Physical Properties of Coated Fabrics

4.1 GENERAL CHARACTERISTICS

COATED textiles are flexible composites, consisting of a textile substrate and a polymeric coating. The coating may be on one side or on both sides with the same or a different polymeric coating per side. A typical construction, coated on both sides, is depicted in Figure 4.1.

The physical properties of a coated fabric depend on the properties of the substrate, the coating formulation, the coating technique, and the processing conditions during coating. The factors responsible for different properties of a coated fabric are given in Table 4.1 [1] .

Due to the application of longitudinal tension during the coating process, the position of the yarns in the textile substrate is considerably altered in both the warp and weft directions. The warp yarns are aligned more parallel, whereas in the weft there is an increase in the crimp. The minimum coating thickness is thus on the top of the filling yarns.

4.2 TENSILE STRENGTH

The strength of a fabric depends on type of fiber, fineness, twist, and tenacity of yarns and also on the weave and yarn density (set). Theoretically, the tensile strength of a fabric should be the sum of the tensile strength of all the yarns added together. However, there is always a loss of strength due to weaving, and as a result, the theoretical strength is never achieved. The conversion penalty due to weave has been calculated and reported in a recent study on plain weave polyester fabric of varying yarn densities [2]. It has been found that the processing penalty in the warp direction is about 10% and in the weft direction is about 15%. The processing penalty increases with yarn density of the fabric.

The reason for this conversion loss is due to the thread strain during the weaving process, i.e., shedding, warp formation, weft insertion, etc., and due to
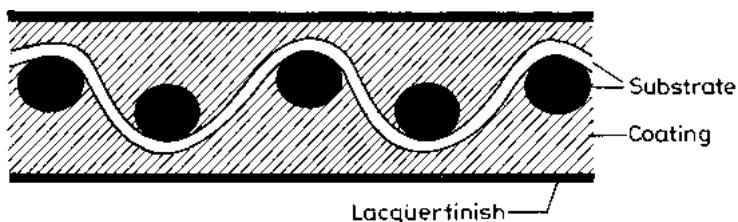
Figure 4.1 A double-sided coated fabric.

the transversal strain at the intersection points. The higher weaving penalty in the weft is due to greater waviness of the weft yarn bending around the stretched warp yarns.

Earlier workers observed that coating increased tensile strength [3–5], however, the reasons for the same were not properly explained. This aspect was thoroughly investigated by Eichert by measuring the strength of coated polyester fabric of different yarn densities [2]. It was observed that the tensile strength of the coated fabric increased from loomstate fabric when calculated on the basis of nominal thread count. Eichert argued that because the difference of break elongation of the yarn and the coating compound is so great, the coating compound cannot contribute to the tensile strength in any way. On further investigation, it

TABLE 4.1. Factors Affecting the Properties of Coated Fabrics.*

Properties	Substrate Construction	Coating Technique/ Processing Conditions	Recipe
1. Tensile strength	●	●	
2. Extension at break	●	●	
3. Dimensional stability	●	●	
4. Burning behavior	●		●
5. Long-time properties	●	●	●
6. Coating adhesion	●	●	●
7. Tear strength	●	●	●
8. Bending resistance	●		●
9. Cold resistance			●
10. Heat resistance			●
11. Chemical resistance	●		●
12. Sea water resistance			●
13. Weather resistance	●		●
14. Abrasion resistance			●
15. Welding properties			●

*Adapted with permission from U. Eichert, *Journal of Coated Fabrics*, vol. 23, April 1994, ©Technomic Publishing Co., Inc. [1].
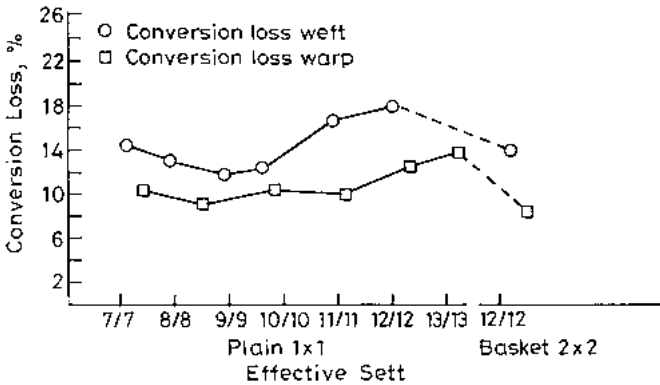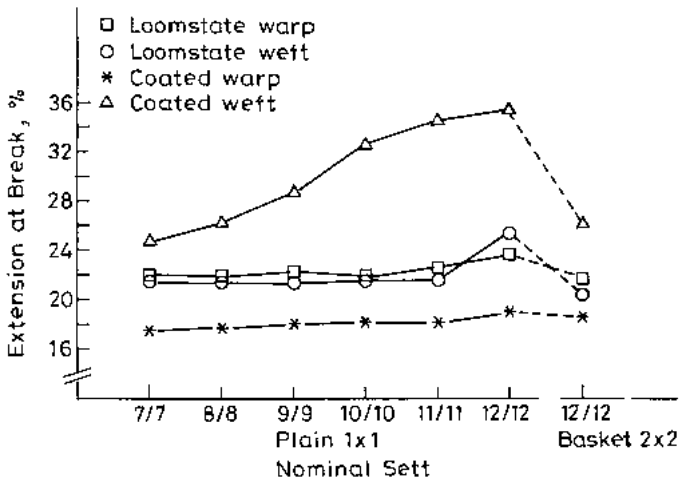
Figure 4.2 Tensile strength of coated fabric conversion loss % vs. effective set (Diolen 174 S 1100 dtex 1210 Z 60). (Adapted with permission from U. Eichert. *Journal of Coated Fabrics*, Vol. 24, July 1994. ©Technomic Publishing Co., Inc. [2].)

was found that there is a shrinkage of fabric in the weft direction due to tension and heat of the coating compound during the coating process. This resulted in an increase in yarn density in the warp direction. A comparison of tensile strength of coated fabric, with that of loomstate fabric, computed from effective thread count showed conversion loss in all fabric densities studied in the warp direction. The conversion loss was found to be more than the weaving penalty. As per Eichert, other reasons for conversion loss due to coating are transversal strain and heating of the yarns in the coating process. The conversion loss is shown in Figure 4.2.

4.3 ELONGATION

The extension of break of coated polyester fabric of different fabric densities has been studied by Eichert (Figure 4.3) [2]. In the uncoated fabric, the elongation only shows a slight increase with thread count both in warp and weft directions. In coated fabric, however, the elongation in the warp direction is much less than that in the loomstate fabric and is similar to the yarn elongation. This is due to the fact that during the coating process, the fabric is subjected to longitudinal tension, stretching the warp threads taut and parallel. Due to the stretching of the warp threads, the looping angle of the weft thread increases, and this phenomenon increases with thread count. This pronounced looping or crimp transfer causes enhanced elongation in the weft direction. Lower elongation of basket weave both in loomstate and coated fabric in weft is due to much lower interlacing.
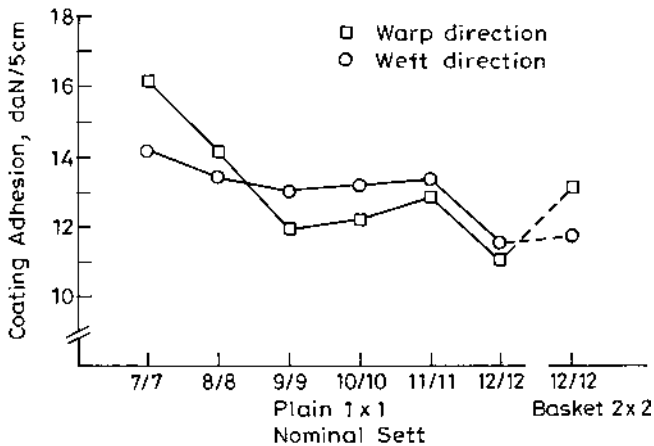
Figure 4.3 Elongation of loomstate vs. coated fabric (Diolen 174 S 1100 dtex 1210 Z 60). (Adapted with permission from U. Eichert. *Journal of Coated Fabrics*, Vol. 24, July 1994. ©Technomic Publishing Co., Inc. [2].)

4.4 ADHESION

The forces of adhesion between the coating compound and the textile substrate are a combination of mechanical and chemical bonding, particularly when bonding agents are added. Mechanical adhesion is predominant in staple fiber yarn and in texturized yarns. Acceptable adhesion values can be achieved between coating and these yarns without the addition of adhesion promoters described earlier. In the case of smooth, high tenacity filament yarns, mechanical adhesion is much lower, and chemical adhesion predominates. Chemical adhesion is obtained by the interaction of the adhesive system with the polar group of the textile substrate and the polymeric coating composition. The effect of mechanical bonding is seen from a study of adhesion in PVC-coated polyester fabric of varying yarn densities (Figure 4.4) [2]. In very loose constructions, the adhesion is very high due to mechanical factors, because of strike-through of the coating composition through the interstices of the fabric. The adhesion decreases with fabric density and becomes more or less level as coating penetration decreases. Thus, even though adhesion on the yarn is at a low level, high adhesion due to mechanical factors can be achieved in scrim fabric.

Chemical adhesion is mainly brought about by treatment of the textile or incorporation of bonding agents in the coating material. The mechanism of the action of the bonding agents has already been described in Chapter 1. Certain coating materials such as polyurethanes and chloroprene also contain reactive groups that promote adhesion. The adhesive system for rubber has already been

Figure 4.4 Effect of yarn density on adhesion (Diolen 174 S 1100 dtex 1210 Z 60). (Adapted with permission from U. Eichert. *Journal of Coated Fabrics*, Vol. 24, July 1994. ©Technomic Publishing Co., Inc. [2].)

described. The adhesive systems used in trade for coating different polymeric formulations can be classified as follows:

(1) One-component system—polyfunctional isocyanates, e.g., Desmodur R (Bayer), Vulcabond VP (ICI), etc., suitable for rubbers, PVC, and polyurethanes

(2) Two-component system—containing polyols and diisocyanates, e.g., Desmodur N, Plastolein, etc., suitable for PVC and polyurethanes

(3) Three-component system—RFL systems, mainly for rubbers

In vinyl coating, the bonding system is added to the plastisol in a range of about 4–6%. These bonding agents may be one- or two-component systems. The incorporation of the additives increases the viscosity of the PVC paste. Moreover, the plastisol temperature affects the pot life of the bonding agent.

Vulcabond VP [6] is an important bonding agent, for vinyl and textile substrates made from synthetic fibers. Chemically, it is a trimer of toluene diisocyanate dispersed in dibutyl phthalate. The reactive -NCO reacts with the hydroxyl and amido groups of polyester and nylon, respectively, and with the active hydrogen atom of the polyvinyl chloride chain, thus promoting adhesion. Optimum dose level of the additive is ∼4%. Higher bonding agent enhances adhesion but causes loss of tear strength of the coated fabric.

The factors affecting adhesion can be summarized as follows [7]

- type of fiber
- fiber surface: moisture, finish, etc.
- construction of fabric

- polymer for coating and its recipe
- bonding agents
- method of coating and coating conditions

Haddad and Black [8,9] have studied the effect of type of yarn, yarn construction, and fabric structure on adhesion. The fabric surface to be tested was pressed against a standard vinyl film. The peel tests were performed as per ASTM 751-79. Effect of weave pattern on adhesion is given in Figure 4.5.

It is seen that adhesion is the same on both sides of a 2×2 twill being a balanced fabric. In 1×3 twill, however, adhesion is higher on the filling side. This is because the picks were unsized and made of core-spun yarns. The effect of yarns on adhesion was studied by making a series of 1×3 twill construction with textured air-entangled polyester as warp and by using different types of filling yarns, viz., multifilament, core-spun, and spun yarns. The highest adhesion was obtained in air-textured yarns, yarns with cotton as the sheath, and open-end spun yarns in the three categories, respectively (the results are given in Table 4.2).

In the case of textured polyester yarns, a relationship between shrinkage (dependent on crimp and bulk) and adhesion has also been found. Clearly, adhesion is dependent on weave and nature of yarn. An open-weave structure and higher yarn surface exposure promote adhesion due to increased mechanical anchoring of the coating compound.
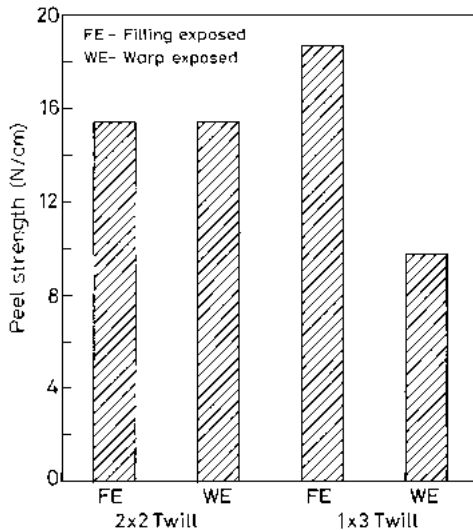
Figure 4.5 Effect of weave pattern and side of laminating on peel strength. Construction: warp—$2 \times 150/34$ textured air-entangled polyester 22.4 ends/cm.; fill—12/1 core spun, sheath 100% pima cotton; core—150/34 stretch polyester, 16.8 picks/cm. (Adapted with permission from Haddad and Black. *Journal of Coated Fabrics*, Vol. 14, April 1985. ©Technomic Publishing Co., Inc. [8].)

TABLE 4.2. Effect of Different Filling Yarns on the Peel Strength on Vinyl Laminated Fabric.* Vinyl Film Applied to the Side Where Filling Is Exposed.

| Type of Filling Yarn	Peel Strength N/cm ASTM D 751−79
A. Multifilament polyester yarn	
1. 2 × 150/34 Friction-textured air-entangled polyester	7.9
2. 2 × 150/34 Friction-textured, plied 2.5 TPI S	9.9
3. 2 × 150/34 Air-textured Taslan	13.3
4. 2 × 150/68 Air-textured Taslan	14.9
B. Core-spun yarns	
1. 17.5/1 Sheath polyester, core 150/34 textured polyester	13.8
2. 17.5/1 Sheath AvrillII; core 150/34 textured polyester	17.0
3. 15/1 Sheath 100% pima cotton, core 150/34 textured polyester	18.5
4. 12/1 Sheath 100% pima cotton, core 150/34 textured polyester	18.6
C. Spun yarns	
1. Ring-spun 12/1 3.5TM S high-tenacity polyester	17.0
2. Ring-spun 12/1 2.75TM S high-tenacity polyeser	14.3
3. Ring-spun 12/1 3.5TM S crimped polyester	18.0
4. Ring-spun 12/1 2.75TM S crimped polyester	16.8
5. Ring-spun 16/1 3.5TM Z regular tenacity polyester	17.0
6. Ring-spun 18/1 3.75TM S regular tenacity polyester	13.9
7. Open-end spun 18/1 3.75TM S regular tenacity polyester	23.2

*Adapted with permission from Haddad and Black, *Journal of Coated Fabrics*, vol. 14, April 1985, ©Technomic Publishing Co., Inc. [8].
Construction: 1 × 3 twill, 16.8 picks/cm. Warp 2 × 150/34 textured air entangled polyester 22.4 ends/cm.

Dartman and Shishoo [10] have carried out adhesion of PVC on various polyester and polyamide knitted and woven fabrics. Studies on the effect of moisture were done by carrying out the coating in an environmental chamber with humidity control. Moisture content in the substrate greatly affects adhesion; environmental moisture, on the other hand, has little effect on adhesion (Figure 4.6). They also noted that knitted fabric with a lower cover factor promotes adhesion.

4.5 TEAR RESISTANCE

Resistance to propagation of tear of a coated fabric is of great importance where these fabrics are under tension, e.g., in covers, shelters, and architectural purposes. If cut or punctured, tear can propagate rapidly under stress, damaging the material and leading to its failure. Factors controlling tear strength are as follows:
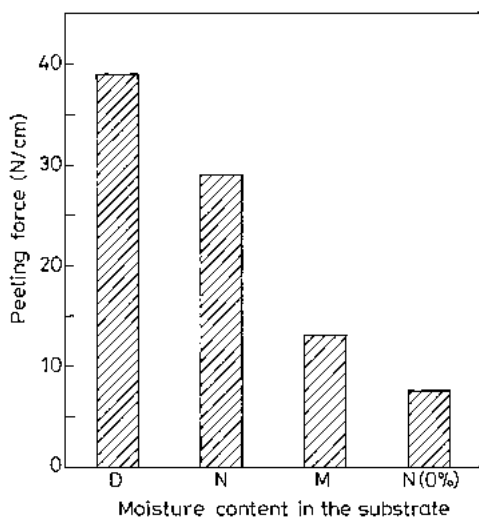
Figure 4.6 Effect of adhesion on the moisture content of substrate. PVC-coated woven polyester, 5% bonding agents in the coating; D = fabric dried at 105°C, N = fabric conditioned at 20°C and 65% RH, M = wet fabric, N (0%) = same fabric as N but with no bonding agent in coating. (Adapted from Dartman and Shishoo. *Journal of Coated Fabrics*, Vol. 22, April 1993. ©Technomic Publishing Co., Inc. [10].)

- construction of the fabric: weave, yarn fineness, and yarn density (Tear strength is related to yarn strength)
- coating material: formulation and bonding system
- adhesion and penetration of coating material on the textile substrate

The effect of various constructional parameters of the fabric on tear strength has been reviewed [11]. A study of three woven constructions, viz., matt 3/3, matt 2/2, and plain-weave fabric, shows that tear strength decreases in the order described due to a lower number of threads at the intersection. Staple fiber yarn has a lower tear compared to filament yarn. Tear strength decreases with weft density of the fabric, but it increases with warp density up to a maximum value and then decreases. The factors that affect tear strength of uncoated fabric also apply to coated fabrics.

Abbott et al. [4] have carried out a detailed study of the tear strength of various woven cotton fabrics coated with PVC plastisols by the knife on blanket method. In the uncoated state, the tear strength of different weaves, with the same cover factor, was found to decrease in the order of basket, twill, and plain weave, due to the reduced deformability of the structures. Coating resulted in loss of tear strength in all cases, but the loss of strength varied with the type of weave. For basket weave, the loss was ~70%, in twill ~60%, and in plain weave ~25%. Yet, the tear strength of the coated fabric was highest for basket, intermediate for twill, and least for plain weave, because of their respective tear strength in
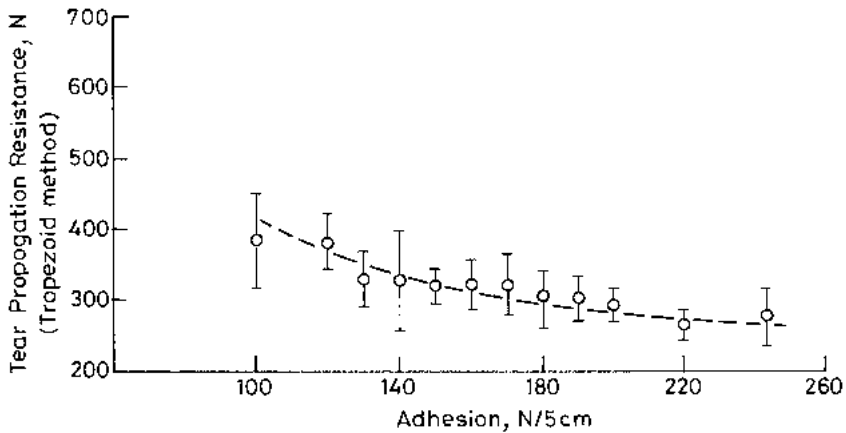
Figure 4.7 Relationship between tear propagation resistance and adhesion (vinyl-coated polyester 1000 d Plain weave 9 ends/cm). (Adapted with permission from Mewes. *Journal of Coated Fabrics*, Vol. 19, Oct. 1989. ©Technomic Publishing Co., Inc. [7].)

the uncoated state. It was also observed that twills and basket weaves made from plied yarns had significantly lower tear strength than those made from single yarns. In all cases, the decrease in tear strength is related to reduced deformability due to the coating.

One of the most important factors controlling the tear strength in a coated fabric is the adhesion of the coating material on the substrate. Mewes [7] has reported a relationship between tear strength and adhesion (Figure 4.7). A linear relationship has been reported by other authors [11,12].

Effect of fabric density on tear strength on PVC-coated fabric has been studied by Eichert [2]. The tear strength in the warp direction decreases with yarn count, but in the weft direction, no general trend is seen (Figure 4.8). In a trapezoid tear test, an increase in ends and picks increases tear strength. This is due to the difference in tear geometry in the two tests. In leg tear, the thread system exposed to testing is not restrained as in the case of the trapezoid test.

The loss in tear strength on coating is much more severe in the weft direction than in the warp. This is explained by the process of spread coating. During spread coating, the coating knife runs parallel to the weft, its dragging action opens the filament/fibers, leading to greater penetration in the weft. Warp yarns, on the other hand, have much lower crimp due to tension applied during coating, moreover, because the knife runs at right angles to the warp, they are not opened, as such, penetration is lower in the warp [3,13]. Abbott et al. [14] have studied the mechanical properties, particularly tearing strength, of different types of cotton fabrics by coating with PVC plastisols of different hardnesses and viscosities; polyvinyl butyral and polyurethane. It was seen that the tear strength is affected primarily by the coating that penetrates the fabric pores, and not on the nature of coating. No direct relation between viscosity and extent of
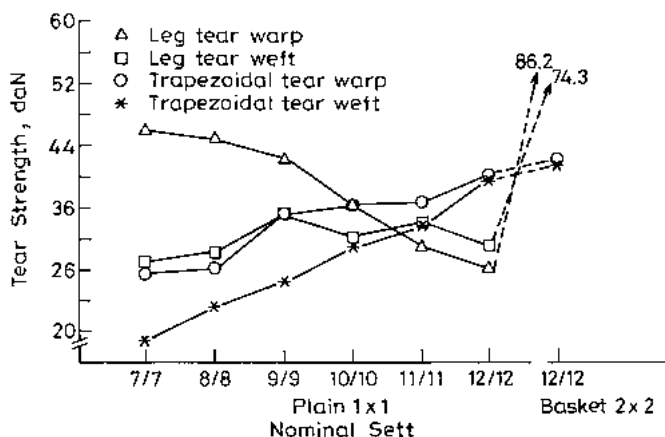
Figure 4.8 Tear strength vs. yarn density in coated fabric. (Adapted from U. Eichert. *Journal of Coated Fabrics*, Vol. 24, July 1994. ©Technomic Publishing Co., Inc. [2].)

penetration could be found. Higher tear strength is observed for coating that is more deformable. In many cases, the penetrated coating was found to be porous and presumably deformable. The use of soft coating alone, or as a base coat with a hard top coat, showed higher tear strength. A novel way of obtaining high tear strength is to fill the fabric interstices with a water-soluble polymer, such as carboxymethyl cellulose prior to plastisol coating, followed by leaching the water-soluble polymer. Thus, high tear strength could be obtained by any type of coating if the shape of the coating-fabric interface and deformability of the penetrated coating are properly controlled.

The studies were continued by the authors to investigate the tear strength and penetration in the coated fabric using different coating techniques, viz., knife on blanket, floating knife, reverse roll, and transfer coating [15]. The tear strength obtained by knife on blanket and floating knife were found to be similar, even though the degree of penetration in floating knife was higher. In transfer-coated fabric, considerable penetration was noted using a binder coat without gelling, but little penetration occurred when the same was pregelled. The reason for higher tear strength, in spite of deep penetration, has been explained as due to the porous, deformable nature of penetrated coating. The factors that determine the tear strength of the coated fabric are the shape of the coating applicator, the nature of the fabric surface, and the rheology of the coating.

4.6 WEATHERING BEHAVIOR

Weathering or degradation of material to outdoor exposure is a complex combination of various components [16].

- solar radiation (In sunlight, ultraviolet radiation is the most important cause of degradation because of its higher energy)
- temperature
- humidity and precipitation—liquid or solid
- wind
- chemicals and pollutants

A coated fabric is essentially a polymeric material. Weathering degrades a polymeric coating by the following process:

a. Volatalization of plasticizer and solvents

b. Rupture of the main macromolecular chain

c. Splitting of the side groups in various ways

d. Formation of new groups and reactions among them

e. Regional orientation—formation of crystalline regions

Studies on the weathering behavior of fibers and fabrics show a rapid degradation in most natural and synthetic fibers resulting in loss of strength [16]. Attempts to correlate outdoor exposure to accelerated weathering tests have not been very successful. A typical result is given in Figure 4.9. The degradation of fabric can be prevented by the application of coating. The thicker the coating, the longer the protection.

Vinyl-coated fabrics are extensively used for covers, tents, shelters, and architectural use. They are, therefore, exposed to weathering. A study of their weathering behavior assumes great significance. The weather resistance of coated fabric is dependent on the coating composition as well as on the nature
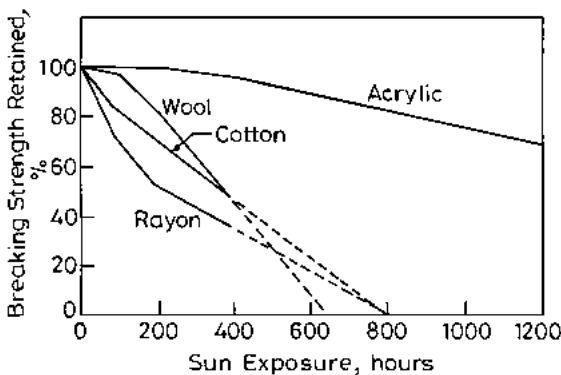
Figure 4.9 Sunlight exposure of wool, cellulosic, and acrylic fibers. (Adapted with permission from "Fibres" by J. H. Ross in *Environmental Effects on Polymeric Materials*, Rosato and Schwartz, Eds. ©John Wiley & Sons, 1968 [16].)

of the textile substrate. Strength and elongation are chiefly contributed by the textile, and the coating protects it from UV radiation during weathering and subsequent loss of strength.

Krummheuer [17] has investigated the weathering of vinyl-coated polyester at different locations of varying sunshine hours and different climatic conditions. The coating composition was a white plasticized PVC with fungicide and UV stabilizer added. The exposure was done at Miami (U.S.), Dormeletto (Italy), Ebnit (Austria), and Wuppertal (Germany). From the results of exposure after five years (Table 4.3), it was found that there was a significant loss of tensile strength and tear strength in thinly coated samples. The loss was maximum at those sites where complete coating was lost, i.e., Dormeletto and Wuppertal. In thickly coated samples, there was loss of coating, but there was no major loss of strength. The rate of loss of strength and tear strength is related to sunshine hours. The rate of deterioration is very rapid after a substantial loss of coating thickness. The author has suggested that for long-term durability, a minimum coating of about 150 μ is required. The outdoor test does not correlate with accelerated weathering by Xenotest because pollutants play an important role. The effect of a UV absorber is significant for short-time exposure, but for long-time exposure, their effect is marginal.

Studies were also carried out by Eichert [1] with similar fabric at the same locations for a period of ten years. The findings are similar to those of Krummheuer. The loss of tensile and tear strength was found to be more severe in the weft direction than in the warp. This is because the fabric warp is located at the center and is better protected than the weft threads.

4.7 MICROBIOLOGICAL DEGRADATION

It has been observed that PVC-coated fabric, used for awnings and marquees, shows discoloration on prolonged use. This is more prominent in white or light-colored fabrics. Such discoloration is due to microbiological attack on the material. In PVC-coated polyester fabric, the plasticizer of PVC is susceptible to microbiological attack, as many of the plasticizers are known nutrients for microbes. Eichert [18] has studied the microbiological susceptibility of white plasticized PVC with and without fungicide. The organisms for study were *Aspergillus niger, Penicillum funiculosum, Paecilomyces varioti, Trichoderma longibrachiatum,* and *Chaetomium globosum.* Profuse growth was observed in coated fabric without fungicide but no growth was seen in uncoated fabric and coated fabric with fungicide. The mechanical properties (tensile strength and tear strength) of the infested fabric, however, did not show any change despite discoloration. The author suggests a longer test to confirm no loss of mechanical damage due to microbiological attack.

TABLE 4.3. Weathering Test for Five Years of PVC Coated Polyester (Plain-Weave Polyester Fabric 1000 d 9/9 Set Coated with White Plasticized PVC).*

Locations	Original Coating Thickness of Samples and (Add on g/m^2) −0.5% UV Absorber								
	20 μ (540)			50 μ (600)			230 μ (900)		
	Res. Thickness	Res. Strength	Res. Tear	Res. Thickness	Res. Strength	Res. Tear	Res. Thickness	Res. Strength	Res. Tear
Wuppertal	0	37%	22%	0	37%	28%	213	113%	87%
Ebnit	22	53%	31%	36	72%	52%	212	87%	94%
Dormeletto	0	21%	14%	0	21%	17%	138	109%	101%
Miami	13	35%	21%	31	51%	36%	204	97%	139%

* Adapted with permission from Krummheuer, *Journal of Coated Fabrics*, vol. 13, 1983, ©Technomic Publishing Co., Inc. [17].

4.8 YELLOWING

For critical applications, yellowing of coated fabrics may be undesirable. In PVC-coated fabric extensively used for architectural application, the yellowing can be due to degradation of the polyvinyl chloride due to heat and light. If properly stabilized, the yellowing of PVC-coated fabric may only be due to the adhesives used in the tie coat formulations. As discussed earlier, these bonding agents are one-component or two-component systems based on polyisocyanates that can be aliphatic or aromatic. Aromatic isocyanates are known to yellow on exposure to light. This aspect has been studied by Eichert [19]. White PVC-coated fabrics with different tie coat formulations were prepared, and their whiteness and light transmission properties were measured after accelerated weathering. The adhesive system affects the yellowing of the fabric, but the aliphatic isocyanates do not show significant nonyellowing properties over many aromatic systems.

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Rheology of Coating

THE science of deformation and flow of matter is termed rheology. It is concerned with the response of a material to an applied stress. In coating, we are concerned mainly with the flow of liquids, solutions, dispersions, and melts. An understanding of the flow property of the coating material is required to control coating thickness, penetration, adhesion, and coating defects.

5.1 RHEOLOGICAL BEHAVIOR OF FLUIDS [1–3]

In order to understand the concept of viscosity, which is the resistance of a liquid to flow, let us consider a situation in which a liquid is confined between two parallel plates—AB and CD. The bottom plate AB is stationary, while the upper plate CD moves (Figure 5.1).

Let the plates be separated by a distance x and the shear force F act tangentially on the top movable plate CD of area A, in a direction, so that plate CD slides sideways with a velocity v as shown in Figure 5.1. The top layer of liquid then moves with the greatest velocity, and the intermediate layers move with intermediate velocities. The velocity gradient dv/dx through the layer is constant, where dv is the incremental change in velocity corresponding to a thickness, dx, of the liquid layer. This term is known as shear rate and is given by
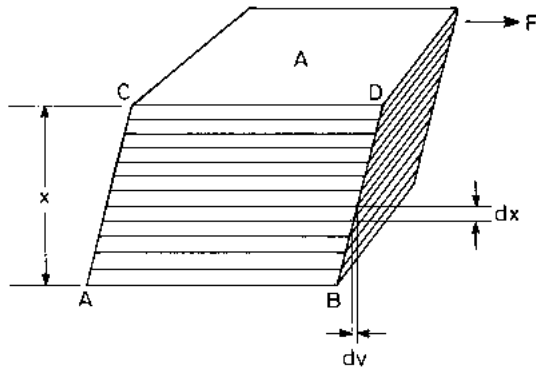
$$\gamma = dv/dx \text{ (shear rate)}$$

The shearing force acting over the unit area is known as the shear stress.

$$\tau = F/A \text{ (shear stress)}$$

Viscosity is defined as the ratio of shear stress to shear rate, i.e.,

$$\eta = \tau/\gamma \text{ (viscosity)}$$

**Figure 5.1** Flow of liquid under shear: A = area, F = force (dynes).

The unit of shear stress is dynes/cm^2, shear rate sec^{-1}, and of viscosity dynes $-$ sec/cm^2 or poise.

Liquids where shear stress is directly proportional to shear rate are known as Newtonian. For a liquid, a plot of shear rate vs. shear stress is a straight line passing through the origin. In other words, the viscosity η for a Newtonian liquid is constant, remaining unchanged with rate of shear (Figure 5.2).

Liquids with viscosity that is not constant but varies as a function of shear rate are known as non-Newtonian liquids. The viscosity value obtained for a non-Newtonian liquid at a particular shear rate is known as the apparent viscosity. For non-Newtonian liquids, because viscosity changes with shear rate, only a viscosity profile is capable of expressing the varying viscosity behavior. The various modes of non-Newtonian behavior are given below.

5.1.1 BINGHAM BODY BEHAVIOR

In this type of flow, a certain minimum stress is necessary before flow begins. This is known as the yield value. Once the yield value is reached, the behavior is Newtonian. Mathematically, it can be expressed as $\tau = \tau_0 + \eta\gamma$, where τ_0 is the yield stress. Examples of material of this type are ketchup and mayonnaise.
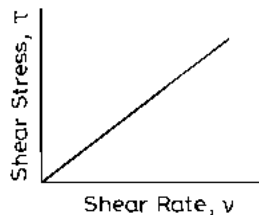
Figure 5.2 A Newtonian liquid.
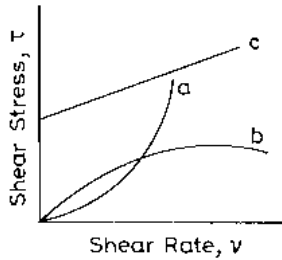
Figure 5.3 Flow behavior of non-Newtonian liquids: (a) dilatant, (b) pseudoplastic, and (c) Bingham body.

## 5.1.2 DILATANCY AND PSEUDOPLASTICITY

In a dilatant liquid, the apparent viscosity increases with shear rate, i.e., shear stress increases with shear rate. A pseudoplastic liquid, on the other hand, shows shear thinning, i.e., a decrease of apparent viscosity/shear stress, with shear rate. In a dilatant fluid, the dispersed molecules or particles are compressed and piled up, with application of shear, creating resistance to flow. The molecules/particles in a pseudoplastic fluid arrange themselves in a favorable pattern for flow on application of shearing force. The different flow patterns of non-Newtonian fluids and change in apparent viscosity with shear are given in Figures 5.3 and 5.4.

Different mathematical relationships have been put forward to describe non-Newtonian flow behavior. An equation, commonly referred to as the Power law equation, has been accepted to be of general relevance and applicabilty. This equation takes the following form:
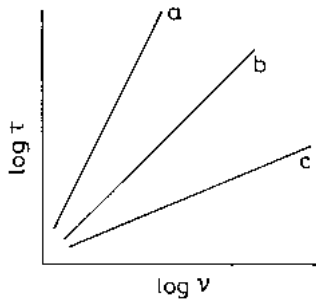
$$\tau = K(\gamma)^n$$

where K and n are constants. In logarithmic form, this law takes the form of

$$\log \tau = \log K + n \log \gamma$$
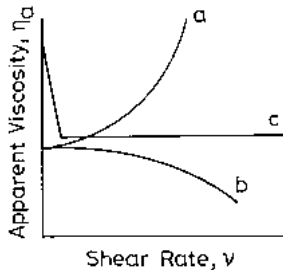
Figure 5.4 Apparent viscosity vs. shear rate of non-Newtonian liquids: (a) dilatant, (b) pseudoplastic, and (c) Bingham body.

Figure 5.5 Power law plot of different types of fluids: (a) dilatant $n > 1$, (b) Newtonian $n = 1$, and (c) pseudoplastic $n < 1$.

Thus, a plot of $\log \tau$ vs. $\log \gamma$ will yield a straight line. If $n = 1$, the liquid is Newtonian. Dilatant and pseudoplastic materials have $n > 1$ and $n < 1$, respectively (Figure 5.5).

5.1.3 THIXOTROPY AND RHEOPEXY

There are a number of fluids whose flow properties, such as apparent viscosity, change with time at a constant rate of shear. In some cases, the change is reversible or at least after cessation of shear, the viscosity returns to the original value over time. A thixotropic material may be considered a special case of pseudoplasticity, where the apparent viscosity also drops with time at a constant rate of shear (Figure 5.6). As the shear force is reduced, the viscosity increases but at a lesser rate, forming a hysteresis loop. The area of the hysteresis loop is a measure of the thixotropy of the coating (Figure 5.7). Thixotropic behavior may be visualized as isothermal gel-sol-gel transformation of a reversible colloidal gel. Under constant shear, the material undergoes a progressive breakdown of structure with better flowability over time.

A common example of thixotropic behavior is the drop of viscosity of paint with stirring. Thixotropic behavior is advantageous in a coating system because lowering of the viscosity during coating facilitates application, whereas, higher viscosity at a lower shear rate prevents sagging and dripping.
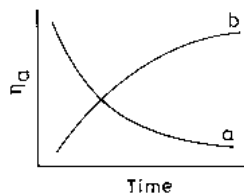
Figure 5.6 Time-dependent flow: (a) thixotropic and (b) rheopectic.
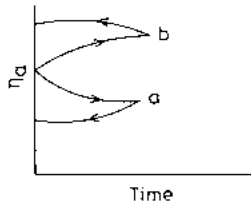
Figure 5.7 Hysteresis curves of of fluids: (a) thixotropic and (b) rheopectic.

Rheopexy is the exact opposite of thixotropy in that under steady shear rate, viscosity increases. This phenomenon is observed in some dilatant systems. Such flow is not of much interest in coating.

5.2 RHEOLOGY OF PLASTISOLS [3–5]

Rheological properties of the coating material are of primary importance for successful coating. The flow properties of coating compositions are greatly influenced by the shear applied during the coating process, as in calender, roller, blade coating, etc. For use of plastisols (pastes) in spread coating, it is useful to know the viscosity at high shear and low shear rates. High shear is encountered at the coating head. A high viscosity at the coating head may cause uneven deposition and may even bend the coating blade. Viscosity at low shear rate and knowledge of yield value is also important. A high yield value prevents strike through in an open-weave fabric, while a low yield value aids leveling of the paste after coating [6]. The rheology of plastisol is the most complex and merits discussion.

Very dilute dispersions containing more than 50% plasticizer show Newtonian behavior. Paste formulations, however, have higher polymer loading. As such, pastes show non-Newtonian behavior. Depending on the formulation, they may be pseudoplastic, dilatant, or thixotropic. The flow behavior normally varies with the shear rate. A paste may show pseudoplastic flow at low shear rates, dilatancy at moderate shear, and again pseudoplastic at still higher shear rates. It may also show dilatancy at low shear rate but pseudoplastic at moderate shear. Pseudoplastic behavior is due to breakdown of a structure in the paste with shear, while dilatancy occurs due to peculiar particle size distribution that does not favor close packing, thus resistance to flow.

5.2.1 APPARENT VISCOSITY OF PLASTISOLS

The viscosity of a simple suspension is given by the well-known Einstein's equation.

$$\eta_s = \eta_o \left(1 + 2.5\phi\right) \tag{1}$$

where η_s = viscosity of suspension, η_o = viscosity of the suspending fluid, and ϕ = the volume fraction of the suspended particles. η_s/η_o is known as the relative viscosity η_r. This equation is true for dilute solutions. At volume fractions >0.025, the η_r becomes much lower than actually observed. Moreover, this equation is applicable when the suspending particles are monodisperse in nature, and there is no interaction between the particles and the medium.

The equation cannot be applied to PVC pastes because of the following reasons:

a. The volume fraction of the suspended particles is quite high >0.2.

b. The suspended particles are not monodisperse.

c. Although paste polymers are resistant to solvation by the plasticizer, slow swelling and dissolution of the polymer particle still occur. Solvation of the polymer increases the viscosity of the plasticizer medium, and swelling increases the volume fraction of the polymer.

Johnston and Brower have developed an equation of apparent viscosity for PVC pastes that is applicable for volume fraction of about 0.2 and for several resin and plasticizer systems.

$$\log_{10} \eta_r = (1.33 - 0.84 \, \phi/\phi_c)(\phi/\phi_c - \phi) \tag{2}$$

ϕ_c is known as critical volume fraction and is defined as the volume fraction of the polymer particle at a stage when it has absorbed plasticizer to the maximum limit, as in a fairly advanced stage of gelation.

The flow property of the paste and its stability are greatly influenced by the formulation of the paste. The important factors are particle size, particle size distribution of the resin, the nature of the plasticizer, and the amount of plasticizer. Additives also affect paste rheology. The effects of various factors are given below.

5.2.2 POLYMER SIZE AND SIZE DISTRIBUTION

As has been described earlier, paste resins are emulsion grade, obtained by spray drying, of particle size ranging from 0.1–3 μm. These particles are known as primary particles. However, during spray drying, aggregates of primary particles are formed that can be much larger in size, 40–50 μm. The aggregates are fragile and break down to primary particles by shearing during paste formation. The ease of breakdown depends on the fragility of the aggregate. The deagglomeration process also affects the paste rheology.

The paste viscosity depends on the size of the primary particles and the size and proportion of the aggregate or secondary particles. The resins may be categorized into the following three types:

(1) High-viscosity resins: the primary particles have size <0.5 μm and are monodispersed in nature. The secondary particles do not significantly affect viscosity.

(2) Medium-viscosity resins: primary particles are polydisperse, having size range of 0.8–1.5 μm. Secondary particles have some effect on viscosity, showing dilatancy at high shear rate.

(3) Low-viscosity resins: they have broader particle size distribution. The secondary particles are larger in proportion and size.

The blending resins have much larger particle size (80–140 μm) than the paste resins. These resins improve the packing of the nearly spherical emulsion particles, reducing the interstitial space and lowering the surface area. Thus, for a given plasticizer content, more of it is freely available, lowering the viscosity.

Apart from particle size, there are other factors of the resin that influence the viscosity of the paste. The surfactant used in the manufacture of the resin is retained in the dried resin. The nature and quantity of the surfactant present in the resin is important as it may reduce or increase the paste viscosity depending on its solubility characteristics, with the plasticizer. Moreover, higher temperature and duration of drying may produce an over-dried resin with reduced plasticizer absorption. The K value of the polymer does not have much influence on the paste viscosity.

5.2.3 PLASTICIZER AND ADDITIVES

The viscosity of the plasticizer and its solvating power affect the viscosity of the paste. For freshly made paste, the viscosity of the paste varies linearly with the viscosity of the plasticizer. However, as the paste ages, this correlation is lost due to the overriding effect of solvation. The higher the solvation (δ closer to PVC ~ 9.7), the greater the viscosity of the paste. Polar plasticizers, such as DBP and TCP, yield highly viscous pastes, with poor viscosity stability, showing dilatancy. For coating purposes, high viscosity and dilatancy are not required. Less polar types such as DOP and DIDP form medium-viscosity pastes with thixotropic properties. As such, they are useful for spread coating. Because of their low δ value, dialkyl esters of adipate and sebacates such as DIDA form low viscosity pastes. An increase of temperature increases aging and viscosity.

The influence of stabilizers, fillers, thickening agents, etc., on paste rheology has already been described (Chapter 1).

5.2.4 VISCOSITY CHANGE DURING FUSION

As the paste is heated, there is initially a lowering of paste viscosity due to a drop in viscosity of the plasticizer with temperature. This is dependent on the nature of the plasticizer (AB in Figure 5.8).
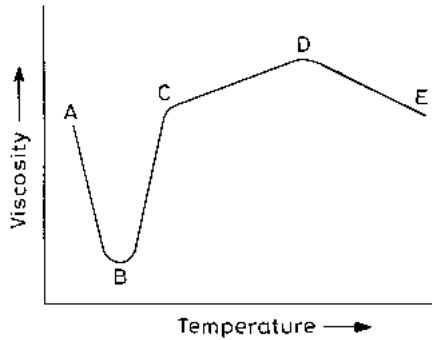
Figure 5.8 Change in viscosity during fusion. (Adapted with permission from *PVC Plastics* by W. V. Titow. ©Kluwer Academic Publishers, Netherlands, 1990 [3].)

A sharp rise of viscosity then occurs mainly due to adsorption of plasticizer by the polymer and due to solution of polymer in the plasticizer-gelation region (BC). The temperature at which the sharp rise occurs is known as the gelation temperature. As the temperature increases, viscosity increases slowly, showing a maxima (D) at the fusion point. A slight drop in viscosity thereafter, is due to the melting of the microcrystalline structure of the polymer. A solvent immersion test is useful for determining complete fusion in a coated fabric. The fusion temperature depends on the nature of the resin and the plasticizer. A paste of a highly solvating plasticizer and fine particle resin of lower K value have lower fusion temperature and require lower fusion time.

5.3 HYDRODYNAMIC ANALYSIS OF COATING

The process of fluid coating is essentially a fluid in motion, and usual unit operation parameters can be applied. An overall macroscopic force balance is obtained by the application of the principle of the conservation of momentum to an elemental volume in the fluid. The force acting on the volume is given by rate of change of the momentum of the fluid surrounding it at any instant, i.e., flux of momentum summed over the entire control surface and the rate of change of momentum within the volume.

The net force F_x, acting in say x direction on the fluid element moving with the velocity of the fluid is a sum of (1) force due to the weight of the volume element (body force) F_{xB} and (2) force due to the stresses acting on it along x direction, F_{xS} [Equation (3)].

$$F_x = F_{xB} + F_{xS} \tag{3}$$

For an element of a differential mass $\rho dx\, dy\, dz$, Equation (3) becomes

$$\rho dx\, dy\, dz(du_x/dt) = \rho dx\, dy\, dz\, g\cos\beta$$
$$+ (\partial\tau_{xx}/\partial_x + \partial\tau_{yx}/\partial_y + \partial\tau_{zx}/\partial_z)dx\, dy\, dz \quad (4)$$

which, on rearranging, reduces to Equation (5),

$$\rho du_x/dt = g\cos\beta + (\partial\tau_{xx}/\partial_x + \partial\tau_{yx}/\partial_y + \partial\tau_{zx}/\partial_z) \quad (5)$$

where

$u_x =$ velocity of the fluid element in x direction
$\rho =$ density of the fluid element
$g =$ acceleration due to gravity
$\beta =$ angle the fluid element makes with the x axis
$t =$ time
$\tau_{xx}, \tau_{yx}, \tau_{zx} =$ components of stress acting in x direction

By substituting the values of stress and rearranging, we get the Navier Stokes equation [Equation (6)]. This is the equation of motion of the elemental volume in x direction and is used for the analysis of the hydrodynamics of coating [7].

$$u_x\partial u_x/\partial x + u_y\partial u_x/\partial y + u_z\partial u_x/\partial z + \partial u_x/\partial t$$
$$= g\cos\beta - 1/\rho\ \partial p/\partial x + \eta/\rho(\partial^2 u_x/\partial x^2 + \partial^2 u_x/\partial y^2 + \partial^2 u_x/\partial z^2)$$
$$+ 1/3\ \eta/\rho\ \partial/\partial x(\partial u_x/\partial x + \partial u_y/\partial y + \partial u_z/\partial z) \quad (6)$$

where u_x, u_y, u_z are velocities of the fluid element in x, y, and z directions; $p =$ pressure generated due to the movement of fluid element in x direction; and $\eta =$ viscosity of the fluid.

In a blade coating, the substrate to be coated moves under tension, below a blade. The coating fluid is either poured manually or pumped at the blade nip. The gap between the blade and substrate controls the coating thickness. A study of the hydrodynamics of blade coating has been done by Hwang using the Navier Stokes equation [8]. In a simple analysis, the coated film thickness is a function of five variables only. These are the gap between blade and the web, web speed, viscosity, density, and surface tension of the coating fluid. The motion of the liquid is considered steady and unidimensional in nature, and the liquid is incompressible. For motion along x axis, with y axis perpendicular to it, Equation (6) reduces to

$$\partial p/\partial x = \eta\ \partial^2 u_x/\partial y^2 + \rho g \quad (7)$$
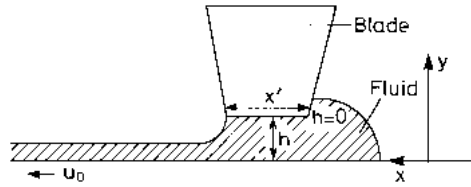
Figure 5.9 Blade coating: h is gap between blade and web; x' is blade width; at the blade $h = 0$, $u = 0$; at the web $y = h$ and $u = u_0$.

The boundary conditions taken are: at the blade, the fluid is motionless, i.e., $u = 0$, the fluid velocity at the web is the same as that of the web velocity, $u = u_0$ at $y = h$. The gap between the blade and the web is h and is small compared to the blade width x' (Figure 5.9).

The coater is more like a channel, and a parallel plane flow model is used. For a Newtonian fluid, by integrating equation [Equation (7)] twice and applying the above boundary conditions, the velocity is obtained as

$$u = u_0 y/h + 1/2\eta \, (dp/dx - \rho g)(y^2 - hy) \tag{8}$$

The total quantity of fluid that passes through the gap per unit length, per unit time, Q is obtained by integrating the above velocity [Equation (8)] between the limits $y = 0$, $u = 0$ and $y = h$, $u = u_0$.

$$Q = \int_0^h u \, dy = u_0 h/2 - (1/12\,\eta)\,(dp/dx - \rho g)h^3 \tag{9}$$

The coating thickness, W, can be obtained by dividing Q by web velocity u_0.

$$W = h/2 - (1/12\eta u_0)(dp/dx - \rho g)h^3 \tag{10}$$

The author has related the pressure gradient to the surface tension of the coating fluid considering the force balance across a parabolic meniscus at the exit of the blade gap and obtained the relation as

$$dp/dx = -\sigma/2h^2 \tag{11}$$

where σ is the surface tension of the fluid.

Thus, the coating thickness obtained in terms of the five paramaters mentioned above is obtained by combining Equations (10) and (11).

$$W = h/2 + (1/12\eta)(\sigma/2h^2 + \rho g)h^3/u_0 \tag{12}$$

The conclusion of the analysis is that for blade coating, the coating thickness is half the coating gap, together with a small term that relates directly to surface tension and gap and inversely to the viscosity and web speed. Hwang has found

a good correlation between the coating thickness obtained from experiments and the thickness calculated from Equation (12).

Middleman has carried out analysis of roll, blade, and dip coating for Newtonian and non-Newtonian fluids [9]. These models have, however, not considered the nature of the textile web, which has an important bearing on the coating thickness.

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Fabrics for Foul Weather Protection

6.1 CLOTHING COMFORT

A person feels comfortable in a particular climatic condition if his energy production and energy exchange with the environment are evenly balanced, so that heating or cooling of the body is within tolerable limits. A core body temperature of approximately 37°C is required by an individual for his well-being. The body maintains this temperature at different work rates and climatic conditions by changing blood flow and evaporating perspiration from the skin. Because the body has a limited ability to cope with the climate, clothing is consciously selected and adjusted to secure comfort and protection in an adverse environment. There are two aspects of clothing comfort, skin sensorial, i.e., mechanical contact with textile surface, and thermophysiological. The thermophysiological aspect considers the heat balance of the microclimate created between the skin, air, and clothing, with the external climate and the metabolic heat generated. The routes of heat loss from the body are conduction, radiation, and evaporation. The environmental factors responsible for this heat flow are (1) temperature difference, (2) air movement, (3) relative humidity, and (4) radiant heat from the sun or other sources of thermal radiation. Clothing interacts with the environment by [1–3]

- thermal resistance—insulation
- resistance to evaporation
- resistance to wind penetration
- structural features, such as, thickness of clothing, clothing weight, clothing surface area, etc.

The total heat transfer through the clothing of the body with the environment, considering the thermal and evaporation resistance of the clothing, has been

$$\frac{T_s - T_a}{I} + \frac{P_s - P_a}{E} \qquad (1)$$

where H = total heat transfer, $T_s - T_a$ = temperature difference between skin and ambient, $p_s - p_a$ = water vapor pressure difference between skin and ambient, I = insulation of the clothing, and E = evaporation resistance of the clothing.

The thermal and water vapor resistance are additive, and clothing assemblies can be evaluated by adding the individual values and the intervening air layers between them. A person wearing light clothing engaged in light activity in a temperate environment loses about 75% of his metabolic heat by transfer of dry heat. The rest is lost by evaporaton of water from the skin and lungs. As the activity level rises, perspiration production increases, and the proportion of heat loss by evaporation increases. Perspiring is the main thermoregulatory process at a high level of work rates. If the clothing is impermeable, evaporative cooling cannot occur, and in a hot and humid climate, heat exhaustion may occur. Insensible perspiration is converted into liquid perspiration below the dew point. In cold climates, wet, perspiration-soaked clothing loses much of its insulation value, leading to hypothermia. Moreover, wetting of garments by perspiration gives a clinging appearance and is a burden on motion. Such a situation is acute in garments with fabrics having compact coated PVC, PU, or rubbers. Typical perspiration values for various activities are given in Table 6.1.

In extremes of climatic conditions, particularly cold weather, apart from proper thermal insulation, the clothing should be windproof so that cold wind does not enter into the space between the skin and the clothing, dissipating the warm air in the vicinity of the skin. Protection against rain, sleet, or snow is also required, as penetration of moisture in the skin gives a clammy feeling, and its evaporation takes away body heat of the wearer, creating conditions of freezing. In sum, cold weather clothing, besides insulating, should ideally have three main features, it should be water vapor permeable, windproof and waterproof. Two types of fabrics are in use for foul weather clothing. They are

TABLE 6.1. Typical Perspiration Levels for Various Activities [4].*

Activity Level	Heat Produced (watts)	Perspiration Rate (ml/h)
Sleeping (cool dry)	60–80	15–30
Walking 5 km/h	280–350	200–500
Hard physical work (hot humid)	580–1045	400–1000
Max. sweat rate (tolerated for short time)	810–1160	1600

*Adapted with permission from G. R. Lomax Textiles, no. 4 1991, © Shirley Institute U.K. [4]. Conversion factor 1.16 W/m^{2}h = 1 kcal/m^{2}h.

impermeable coated fabrics and the breathable fabrics. An impermeable fabric is both wind- and waterproof but not water vapor permeable. A breathable fabric, on the other hand, meets all of the features of foul weather clothing and is water vapor permeable.

6.2 IMPERMEABLE COATING

These fabrics function by blocking the pores of the textile material by a compact polymeric coating that forms a physical barrier to wind and water. Even though these fabrics are not breathable, they are comparatively inexpensive, and are widely used for rainwear and foul weather clothing.

Various materials are available for rainwear offering different levels of protection. Generally, single- or double-textured rubberized fabrics are used. A single-textured fabric consists of a coating material of natural or synthetic rubber coated on one side of a base fabric of cotton, viscose, or nylon fabric. A typical fabric has a weight of 250 g/m^2, with a proofing content of 140 g/m^2. A double-textured fabric has a rubber coating in between two layers of cotton or viscose fabric. Such a fabric is heavy (400–575 g/m^2) but gives excellent protection against rain [5]. By providing proper ventilation in rainwear, it is possible to transfer condensed sweat outside, minimizing discomfort to the wearer.

Clothing for protection against extreme cold consists of two parts: an inner insulation material and an outer fabric layer to preserve the insulation from wind or rain. The outer layers are usually PU-, PVC-, or neoprene-coated fabrics. PVC- and neoprene-coated fabrics have some limitations in use in extreme cold conditions. PVC-coated fabrics have poor low temperature properties and are affected by solvents. Neoprene-coated fabrics, on the other hand, are rather heavy. Polyurethane-coated nylon is the fabric of choice because of its light weight, thin coating, and excellent low temperature flexibility [6,7]. Some popular PU-coated nylon fabrics have weights ranging from 100–250 g/m^2 with a PU coating between 10–30 g/m^2. These fabrics are also used by the military for various items of cold weather clothing, such as jackets, trousers, caps, and gaiters. Figure 6.1 shows cold weather clothing for the services made of PU-coated nylon fabric.

6.3 BREATHABLE FABRICS

The main features of a breathable fabric are depicted in Figure 6.2.

Extensive research is being done worldwide to develop fabrics that provide comfort to the wearer, while offering protection against foul weather. Although poromerics for shoe uppers were developed in the 1960s, the search for lightweight breathable fabric for apparel got a fillip from the development

Figure 6.1 Cold weather clothing ensemble.

of the versatile GORE-TEX® laminates in 1976. Numerous brand products have been developed and patents filed ever since. In the ensuing sections, an overview of the technology of these fabrics is discussed.

6.3.1 USES AND REQUIREMENTS

These fabrics find extensive use in sports and leisure wear. Army personnel on outdoor duty are exposed to foul weather for days or weeks, especially when on patrol duty. Breathable fabrics have great application for protective clothing for the services. Another emerging field for breathable fabric is protective apparel for healthcare workers, against body fluids and bacterial and viral infections. ASTM has adopted two new specifications to evaluate the barrier effectiveness of such clothing. They are ASTM F 1670-97 and F 1671-97a [8].
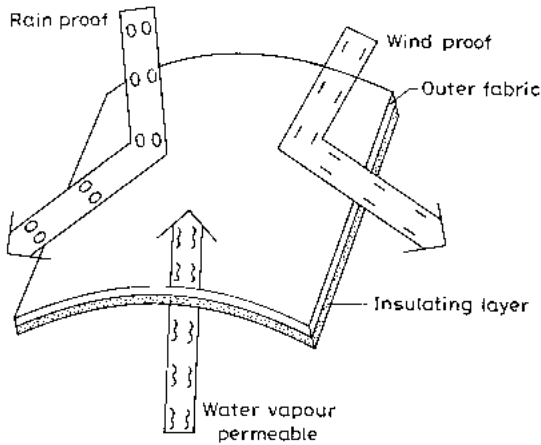
Figure 6.2 Main features of a breathable fabric.

In quantitative terms, a breathable fabric should have the following attributes [4,9,10]:

(1) Water vapor permeability—min. 5000 g/m^2/24 h

(2) Waterproofness—min. 130 cm. hydrostatic pressure

(3) Windproofness—less than 1.5 ml/cm^2/sec at 1 mbar; measured by air permeability

Other properties required are as follows:

(1) Durability: tear, tensile, and peel strength; flex and abrasion resistance

(2) Launderability

(3) Tape sealability

6.3.2 DESIGNING A BREATHABLE FABRIC

A discusssion of the mechanism of water vapor permeability and water repellency is useful in understanding the principle of designing breathable fabric. Water vapor transport through a fabric/clothing system may occur due to diffusion (driven by vapor concentration gradients) and convection (driven by pressure difference). A discussion of the mechanism of diffusion of water vapor through fabric and membranes is given below.

6.3.2.1 Diffusion of Water Vapor through a Fabric

This occurs by the following ways [1,11].

(1) Interyarn space: the diffusion of water vapor occurs through these spaces due to the water vapor pressure gradient across the two sides of the fabric by molecular diffusion.

(2) Interfiber space: the contribution of diffusion through a fiber bundle is much less than the void between the yarns. However, liquid water can permeate the fabric by the wicking action of capillaries of the fiber bundle and subsequent evaporation at the outer surface.

(3) Intrafiber diffusion: in this process, water vapor is absorbed by the fiber and desorbed at the outer surface. The process is dependent on the nature of the fiber, i.e., hydrophilic or hydrophobic, and is related to moisture regain. It is obvious that diffusion of air and water vapor follow different mechanisms.

A detailed study of diffusion of water vapor through fabric was carried out by Whelan et al. [12]. To arrive at a theoretical model, studies were done using perforated metal plates of different thickness and hole diameter. It was found that water vapor resistance is directly related to the thickness of the plate and inversely to the percent pore area. For plates having constant perforated area, the resistance to water vapor diffusion increases linearly with the diameter of the perforation. An empirical formula [Equation (2)] was derived from the experimental data.

$$R = \frac{T}{\beta} + 0.71d\left(\frac{1}{\beta} - \frac{1}{\sqrt{\beta}}\right) \tag{2}$$

where R = water vapor resistance, d = diameter of holes, and β = ratio of void area to total area.

Studies of permeation with fabrics revealed that water vapor resistance is related to the thickness of the fabric, provided fiber volumes are similar. In the case of fabrics, because the air path is irregular, the resistance is related to the percent fiber volume (V_f), rather than percent pore areas found in case of metal plate. An empirical relation derived [Equation (3)] fits the experimental data.

$$R = \frac{100}{100 - V_f}(0.9 + 0.034V_f)T + 0.5 \tag{3}$$

The results indicate that fabric thickness and the air space in the fabric are important parameters for movement of water vapor. The diffusion of water vapor through the pores of a polymer foam structure is related to the thickness and percent pore volume and follows the empirical equation of the metal plate as given in Equation (2) [13].

6.3.2.2 Diffusion through Membranes [14]

Diffusion of gases and vapor through a nonporous membrane occurs through a different route. The gas is initially dissolved in the exposed polymer surface. The concentration built up on the surface is directly proportional to gas pressure, i.e., Henry's law. The gas then migrates to the opposite surface under concentration gradient. The migration of the penetrant can be visualized as a sequence of

steps during which the molecule passes over a potential barrier separating one position from the next. A successful jump requires that a passage of sufficient size be available, and this is dependent on the thermal motion of the polymer chains. The diffusivity is temperature dependent, which follows an Arrhenius-type expression. For large molecules, the size of the penetrant determines the hole size required. Diffusion rates are higher for good solvents of the polymers, rather than for permanent gases, as they diffuse by plasticizing the polymer. The steady state flux J is given by the expression as

$$J = DS(p_1 - p_2)/l \qquad (4)$$

where D = diffusivity, S = solubility coefficient/Henry's law constant, l = thickness of the membrane, p_1 and p_2 are partial pressure of the diffusing gas at two sides of the membrane.

It is common practice to describe the diffusional character of the membrane at equilibrium in terms of a quantity known as permeability. The permeability coefficient is given by $P = DS$. The structure of the polymer has great influence on the permeability. The factors that increase the segmental mobility, enhance the diffusion rate. Thus, permeation is higher at temperatures higher than the glass transition temperature T_g. Increase of structural symmetry and cohesive energy of the polymer decreases the permeation rate. The crystalline domains in the polymer are inaccessible to penetrants and are an impermeable barrier for the diffusion process. The presence of cross-links reduces the segmental mobility, reducing the diffusion rate. The permeation of water vapor varies from polymer to polymer, depending on the presence of certain polar groups (amino, hydroxyl, carboxyl) in the polymer chain that can interact with water molecules, forming reversible, hydrogen bonds. These groups act as stepping stones for transport of water vapor through the polymer. Water vapor initially absorbed acts as a plasticizer, increasing the intermolecular holes, through which nonhydrogen-bonded water molecules can also pass [11].

6.3.2.3 Water Vapor Transport through Textiles

The water vapor diffusion through textiles is determined by diffusion tests such as ASTM-E-96 and ISO-11092. Such tests can lead to erroneous results for high air permeability textile materials, because a very small pressure gradient can produce large convective flows through the porous structure, far outweighing diffusive transport. Therefore, to characterize the potential of a given material to transport water vapor through its structure, it is necessary to carry out both diffusion and air permeability tests.

In recent years, extensive work has been done by Gibson on the water vapor transport properties of textiles [15–18]. He has developed a fully automated test method known as "dynamic moisture permeation cell," that enables

determination of diffusion and convective properties from the same test, of diverse types of materials, such as air-impermeable laminates, very high air-permeable knitted fabrics, woven fabrics, and polymer foams.

In the test method, the sample is placed in a cell. Nitrogen streams consisting of a mixture of dry nitrogen and water-saturated nitrogen are passed over the top and bottom surfaces of the sample. The relative humidities of these streams are varied by controlling the proportion of saturated and dry components. By knowing the temperature and water vapor concentration of nitrogen flows entering and leaving the cell, the flux of water vapor diffusing through the test sample is measured. It is also possible to vary the temperature of the cell and pressure drop across the sample. With this test method, Gibson has been able to measure the following parameters of various materials:

(1) Combined convection and diffusion: these studies are done by varying the pressure drop, across the sample. With a specified pressure drop, transport takes place both by diffusion and by convection. If there is no pressure drop across the sample, the transport is only by diffusion. For convective transport of water vapor, Gibson has used Darcy's Law [Equation (5)] for calculation of permeability.

$$v = (-k_D \Delta p)/\mu \Delta x \qquad (5)$$

where v = apparent gas flow, k_D = permeability constant, Δp = pressure difference across sample, and Δx = thickness. The results on various types of fabrics clearly show that for high air permeability textiles, convective water transport dominates.

(2) Humidity-dependent air permeability: this parameter is important for porous hygroscopic materials that often exhibit humidity-dependent air permeability due to the swelling of fiber as it takes up water from the environment.

(3) Concentration-dependent diffusion: vapor transport across nonporous hygroscopic polymer membrane is often highly dependent on the amount of water present in the polymer. Studies on several such membranes confirm the same.

(4) Temperature-dependent diffusion studies: for hydrophilic films and membranes, water vapor transport is significantly affected by temperature. The water vapor transport is lower at lower temperatures. This effect is important for the ability of cold weather clothing to dissipate water vapor during active wear.

(5) Transient sorption and desorption: The method can be used to conduct testing of materials under nonsteady state conditions, such as change in relative humidity, temperature, or pressure difference across the sample. In these transient situations, the variable properties of the material become very important, along with factors like sorption rate at which fiber takes up and releases water.

6.3.2.4 Repellency [19]

A liquid spreads on a solid surface when its surface energy (γ_{SA}) is higher than that of the liquid (γ_{LA}). The spreading process lowers the free energy. The spreading coefficient is given by

$$S = \gamma_{SA} - (\gamma_{LA} + \gamma_{SL}) \tag{6}$$

where γ_{SA}, γ_{LA} are the surface tension of the solid and the liquid in contact with air, and γ_{SL} is the interfacial tension. If the spreading coefficient is positive, spreading occurs, and the contact angle is $<90°$. For low energy solids, the spreading coefficient is negative, the liquid is repelled, and the contact angle is $>90°$. Critical surface tension of a solid surface is equal to the surface tension of a liquid that exhibits zero contact angle on the solid. It is a measure of the repellent property of the solid surface. A repellent functions by lowering the critical surface tension of the solid. For instance, a fluorochemical emulsion lowers the critical surface tension of a nylon fabric to <10 dyne /cm, as such, it can repel water and hydrocarbon oils having surface tension 72 dynes/cm and $\sim$20 dynes/cm respectively.

A textile surface is not smooth, liquid can migrate into its pores, even though the contact angle on the surface is $> 0°$. The transport of a liquid through a capillary is given by

$$\Delta P = 2\gamma_{LA} \cos / r \tag{7}$$

where ΔP is the pressure required to force the liquid into the capillary, and r is the pore radius.

Penetration of water into the capillaries of the textile can be prevented by reducing the size of the pores and increasing the contact angle through a water repellent treatment. Water repellent finishes are of various types, viz., pyridinium compounds, wax and wax emulsions, silicones, fluorochemicals, etc. Several commercial finishes are based on molecules containing polar and nonpolar moieties. The polar ends of the molecule attach to the textile, whereas the nonpolar part sticking outwards repels the water. Silicones are available in solution or aqueous emulsion and are commonly a blend of polymethyl hydrogen siloxanes and polydimethyl siloxanes. A variety of fluorochemicals are used as repellents, and several brand products exist. Copolymer of fluoro alkyl acrylates and methacrylates are primarily used for textiles. Fluorochemicals have an added advantage in that they are oil repellent as well.

As mentioned earlier, a compact coated fabric is wind- and waterproof but impermeable to water vapor. The contradictory requirements of water vapor permeability and waterproofness are achieved, in a breathable fabric, by specifically designing the coated fabric to have interconnecting pores of 0.2 to 10 μm. These pores permit much smaller water molecules $\sim$0.004 μm to permeate from

inside of the clothing and at the same time prevent ingress of much larger water droplets ~100 μm (for a fine drizzle) to the body. Because the size of water molecules are of the same order as those of the constituents of air, these microporous coatings/films are permeable to air. However, their permeability is so low that they impart windproofness to the fabric. Another concept that has emerged recently are hydrophilic coatings. These are compact coatings that transport water vapor by permeation through polymeric membranes as discussed earlier. Breathable fabric can be engineered from closely woven uncoated textiles, known as ventile fabrics in common parlance.

6.3.3 TYPES OF BREATHABLE FABRICS

Breathable fabrics can be categorized into four main types:

(1) Closely woven fabrics with water repellent treatment
(2) Microporous film laminates and coatings
(3) Hydrophilic film laminates and coatings
(4) A combination of microporous coating with a hydrophilic top coat

6.3.3.1 Closely Woven Fabrics

The earliest of the waterproof, water vapor permeable fabrics were the Ventile fabrics developed by the Shirley Institute U.K. [3,11] during World War II. The development was an outcome of an urgent need to protect the survivors of air crew forced to ditch in the cold North Seas from hypothermia. Immersion suits of Ventile fabric are still in use in the U.K. These fabrics are made from long staple Egyptian cotton, using low twist mercerized yarns, woven in a dense oxford construction. The fabric weight ranges from 170 to 295 g/m^2 for different uses. The interyarn pores of the fabric in dry state are about 10 μm. The air permeability is low, but the interyarn spaces and hydrophilic nature of the fiber allows adequate water vapor permeability. On wetting the fabric, by rain or immersion in water, the cotton yarn swells, reducing the pore size to 3–4 μm. The swollen fabric in combination with repellent finish, prevents further penetration of water by rain or seawater. The choice of repellent treatment is critical, as it should still allow absorption of water by cotton yarn to swell and constrict the interyarn pores. The waterproofness of these fabrics is low and can stand only moderate hydrostatic pressure.

A new generation of high density fabrics made from microfibers of 0.05 to 1 d polyester, polyamide, viscose, or acrylics has recently emerged as breathable fabric with improved functional properties. The microfibers are obtained by melt spinning of two incompatible polymers into a single fine fiber, known as a bicomponent fiber [20,21]. The cross section of the fiber may be either side by side, core sheath, or matrix fibril type. One of the polymers is then separated by dissolving in a specific solvent, leaving behind microfiber. The yarn is woven

Microfiber	Fabric	Supplier
1. Trevira finesse	Clima guard	Hoechst
2. Tactel micro	Micro spirit	I.C.I.
3. Dyna bright	H_2 OFF	Toray
4. Supplex	—	Dupont

into various dense fabric constructions like taffeta, twill, or oxford, and given a repellent finish of silicones or fluorochemicals. These fabrics have better water repellency than the cotton ventile fabrics and have very soft handle. Some of the important microfibers and fabrics are listed in Table 6.2 [22].

6.3.3.2 Microporous Coatings and Laminates

These are porous membranes laminated to a fabric or porous coating. The pore size ranges from 0.1 to 50 μm. The most widely used are polyurethanes, poytetrafluoroethylenes, acrylics, and polyamino acids. Among these, polyurethane is the most popular polymer because of toughness, flexibility of the film, and capability of tailor making the property of the film to suit the end use requirement. Various methods of generating microporosity have been reported in the literature, and these are discussed below [3].

6.3.3.2.1 Wet Coagulation Process

Microporous polyurethane coating by direct or transfer process has been discussed in detail under poromerics in synthetic leather (Chapter 7). A film, on the other hand, is obtained by casting, using the transfer coating process on a release paper, which is subsequently adhered to the fabric to make laminates. Some commercial products in this class are Cyclone (Carrington), Entrant (Toray), Keelatex, etc. Incorporation of water-soluble salts in the PU coating solution has also been described (Chapter 7). Microporosity is created by leaching the salts on treatment of the film with water. Products in this class are Porvair, Porelle, Permair, etc. [3,11]. Various improvements in the process have been reported in the literature. Addition of a water-repellent agent and nonionic surfactants in the coating solution, imparts water repellency to the pores, resulting in better waterproofness of the coated fabric. A water repellent treatment of the coated layer further improves the waterproofness [23]. A much higher water vapor permeability and waterproofness have been reported by Furuta et al. [24] by incorporation of about 1% nonporous inorganic filler, e.g., silica (Aerosil) or magnesium oxide of particle size <0.1 μm in the polyurethane resin. The coating obtained on wet coagulation shows ultrafine pores of <1 μm, in addition to a honeycomb skin core structure of 1–20 μm pores. The formation

of these micropores has been explained as due to the subtle difference in the rates of coagulation at the resin particle interface. The enhanced water vapor permeability (>6000 g/m^2/24 h) and water pressure resistance (>0.6 kg/cm^2) are attributed to the formation of these additional micropores.

The phase separation method for forming microporous coating has been developed by UCB Chemicals, Belgium, for their product Ucecoat 2000 [11]. In this process, polyurethane is dissolved in a solvent mixture of methyl ethyl ketone, toluene, and water, having 15–20% solids and coated on the fabric. The low boiling solvent evaporates leading to precipitation of polyurethane in the nonsolvent. The nonsolvent is then removed by drying, to yield a microporous coated fabric. This process has an advantage over the wet coagulation process in that immersion and washing baths are not required. The number of pores and their size in microporous coating obtained by the wet coagulation process are $\sim 10^6$ pores/cm^2 and 3 to 40 μm, respectively [9].

A combination of polyamino acid (poly-γ-methyl-L-glutamate) and polyurethane resin in the ratio of 60:40 to 40:60 has been used by Unitika Co., Japan, for production of their Exceltech brand of microporous coated fabric by wet coagulation process [25]. An optimum quantity of surfactant is added for improved water vapor permeability by controlling the porosity. The base fabric used is 70 d taffeta. A scanning electron micrograph shows 10^7 pores/cm^2 in the product. Because PAU is hydrophilic in nature, Exceltech has higher moisture permeability, 8000–12,000 g/m^2/24 h, compared to 4000–6000 g/m^2/24 h for microporous PU coating. The other properties are water entry pressure of 200 cm and air permeability of <0.07 ml/cm^2/sec which are comparable to microporous PU coating.

Microporous polyamide coating by wet coagualation process has also been reported [26]. The process consists of application of an hydrochloric acid solution (5–7.5 N) of polyamide containing 20–30% solids on a textile substrate by knife coating. The coated fabric is immediately dipped into 5–10 N caustic soda solution bath, to coagulate the polyamide. The excess caustic soda solution is then squeezed out from the coated fabric by passage through rolls, washed with water, and excess water is removed. To prevent damage of the fabric by the acid solution, the neutralization process is carried out quickly. The coating is about 20 μm thick, containing two distintict types of pores. The outer layer consists of small ovoid pores of about 0.02 μm due to instant coagulation, while the inner layer has large elongated pores with average diameter of ~ 1 μm.

6.3.3.2.2 Microporous Polyurethane from Aqueous Dispersions

The process consists of impregnation of a textile web with aqueous dispersions of polyurethane containing solubility enhancing ionizable groups and coagulating the polymer by acid or alkali solution, depending on the charge. Such methods are environment friendly as no solvents are used, but the coated

film has poor adhesion and durability. Dahmen et al. [27] have developed a method that gives much better adhesion and durability of the coating. The textile is coated with aqueous dispersions of polyurethane having ionic groups of opposite charge, i.e., both anionic and cationic dispersions. Commercially available dispersions are taken, and their viscosity is adjusted by the addition of nonionic thickeners to render them suitable for knife coating. Anionic dispersion is applied as the first coat on the textile, followed by a second coat of cationic dispersion in wet condition, without any intermediate drying or vice versa. The weight ratios of the two dispersions are so adjusted that the anionic and cationic groups are stoichiometrically equivalent. The coated fabric is then air dried at about $140°C$, given a flourocarbon treatment, and calendered lightly. The process has an advantage in that existing solvent-based equipment can be used and the time-consuming rinsing process is avoided. The fabric is waterproof and water vapor permeable (water vapor permeability ~ 2400 g/m^2/24 h).

6.3.3.2.3 Microporous polytetrafluoroethylene [3,22]

Thin films of 5–15 μm PTFE are extruded through a slit die and biaxially stretched. This results in the formation of microtears of pore size 0.1–1 μm and $\sim 10^9$ pores/cm^2 in the film. The film is mechanically weak and therefore laminated to textile fabric by adhesives. The film is hydrophobic in nature, and its water repellency is far superior. GORE-TEX® (W. L. Gore, U.S.) brand product is the most widely used and versatile laminate of this type. The process [28] consists of extruding PTFE paste-dispersion in mineral spirit. The extrudate is dried to form a film of unsintered PTFE. The film is then clamped and stretched. The stretching can be done in one direction (uniaxial stretching) or in two directions, right angles to each other (biaxial stretching). The stretching is done at an elevated temperature, below the melting point of the polymer, at a high rate. While still stretched, the film is heated slightly above the melting point of the polymer and cooled rapidly in stretched condition. The process gives a film containing porous microstructure, with a considerable increase in strength. The microstructure of the uniaxially stretched film consists of nodes elongated at right angles in the direction of the stretch. These nodes are interconnected by fibrils that are oriented parallel to the direction of the stretch. Typically, the size of the nodes vary from 50–400 μm. The fibrils have widths of about 0.1 μm and lengths ranging from 5–500 μm. The development of porosity occurs due to void formation between nodes and fibrils. When the films are biaxially stretched, similar fibril formation occurs in the other direction with the production of cobweb-like or cross-linked configurations with an increase in strength. Porosity also increases as the voids between the nodes and fibrils become more numerous and larger in size. The factors affecting the porosity and strength of the film are as follows:
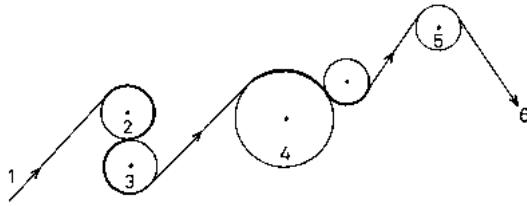
Figure 6.3 Production of stretched PTFE film: (1) unsintered film, (2, 3) heated calender rolls, (4) heated roll for heat treatment, and (5) water-cooled roll.

(1) The polymer should have high crystallinity, preferably >98%.

(2) The temperature and rate of stretching: higher temperature and higher rate of stretch lead to a more homogeneous structure with smaller, closely spaced nodes, interconnected with a greater number of fibrils, increasing the strength of the polymer matrix. Typically, stretching is done between 200–300°C.

(3) The temperature and duration of heat treatment: during heat treatment, which is done above the melting point of the polymer (350–370°C), an increase in amorphous content of the polymer occurs. The amorphous region reinforces the crystalline region, enhancing the strength without substantially altering the microstructure.

Continuous length of the porous film can be obtained by passing the unsintered film through the nip of heated calender rolls moving at different speeds. The film is stretched in the gap of the rolls. The extent and rate of stretch depends on the friction ratio and the gap between rolls. The stretched film coming out of the calender is passed on a heated roll for heat treatment at ~370°C and then over a water-cooled roll for cooling (Figure 6.3). Nitto Elec Ind., Japan, has come out with a similar product known as Microtex.

Figure 6.4 shows an extreme cold weather suit with an outer GORE-TEX® laminate and insulation layer.

6.3.3.2.4 UV/E Beam Polymerized Membranes [29,30]

A rapid method of making microporous films has been developed by Gelman Science, U.S., and patented in 1984 as the Sunbeam process. Monomers and oligomers are cross-linked under a radiation source, UV/E beam and cured in milliseconds. The polymer is based on acrylates. The pores are of the order of 0.2 micron, and the film can be very thin, of the order of a few angstroms. The technology permits production at a rapid rate of about 350 ft/min in 1 m width and is suitable for making films as well as coating. The film is highly repellent and is not wetted by water and most chemicals, only solvents with a S.T. < 18.5 dynes/cm wet the film. The water vapor permeability of these films are ~1100 g/m²/24 h, and the films can be dry cleaned. These films are

Figure 6.4 GORE-TEX® suit for cold weather.

marketed as "Repel" and can be laminated on nonwovens for making disposable protective clothings for a variety of applications such as clean room garments, medical gowns, chemical splash suits, etc.

6.3.3.2.5 Perforation in Compact Coated Fabric [9,11]

A method has been developed to create micropores of the order of 1 million pores/m^2 by passage of nonporous coated fabric between two electrodes, generating high voltage. The electron beam creates pores through the coating without damaging the fabric. This method gives smooth straight through perforations. The functional properties are therefore poor.

6.3.3.2.6 Extraction of Soluble Component from a Polymer Mixture

A process for making breathable fabric with a microporous polyethylene-tetraflouroethylene (ETFE) layer has been reported by Kafchinski et al. [31]. The process consists of making a dope containing a suspension of ETFE ~0.5–1 μm in an extractable polymeric binder. The dope is cast onto a release paper and dried. The film is next calendered above the flow temperature of ETFE, i.e., about 300°C, and laminated to a fabric substrate using heated calender rolls. The binder is then extracted by a suitable solvent which is a nonsolvent for ETFE and does not damage the fabric. This leaves behind a microporous ETFE layer on the fabric. Various extractable polymeric binders can be used such as polycarbonate, polymethyl methacrylate, etc. However, water-soluble polymer, such as polyethyl oxazoline, cellulose acetate, etc., are preferred because they can be extracted by immersion in water. The fabrics preferred are polybenzimidazole, Kevlar,[®] Nomex[®], etc. The resultant laminated fabric is flame resistant as well as breathable. The microporous film can be bonded to the fabric by adhesive as well.

In another process, fabric is coated with an aqueous-based composition containing a film-forming polymer and a suitable proportion of a water-soluble polymer. The coated film is dipped in an aqueous solution of an enzyme, which degrades the water-soluble polymer. Washing of the degradation product leaves behind a microporous coating. The film-forming compositions are emulsions of acrylics, silicones, polyurethanes, or their mixtures. Water-soluble polymers include starch, carboxymethyl cellulose, sodium alginate, etc. The enzymes used are specific for the water-soluble polymers, e.g., for starch it is amylase, and for cellulose derivatives cellulase is used. The water vapor permeability obtained is of the order of 4500 g/m^2/24 h, which is substantially higher than that obtained on washing the coated film with plain water [32].

6.3.3.3 Hydrophilic Coatings and Films

The mechanism of permeation of water vapor through a nonporous polymer film has been discussed. None of the conventional coatings like PVC, PU, and rubbers have the polar groups required for activating the hydrophilic mechanism for the transport of water. Although a number of hydrophilic polymers, like polyvinyl alcohol and polyethylene oxide are available, they are highly sensitive to water and would either dissolve completely in contact with rain or swell so heavily that the flex and abrasion resistance would be very poor. A proper hydrophilic polymer for coating should, therefore, have adequate swelling to allow transmission of water vapor and at the same time retain suitable film strength. Cellulosic derivatives, with a high percentage of crystallinity, lead to stiff coatings. To achieve the proper functional property of the film, an optimization of hydrophilic-hydrophobic balance is required. The approaches available are the use of polymer blends, incorporation of pendant hydrophilic

groups, or the use of segmented copolymers [3]. Out of these possibilities, use of segmented copolymer, incorporating polyethylene oxide into a hydrophobic polymer chain has been found successful. The polyethylene oxide segment has a low binding energy for water, permitting rapid diffusion of water vapor, and it is flexible, so that the end product has soft handle [11,33].

6.3.3.3.1 Hydrophilic Polyurethanes

These are segmented copolymers of polyester or polyether urethanes with polyethylene oxide. The hydrophilicity can be varied either by increasing the overall hydrophilic content or by changing the length of the hydrophilic segments. A process for their synthesis has been described in a patent to Shirley Institute, U.K. [34]. A prepolymer is prepared by reacting polyethylene glycol of molecular weight varying from 1000–2000, with an excess of diisocyanate (preferably 4,4-diisocyanato-dicyclohexyl methane). The prepolymer is chain extended by a low molecular weight diol. Cross-linking can be done using a tri-isocyanate. The polyethylene glycol content is maintained within 25–45 wt.% for optimum properties. An example of this product is Witcoflex [11,33], a series of coatings manufactured by Baxenden Chemicals, U.K. There are two products, viz., Staycool and Super dry. The coating formulations resemble two-component polyurethane systems. The coating can be applied by direct or by transfer coating in MEK/DMF solution. The tie coat contains isocyanate cross-linkers. Bion II film of Toyo also falls in this category [22]. Krishnan [8,35] has reported the synthesis of hydrophilic-polyurethane film based on polyurethane and dimethyl siloxane. Polyalkylene ether glycol (C atoms in the alkylene group at least 3) and polyoxyethylene glycol are reacted with a stoichiometric excess of diisocyanate and chain extended by diamine or diols. In a similar manner, polyalkylene ether glycol, polydimethyl siloxane diol, and polyethylene glycol are reacted with an excess of diisocyanate and chain extended. The two systems are then blended and cross-linked with isocyanates. By controlling the molar ratio of the polyols, a proper combination of hydrophilicity and hydrophobicity is achieved by this process. The product is made by Raffi and Swanson and is marketed as Comfortex. The system is suitable for direct coating as well as for film lamination. The laminate can be used for medical protective clothing. A similar process has been described by Ward et. al. [36]. The soft segment of a block copolymer of polyether urethane consists of a hydrophobic component obtained from either polydimethyl siloxane or polytetramethylene oxide and a hydrophilic part provided by polyethylene oxide. This polymer is mixed with a compatible base polymer, preferably polyether urethane urea. A solution of the two polymers in dimethyl acetamide is suitable for coating or for casting as a film. Incorporation of 0.5% LiBr in the coating solution enhances the water vapor permeability. Another approach of preparing hydrohilic PU is by incorporating polyamino acid in polyester polyurethane. The higher the PAU content, the higher the water vapor permeability, but the lower the elasticity of the film

[37]. Film obtained by transfer coating is laminated on fabric. Excepor U of Mitsubishi is a product of this type [22].

Desai and Athawale [38] prepared a series of PU coating compositions of varying hydrophilicity by incorporating polyethylene glycol of different molecular weight in castor-oil-based polyester polyurethane. These compositions were coated on nylon fabric, and their properties were studied. The water vapor permeability showed an increasing trend with an increase of molecular weight of PEG. In washfastness test, the weight loss of polymer increased with an increase of molecular weight of PEG, indicating that an increase in hydrophilic segments lowers its adhesive strength. In a similar study on cast films by Hayashi et al. [39], it was found that moisture permeability increases linearly with both the concentration of polyethylene glycol and its molecular weight. Setting of the T_g of the polymer at ambient increases its moisture permeability above room temperature but lowers the same at cold temperature. Such shape memory polymers may find applications in foul weather clothing.

6.3.3.3.2 Hydrophilic Polyester

Sympatex membrane devloped by Akzo/Enka Germany [40,41] is a hydrophilic polyester into which polyether groups have been incorporated to impart hydrophilicity to the membrane. Commercial films, 10–25 μm thick, are produced by extrusion process. The membrane is colorless and opaque. It has a water vapor permeability of over 2500 g/m^2/24 h, accompanied by about 5% swelling. It is watertight up to 1000 cm. The film is laminated to the fabric.

Hoeschele and Ostapchenko [42] have synthesized breathable waterproof film of thermoplastic hydrophilic polyetherimide ester elastomers. The elastomeric film is made by the reaction of a diol with a dicarboxylic acid and a polyoxyalkylene imide diacid. The preferred diol and dicarboxylic acid are 1,4-butane diol and terephthalic acid. The polyoxyalkelene imide diacid is obtained by the imidization of trimellitic or pyromellitic acid with polyoxyalkylene diamine. The diamine has molecular weight between 900–4000 and is obtained from polyethylene glycol and polypropylene glycol. The polyoxyalkylene imide diacid can be depicted by the general formula
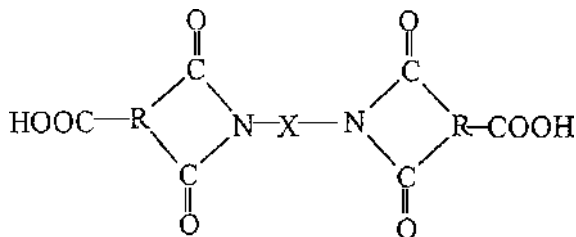
Polyoxyalkylene imide diacid: X = polyether chain, R = acid residue

A large stoichiometric excess of diol is reacted with polyoxyalkylene imide diacid and a dicarboxylic acid, in the weight ratio of 0.8 to 3.0. The resulting

polyetherimide ester elastomer containing 25–60 wt.% of ethylene oxide has optimum properties. The elastomer is compounded with UV stabilizers and fillers and extruded as film. The film is laminated to a textile substrate. Water vapor permeability of 3500 gm/m^2/24 h as per ASTM E 96-66 has been claimed.

Hydrophilic films and coatings have certain advantages over microporous materials [11,33]. In the wet coagulation method, coagulation baths, washing lines, and DMF recovery plants are required. Moreover, precise control over the coating operation is required to generate a consistent, uniform pore structure, preferably below 3 μm for optimum balance of breathability and waterproofness. The entrapment of residues of detergent and sweat into the pores alters the surface property considerably and reduces the water penetration pressure. Hydrophilic coatings, on the other hand, can be applied by conventional solvent coating equipment, being nonporous, they do not lose their properties on cleaning. A hydrophilic film is sometimes applied on microporous films to upgrade the water resistance. Thintech of 3M is a microporous polyolefin coated with a hydrophilic polyurethane. Similarly, UCB Chemicals have also developed a product in which Ucecoat NPU hydrophilic finish is applied to microporous Ucecoat 2000 [22].

6.3.4 USING BREATHABLE FABRIC FOR APPAREL

A breathable coated fabric is used as an ensemble with a liner. The coated surface is always inside, to protect from abrasion. The coating can be on the outer fabric or on the liner. A repellent treatment is generally applied to the outer fabric. Breathable films/membranes are not used as such. They are converted into laminates by bonding them to fabric before use. Lamination is done by powder dot, paste dot, adhesion nets, etc. The resistance of water vapor of these laminates depends on the nature and thickness of the membrane, area of the membrane covered by the adhesive, and nature of the textile component. There are different methods of making laminates. In a garment, the membrane is always the second layer, from outside, placed directly below the outer fabric. The various types of laminates [9,40] are shown in Figure 6.5.
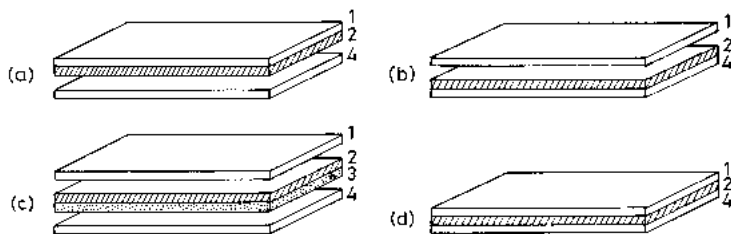
Figure 6.5 Types of laminates: (a) outer fabric laminate, (b) lining laminate, (c) insert laminate, (d) three-layer laminate, (1) outer fabric, (2) breathable film, (3) insert fabric, and (4) lining material. (Adapted with permission from M. Drinkmann. *Journal of Coated Fabrics,* Vol. 21, Jan 1992. ©Technomic Publishing Co., Inc.) [40].

The membrane may be bonded to the outer fabric [Figure 6.5(a)], to the liner [Figure 6.5(b)], on a lightweight knitted material (insert laminates) [Figure 6.5(c)], or may be bonded to both outer and inner fabric into a trilaminate [Figure 6.5(d)]. The type of laminate to be selected depends on the intended application. In the outer fabric laminate, functional aspects are paramount. The liner and insert laminates give softer handle and better fashion appeal.

6.3.5 EVALUATION

The fabric properties of breathable material can be evaluated by B.S. 3546. There are, however, different test methods for measuring water vapor permeability. Because the conditions of tests are different, they give different values. A new specification, B.S. 7209-90, has appeared specially for breathable fabrics [33]. This specification deals with two grades of water resistant, water vapor permeable apparel fabrics. The main requirements of the specification are (1) water vapor permeability index %; (2) resistance to water penetration as received, after cleaning, after abrasion, and after flexing; (3) cold crack temperature; (4) surface wetting (spray rating) as received and after cleaning; and (5) colorfastness to light, washing, dry cleaning, and rubbing. The method of determining the water vapor permeability index has been discussed in the chapter on test methods.

A comparative evaluation of several breathable fabrics available in trade has been done by Keighley [2]. The fabrics have been categorized into three types, viz., Ventile, PTFE film laminates, and PU coating. Some of his important findings are given in Table 6.3. It is seen that cotton Ventiles have low waterproofness but higher permeability. GORE-TEX® laminates have both very high permeability and waterproofness but are expensive.

TABLE 6.3. Comparative Properties of Different Breathable Fabrics.*

	Fabrics		
Properties	Cotton Ventile	PTFE Laminates (GORE-TEX®)	PU Coating
1. Waterproofness hydrostatic head cm	160–200	>2127	630–>2127
2. Water vapor permeability British MOD specification upright cup at 35°C. g/m^2/24 h	4100–5150	4850–5550	2500–4650

6.3.6 COMPARISON WITH IMPERMEABLES

A comprehensive study has been carried out by several TNO laboratories of The Netherlands on the comfort property of rainwear. Rainwear was made from waterproof fabrics of different technologies, viz., microporosity, continuous impermeable films, and microfiber weaves. In a wear trial, it was shown that breathable garments caused equal thermal strain as impermeable clothing in cold environments but less strain in hot conditions. During hard work, the moisture accumulation in breathable fabrics is lower but still large enough to cause discomfort. However, when worn for a whole day, with continually changing moisture production and climate, a breathable garment dissipates moisture all of the time, whereas in impermeable garments, only accumulation takes place. For extended periods of wear, breathable fabrics give a more comfortable, dry feeling. Ventilation at appropriate places in the garment has been designed as an alternative means to transport water vapor [43].

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