously into a hot emulsion or suspension of polyethylene in carbon tetrachloride.

The chlorosulphonyl groups (—CH$_2$CH(SO$_2$Cl)—) make up about 1–2% of the ethylene polymer, whereas the chlorinated groups (—CH$_2$CH(Cl)—) make up about 25–45% of the ethylene units. The SO$_2$Cl groups provide reactive sites for crosslinking, very much as in general purpose rubbers.

**7.6.6.1 Properties.** Compared with straight polyethylene, these polymers possess outstanding resistance to heat ageing, and they have a degree of flame retardance. They are highly resistant to weathering, ozone, abrasion and general chemical attack.

They are utilised where flame retardance, good weathering properties, and chemical resistance are required. Coated fabrics are used for tentage, chemical protective clothing, collapsible fuel tanks, roofing and flooring, amongst other uses.

### 7.7 Liquid proof/vapour permeable coated fabrics

Coated and laminated fabrics are widely used in functional clothing and covers to protect the wearer from rain, water and other liquids. When such garments or covers are worn by humans or animals, there is a physiological problem associated with the inability to allow the free passage of perspiration vapour through the clothing. The consequence of this for active wearers is progressive dampening of the underclothing. In the mildest cases this can cause discomfort, but in the worst survival situations it can result in injury, incapacitation or death by hypothermia or hyperthermia. These conditions are explained in Table 7.6.

**Table 7.6** Effects of waterproof clothing in different conditions

| Conditions | Activity | Consequence |
|---|---|---|
| Cold/wet climate | Medium activity | Discomfort |
| Cold/wet climate in sweat-wetted waterproof clothing | High activity followed by low activity | Hypothermia (cold stress) |
| Hot/moist climate (when protective clothing required) | High activity | Hyperthermia (heat stress) |

The most demanding situations tend to be faced by those with professional outdoor occupations such as military personnel, police, fire services, and those involved in professional sport and expeditions.

One of the biggest growth areas in coated fabrics is that of waterproof/vapour permeable materials, commonly called waterproof/breathable fabrics.

Historically, the first such fabrics consisted of cotton fabrics impregnated with waxes and oils to provide a degree of waterproofness and vapour permeability.

The first microporous polymeric membranes were commercialised by Sartorius-Werkes in Germany in 1927. They were used in microfiltration of liquids and were based upon nitrocellulose polymers. This technology has been developed and modified over the years to produce a wide range of advanced polymeric films and coatings with high vapour permeability and high waterproofness.

The Second World War saw the urgent need to provide comfortable waterproof clothing for RAF Hurricane and Spitfire pilots escorting convoys to Northern Russia. Many pilots were lost through ditching in the sea and dying of hypothermia. A fabric was developed using the finest long staple (Sea Island) cotton, which was carefully spun and doubled before being woven into a dense parchment-feel Oxford weave fabric. The fabric was then finished with a permanent water-repellent finish based upon stearamido derivatives. Such 'Ventile' fabrics (Anon, 1993) have a high vapour permeability in air but, when immersed in water, swell to block the interstitial voids between cotton threads, thus providing a degree of waterproofness. Production started in 1943, and it was still widely used in the 1990s for military aviation, expedition clothing and tentage.

### 7.7.1 Physiological aspects

Comfort is difficult to define; in fact, it is often referred to as 'the lack of discomfort'. Comfort is highly subjective, but in clothing is directly related to the temperature and humidity conditions inside garments. The balance between a person's energy production and its exchange with the environment can be controlled by clothing. Woodcock's formula (Woodcock, 1962) shows

this relationship:

$$H = \frac{T_s - T_a}{I} + \frac{p_s - p_a}{E}$$

where: $H$ = total rate of heat transfer per unit area; $T_s$ = skin temperature; $T_a$ = ambient temperature; $I$ = insulation of clothing plus overlying air layers; $p_s$ = water vapour pressure at skin boundary; $p_a$ = water vapour pressure of ambient air; $E$ = resistance to moisture vapour transmission of clothing and overlying air layer.

In this formula $H$, $T_s$ and $p_s$ are physiological parameters controlled by the individual. $T_a$ and $p_a$ are controlled by the environment. $I$ and $E$ are controlled by the clothing, including air layers. The levels of perspiration produced by a human are as shown in Table 7.7.

Table 7.7 indicates that the human skin exudes a small amount of insensible perspiration even when inactive and in a cool environment. Under continuous strenuous conditions almost 1.5 l/h of sweat can be liberated. For it to cause cooling of the skin, and hence the core of the body, the sweat must leave the skin as a vapour. In impermeable clothing, evaporative cooling cannot take place and overheating results. At the cool end of the climatic scale, sweat-wetted clothing loses up to 70% of its dry thermal insulation. During periods of low activity, chilling and rapid cooling can occur, leading to hypothermia and finally death.

### 7.7.2  Types of waterproof/vapour permeable fabrics

There are four main types of 'breathable' fabric:

(a)  High-density woven fabrics
(b)  Microporous coatings and films
(c)  Hydrophilic coatings and films
(d)  Combined microporous/hydrophilic layers

For the purposes of this chapter, we shall concentrate on (b), (c) and (d).

**Table 7.7**  Sweating rates for humans

| Activity | Sweat rate (ml/h) |
| --- | --- |
| Sleeping (cool, comfort zone) | 15–30 |
| Walking at 5 km/h (comfort zone) | 200–500 |
| Hard physical work (hot, humid conditions) | 400–1000 |
| Maximum sweat rate (only possible for a few minutes) | ~1800 |

### 7.7.3 *Microporous coatings and films (poromerics)*

Microporous membranes are defined as having a narrow pore-size distribution, usually in the sub-micrometre range, although they can range from 0.1 to 10 µm. It is common for microporous films to have 1–2 billion pores per square centimetre in a film 10–50 µm thick. The most widely used polymers for microporous fabrics are as follows.

Polyurethanes, which offer toughness, flexibility and wide variation in formulation, allowing 'tailor-made' polymers.
PTFE, which offers an inert, extremely hydrophobic polymer with very open porous structures.

Other polymers used include:

Acrylics.
Polyamino acids.
Polyolefins

### 7.7.3.1 *Microporous polyurethanes.* There are several methods used to render polyurethane films and coatings microporous. The main commercial techniques are as follows.

(*a*) *Wet-cast coagulation.* A large proportion of polyurethene microfiltration membranes are produced by this technique (at the time of writing). A polyurethane polymer, usually thermoplastic, is dissolved in an organic solvent which is also water-soluble.

The resulting viscous solution is coated on to a fabric directly, or cast as a thin film on a release paper. Whilst still liquid, the film is exposed to water vapour or steam in a controlled manner. The water vapour dissolves in the film, causing phase separation of the polymer, producing a coagulated gel with microporous voids, channels and blow holes. The film is then washed and dried (see Figure 7.7).

The process requires careful control, and is relatively slow. It produces coatings or films with pores in the 0.1–10 µm range. Examples of commercial products are Cyclone®, Entrant® and Keelatex®.

(*b*) *Salt dissolution process.* In this process a polyester or polyether urethane polymer is cast as a film from an organic solvent such as dimethyl formamide (DMF). The polyurethane film contains a water-soluble finely-divided inorganic crystal substance such as sodium chloride. This is subsequently leached out of the film using water. This leaves microporous voids in the film. Examples of commercial products made by this process are Porvair Porelle® and Permair® (Threlfall and Clarke, 1989).

Microporous polyurethanes, having a high permeability to water vapour, tend to suffer from a corresponding decrease in resistance to water ingress. Waterproofness can also suffer during use when contaminants, including
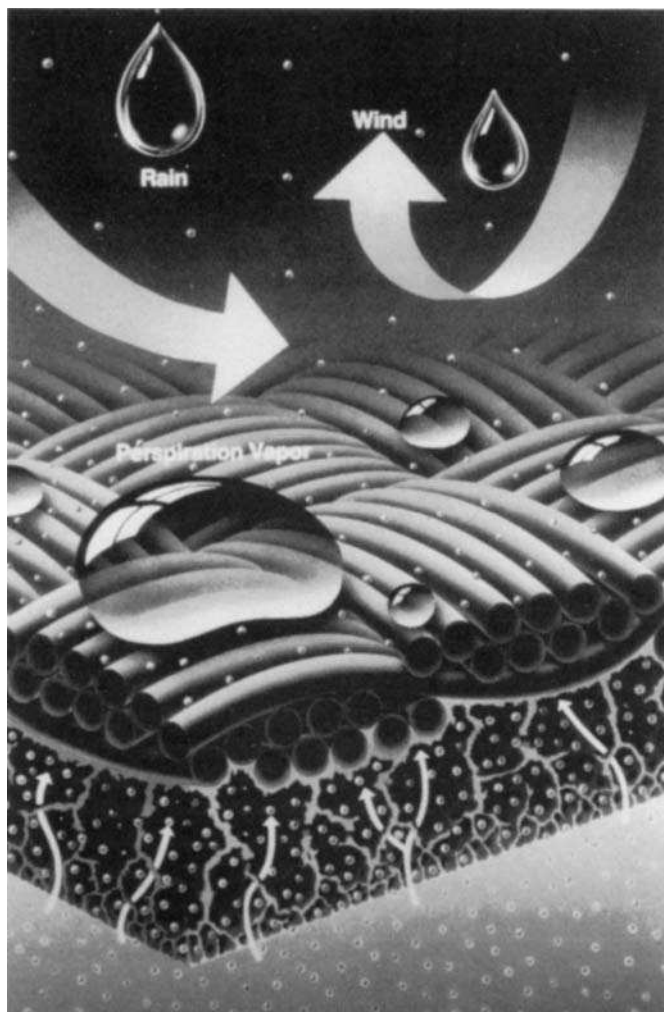
**Figure 7.7**   Microporous polyurethane coated fabric.

sweat residues, migrate into the pores, overcoming surface tension forces. These effects can be offset by applying a surface skin, either directly or indirectly. A thin continuous solid skin must decrease the vapour permeability by a significant amount, but it is a compromise which results from seeking the optimum performance in rainwear. Some microporous products are finished with a thin hydrophilic polyurethane top coat, which in itself has a relatively high water-vapour permeability (see Figure 7.8).
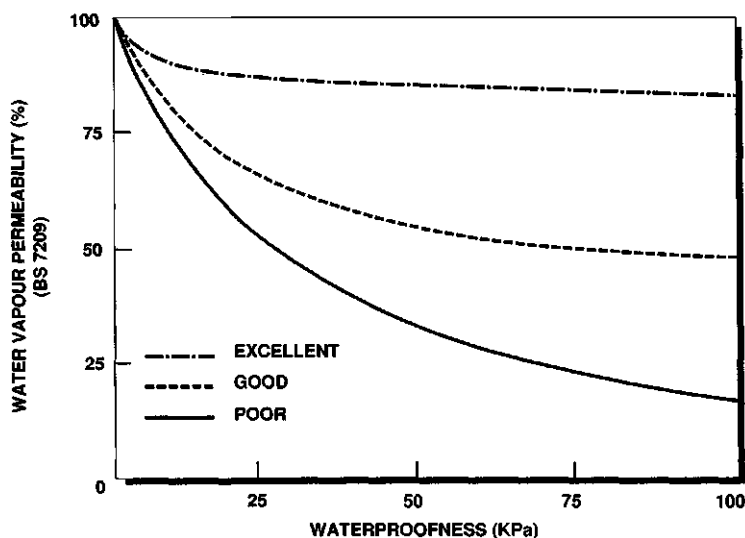
**Figure 7.8** Typical curves of water-vapour permeability versus waterproofness.

**7.7.3.2 Microporous poly(tetrafluoroethylene) (PTFE).** Very thin films of PTFE (5–15 µm) can be made by extruding a paste of PTFE dispersion and oils through a slit die. The extrudate is leached to remove the oil and biaxially stretched. This causes microporous tears or fibrils in the film, which have effective pore sizes of 0.1–1 µm (Gohlke and Tanner, 1976) (Figure 7.9). The material has a very high void volume, but is mechanically weak, and has to be laminated to one or more textile fabrics to be used for rainwear. Certain PTFE films also incorporate thin continuous layers of a hydrophilic/oleophobic polymer on the side facing the sweat. This resists sweat contamination and improves the penetration resistance to low surface tension organic liquids. At the time of writing, this hybrid microporous/hydrophilic membrane is patented.

Such films are adhesively laminated using discrete dots of adhesive applied by a very fine gravure roll. The technique is highly critical, in that there must be sufficient adhesive to bond the hydrophobic 'non-stick' film to a textile fabric, but the adhesive dot coverage has to be kept low to minimise the area of blocked micropores. One of the most widely recognised PTFE laminates is Gore-Tex®.

**7.7.3.3 Ultraviolet-beam polymerised microporous films.** Traditional processes for producing microporous films and coatings tend to be relatively slow, and hence expensive. A process was developed in the late 1980s which was based upon long-standing non-porous coating technology, where monomers and
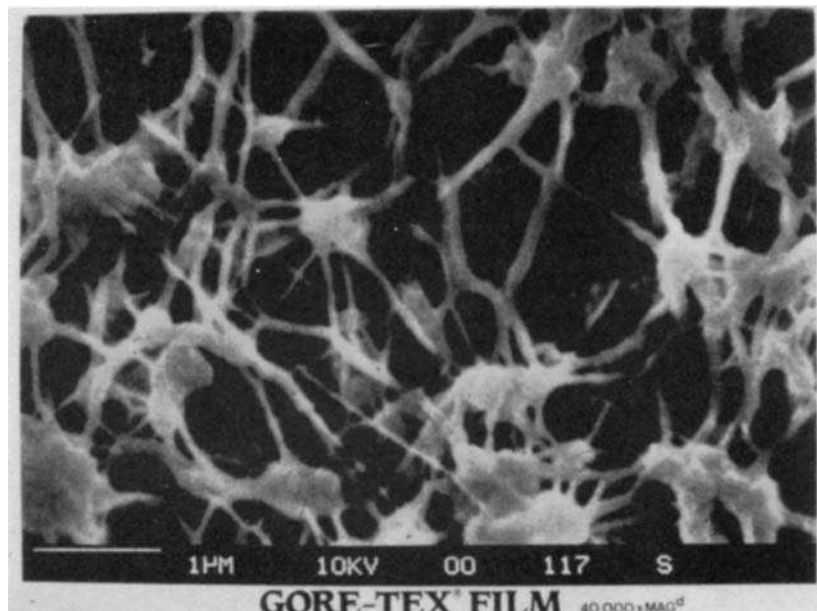
**Figure 7.9** Microporous PTFE membrane.

oligomers are crosslinked under a radiation source and cured in milliseconds. In the Sunbeam® process the film is cured by an ultraviolet beam to produce controlled pores of about 0.2 μm in very thin films of acrylic-based polymers (Lovell, 1984; Gregor *et al.*, 1988). The process can run at speeds of more than 350 feet/min and in widths of up to 100 cm.

Such ultraviolet cured films are very cheap and can be laminated to non-woven substrates for disposable protective clothing. The materials possess high water-vapour permeabilities and good barrier properties. A commercial product is marketed as Gelman Repel®.

### 7.7.4 Hydrophilic coatings and films

In contrast to microporous films, the hydrophilic films are continuous, pore-free solid films. As such, they have the potential for a high resistance to ingress of liquids, provided that they are free from pin-holes and that the film has a certain minimum thickness. However, water-vapour permeability rates through hydrophilic films are inversely proportional to their thickness (Lovell, 1984; Lomax, 1990).

Diffusion of water vapour through a solid film is achieved by the incorporation of hydrophilic functional groups along the molecular chain.

Such groups can be —O—, —CO, —OH or —NH$_2$, all of which can form reversible hydrogen bonds with water molecules. These bonds are comparatively weak, and can readily be broken down by thermal motion. Water molecules diffusing through the film pass stepwise along the molecular chains, a process which is facilitated by introducing pendant side groups, which prevent close-packing of adjacent chains.

The passage of water molecules through solid films is governed by Fick's Laws of Diffusion (Crank and Park, 1968), such that the rate of diffusion is proportional to the concentration gradient of water vapour between the two surfaces of the film. Expressed mathematically this is:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -DA(C_1 - C_2)$$

where: $\mathrm{d}s/\mathrm{d}t$ is the diffusion rate across an area $A$ of film; $(C_1 - C_2)$ is the concentration gradient of vapour between the two surfaces; and $D$ is the absolute diffusion coefficient.

7.7.4.1 *Hydrophilic polyurethanes.* Of the various possible routes to hydrophilic coatings and films, segmented copolymers of polyester or polyether polyurethanes with poly(ethylene oxide) are the most widely used for breathable apparel. The hydrophilicity of these products can be varied, either by increasing the overall content of the hydrophilic component, or by altering the length of the hydrophilic segments (Lovell, 1984; Lomax, 1990).

An important feature of hydrophilic films and coatings is that there has to be a balance between swelling of the membrane, which encourages the passage of water vapour, and dissolution of the polymer in water. Constant swelling and shrinking of the polymer coating can also lead to delamination from the textile substrate. Modern formulations are designed to provide low swelling with high vapour transmission rates. An example of a commercial polymer product is Witcoflex Staycool®, which can be applied as a direct coating, or as a transfer film.

7.7.4.2 *Hydrophilic polyesters.* Another type of hydrophilic copolymer is based on a modified type of polyester into which polyether groups have been incorporated to impart hydrophilic properties with a limited degree of swelling (Drinkmann, 1992). Commerical products such as Sympatex® are available as pre-prepared films which are 10–25 μm thick (Figure 7.10), The thinner films are used for apparel, and can be laminated to textiles in a variety of ways such as two-layer or three-layer laminates, but can also be used as lightweight linings or inserts in waterproof clothing. As with hydrophilic polyurethanes, the water vapour transmission rates are inversely proportional to the film thickness (Figure 7.11).
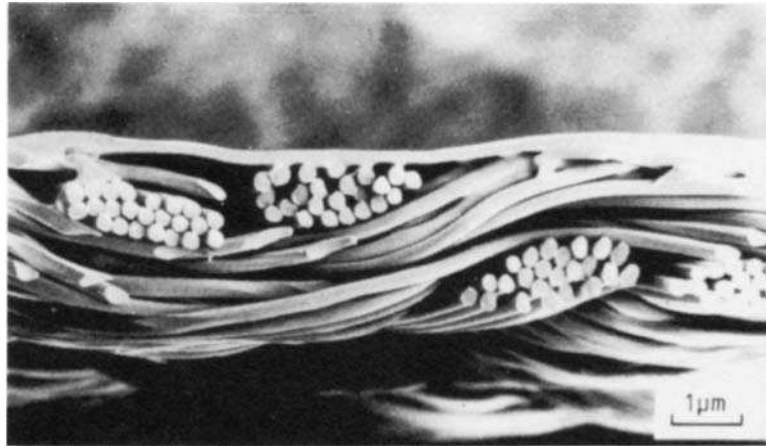
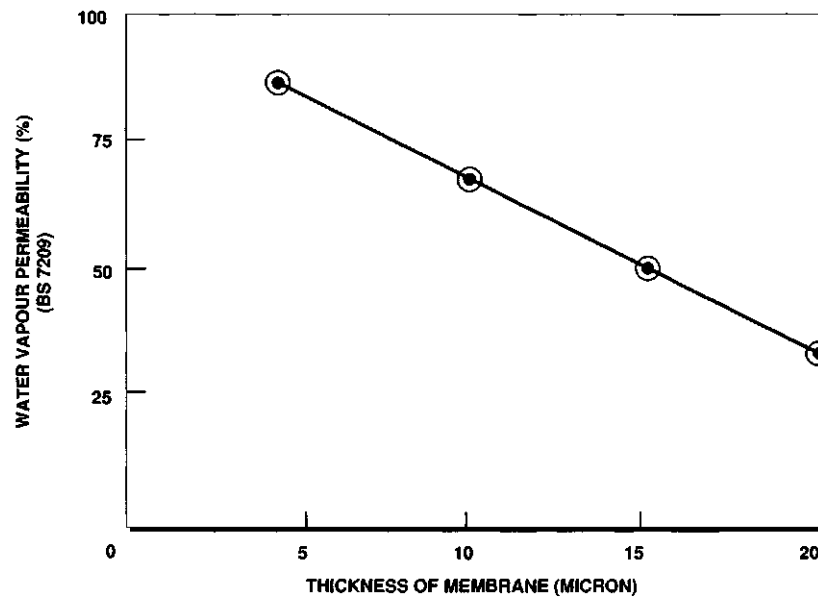**Figure 7.10**    Solid hydrophilic polyester coated fabric.



**Figure 7.11**    Typical graph of water-vapour permeability versus membrane thickness.

**Table 7.8** Star rating of breathable barrier fabrics. One star = poor; five stars = excellent

| Type of breathable barrier fabric | Water-vapour permeability | Waterproofness | Cost | Comments |
|---|---|---|---|---|
| PTFE laminates | ***** | ***** | Very high | Market leader; versatile usage; expensive |
| Microporous polyurethanes | ** to ***** | ** to ***** | Medium to high | Widely used; reasonable durability; coated or laminated forms |
| Hydrophilic polyurethanes and polyesters | ** to *** | *** to ***** | Low to medium | Polyurethanes very cheap; some delamination can occur in use |
| Conventional impermeable coatings | Not significant | ** to ***** | Low to medium | Waterproof but uncomfortable |

## 7.7.5 Relative performance of breathable barrier fabrics

A wide range of coated and laminated products is available worldwide, and their performance improves with development (Scott, 1991). It is not possible to give detailed specific performance figures for all products in this chapter, but they can be compared in general representative groups using a star-rating (shown in Table 7.8).

## 7.8 Test methods for coated and laminated fabrics

The performance of coated and laminated fabrics is quantified by a large range of laboratory tests. Such test methods are widely used by purchasers, suppliers and users of such fabrics. Many public bodies, such as government departments and private sector companies and corporations, purchase materials to detailed specifications which call upon national standard tests, and quote required minimum performance figures.

Table 7.9 lists contain details of those tests which are most widely used.

## 7.9 End-use applications for rubber-coated fabrics

Natural rubber has poor resistance to ozone, oxidation, sunlight, elevated temperatures, hydrocarbons and micro-organisms. This limits its usefulness, as the synthetic rubbers possess better performance in specific areas.

Butyl rubbers have excellent gas- and liquid-holding properties and can operate over a wide range of temperatures.

Neoprene rubbers have good oil and solvent resistance, and possess a degree of flame retardance.

Uses are summarised in Table 7.10. Gillette (1992) also discusses end-uses.

**Table 7.9**   Test methods for coated and laminated fabrics

| Test method title | Standard test reference | Comments |
|---|---|---|
| Coated fabrics for use in the manufacture of water penetration resistant clothing | BS 3546: Part 1 | Specification for polyurethane and silicone elastomer fabrics |
| | BS 3546: Part 2 | Specification for non-water vapour permeable fabrics |
| | BS 3546: Part 3 | Specification for natural and synthetic rubber polymer fabrics |
| | BS 3546: Part 4 | Specification for water vapour permeable fabrics |
| Mass per unit area | BS 3424: Part 3 ISO 2286 | Includes measurements on total mass, mass of coating and mass of substrate |
| Breaking strength and elongation at break | BS 3424: Part 4 ISO 1421 | Test methods for CRL, CRT and CRE machines |
| Methods for the determination of tear strength | BS 3424: Part 5 | Three methods of test, and advice on analysis of autographic traces |
| Coating adhesion strength | BS 3424: Part 7 ISO 2411 | Includes several test procedures |
| Low temperature performance | BS 3424: Part 8 ISO 4646 | Cold crack tests — three methods listed |
| Resistance to damage by flexing | BS 3424: Part 9 ISO 7854 | Four methods to assess dynamic flex fatigue properties |
| Resistance to accelerated ageing | BS 3424: Part 12 ISO 1419 | Ageing in dry heat, tropical conditions and ultraviolet exposure |
| Resistance to blocking | BS 3424: Part 11 ISO 5978 | Two methods to determine the resistance of polymeric coatings to self-adhesion |
| Fusion of PVC coatings and the state of cure of vulcanised rubber coatings | BS 3424: Part 22 ISO 6451 | Checks for tackiness, cracking, or disintegration of the coating |
| Resistance to water penetration and surface wetting | BS 3424: Part 26 | Hydrostatic head tests at different pressures and conditions. One method to measure surface wetting (repellency) |
| Method for the determination of surface wetting | BS 3702 | Water repellency test |
| Resistance to wicking and lateral leakage | BS 3424: Part 18 | Two methods for fabrics coated on one or both sides, or double textured or plied fabrics |
| Water entry pressure of coated fabrics | Federal Standard 191 Method 5512 | Mullen Test; produces pressures up to 400 psi |
| Water vapour permeability index (WVPI) | BS 3424: Part 37 BS 7209 | Water vapour permeability compared with that of an open polyester mesh fabric |
| Moisture vapour transmission rate | ASTM 96-66BW | Modified Inverted Cup Test (USA) |
| Water vapour resistance | CGSB CAN–4.2 (M77) Method 49 | Canadian 'Turl' Dish Method; measures resistance in equivalent thickness of still air layer |
| Measurement of stationary thermal and water vapour resistance by means of a thermoregulatory model of human skin | DIN 54101 ISO/DIS 11092 | Hohenstein skin model measures water vapour resistance |

**Table 7.10**  Use of rubber coatings

| Rubber coating | End-use applications |
|---|---|
| Natural rubber | Conveyor belts, inflatable balloons, surgical gloves, hoses, flooring, mats, groundsheets, immersion and diving suits, gaskets, aprons |
| Styrene–butadiene rubbers | Similar uses to natural rubber |
| Neoprene rubber | Waterproof clothing, oil- and fuel-resistant clothing, gloves, tents, shelters, inflatables, fuel tanks, conveyor belts, life jackets, gaskets |
| Butyl rubber | Gas-holding bags, chemical warfare protective clothing and shelters, pond and reservoir liners, water tanks, inflatable boats, covers, bellows, conveyor belts, air cushions, gaskets |
| Nitrile rubber | Oil-resistant clothing, gloves, aprons, fuel-cell liners, gaskets |

**Table 7.11**  Uses of polymer coatings

| Polymer coating | End-use applications |
|---|---|
| Polyurethanes | Lightweight waterproof clothing, covers, tents, bags, load carriage pouches, immersion clothing, inflatable boats and tanks, camouflage nets, acoustic insulation, vibration-absorbing materials |
| Poly(vinyl chloride) | Truck covers, tents, shelters, tarpaulins, waterproof clothing, leather-cloth upholstery, blinds, awnings, bags, shoes, belts, aprons |
| Silicones | Tents, covers, heating ducts, diaphragms, nonstick conveyor belts, gaskets, medical products |
| Polyethylene | Chemical protective clothing (disposable), disposable covers, shelters, gaskets, linings |
| Acrylates | Blinds, awnings, white hat covers, camouflage nets (snow) |
| Poly(tetrafluoro-ethylene) | Lightweight waterproof clothing, chemical protective clothing, tents, shelters, tensioned covers, conveyor belts, medical products, gaskets, seals |
| Chlorosulphonated polyethylene | Tents, covers, tarpaulins, shelters, inflatables, gaskets, ducting |

**Table 7.12**    Properties of rubbers for coated fabrics

| Properties | Natural rubber | Styrene–butadiene (SBR) | Butyl rubber | Nitrile rubber | Neoprene rubber |
|---|---|---|---|---|---|
| Adhesion to textiles | Excellent | Good | Good | Good | Excellent |
| Tear resistance (alone) | V. good | Fair | Good | Fair | Good |
| Abrasion resistance | Excellent | V. good | Good | Good | Excellent |
| Electrical insulation | V. good | V. good | V. good | Poor | Fair |
| Permeability to gases | Medium | Medium | V. low | Low | Low |
| Acid resistance | | | | | |
| Dilute | Medium | Medium | Excellent | Good | Excellent |
| Concentrated | Medium | Medium | Good | Good | Good |
| Solvent resistance | | | | | |
| Aliphatic hydrocarbons | Poor | Poor | Poor | Excellent | Medium |
| Aromatic hydrocarbons | Poor | Poor | Poor | Good | Fair |
| Ketones, ethers | Good | Good | Good | Poor | Poor |
| Resistance to swelling | | | | | |
| Mineral oils and gasoline | Poor | Poor | Poor | Excellent | Good |
| Animal and vegetable oils | Fair | Fair | V. good | V. good | Good |
| Water absorption | V. low | V. low | V. low | Low | Low |
| Resistance to | | | | | |
| Oxidation | Good | Fair | Excellent | Good | V. good |
| Ozone | Poor | Poor | Excellent | Fair | V. good |
| Sunlight ageing | Poor | Poor | V. good | Poor | V. good |
| Heat ageing | Fair | Medium | V. good | Good | Good |
| Low temperature | V. good | V. good | Good | Medium | Good |
| Flame | Poor | Poor | Poor | Poor | Good |

## 7.10    End-use applications for polymer-coated fabrics

Many coating and laminating polymers have specific properties that make them suitable for specific purposes. Polyurethanes are used in lightweight waterproof fabrics which can remain flexible and durable over a wide range of operating temperatures and conditions.

PVC is a good general-purpose, low cost, heavy covering material with a degree of flame resistance.

Silicones produce very lightweight waterproof/liquid proof fabrics. They can operate at high and low temperatures, and can be used in the food and medical industries. Polyethylenes possess good chemical resistance.

## 7.11    Summary

Tables 7.12 and 7.13 summarise the properties of rubber and polymer coatings, respectively.

**Table 7.13** Properties of polymers used for coated fabrics

| Properties | Poly-urethanes | PVC | PTFE | Chloro-sulphonated polyethylene | Silicone elastomer | Poly-ethylene |
|---|---|---|---|---|---|---|
| Adhesion to textiles | V. good | V. good | Fair | Good | Excellent | Good |
| Tear resistance | | | | | | |
| (alone) | Excellent | Good | Medium | Fair | Fairly low | V. good |
| Abrasion resistance | Excellent | Good | Good | Excellent | Fair | Good |
| Electrical insulation | Good | Good | Excellent | Good | Excellent | Excellent |
| Permeability to gases | Fairly low | Fairly low | V. low | Fairly low | Fairly low | V. low |
| Acid resistance | | | | | | |
| Dilute | Fair | Excellent | Excellent | Excellent | Excellent | Excellent |
| Concentrated | Poor | V. good | Excellent | Good | Fair | V. good |
| Solvent resistance | | | | | | |
| Aliphatic hydrocarbons | Fair | Good | Excellent | Fairly good | Poor | Fair |
| Aromatic hydrocarbons | Poor | Fair | Excellent | Fair | Poor | Fair |
| Ketones, ethers | Poor | Poor | Poor | Fair | Fair | Good |
| Resistance to swelling | | | | | | |
| Mineral oils and gasoline | V. good | Poor | Excellent | Good | Fair | V. good |
| Animal and vegetable oils | V. good | Poor | Excellent | Good | V. good | V. good |
| Water absorption | Low | Low | V. low | Low | V. low | V. low |
| Resistance to | | | | | | |
| Oxidation | Excellent | Fair | Outstanding | Excellent | Excellent | Poor |
| Ozone | Excellent | Fair | Outstanding | Outstanding | Excellent | Good |
| Sunlight ageing | V. Good | Poor | Outstanding | Outstanding | Excellent | Fair |
| Heat ageing | Fairly good | Fair | Outstanding | V. good | Outstanding | Medium |
| Low temperature | Excellent | Poor | Fairly good | Good | Outstanding | V. good |
| Flame | Fairly poor | V. good | Excellent | V. good | Fair | Poor |

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