11

Textile-reinforced composite materials

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11.1 Composite materials

Textile-reinforced composite materials (TRCM) are part of the general class of engineering materials called composite materials. It is usual to divide all engineering materials into four classes: metals, polymers, ceramics and composites. A rigorous definition of composite materials is difficult to achieve because the first three classes of homogeneous materials are sometimes heterogeneous at submicron dimensions (e.g. precipitates in metals). A useful working definition is to say that composite materials are characterised by being multiphase materials within which the phase distribution and geometry has been deliberately tailored to optimise one or more properties.[1] This is clearly an appropriate definition for textile-reinforced composites for which there is one phase, called the matrix, reinforced by a fibrous reinforcement in the form of a textile.

In principle, there are as many combinations of fibre and matrix available for textile-reinforced composites as there are available for the general class of composite materials. In addition to a wide choice of materials, there is the added factor of the manufacturing route to consider, because a valued feature of composite materials is the ability to manufacture the article at the same time as the material itself is being processed. This feature contrasts with the other classes of engineering materials, where it is usual for the material to be produced first (e.g. steel sheet) followed by the forming of the desired shape.

The full range of possibilities for composite materials is very large. In terms of reinforcements we must include S-glass, R-glass, a wide range of carbon fibres, boron fibres, ceramic fibres (e.g. alumina, silicon carbide) and aramid fibres, and recognise that the reinforcement can come in the form of long (or continuous) fibres, short fibres, disks or plates, spheres or ellipsoids. Matrices include a wide ranges of polymers (epoxides, polyesters, nylons, etc), metals (aluminium alloys, magnesium alloys, titanium, etc) and ceramics (SiC, glass ceramics, etc). Processing methods include hand lay-up, autoclave, resin transfer moulding (RTM), injection moulding for polymer matrices, squeeze casting and powder metallurgy routes for metals, chemical vapour infiltration and prepregging routes for ceramics. A reader interested in a general introduction to composite materials should consult one of a number of wide ranging texts (e.g. Matthews and Rawlings,[2] Hull and Clyne,[3]). A good introduction to the fabrication of polymer matrix composites is provided by Bader *et al*.[4]

The market for composite materials can be loosely divided into two categories: 'reinforced plastics' based on short fibre E-glass reinforced unsaturated polyester resins (which account for over 95% of the volume) and 'advanced composites' which make use of the advanced fibres (carbon, boron, aramid, SiC, etc), or advanced matrices (e.g. high temperature polymer matrices, metallic or ceramic matrices), or advanced design or processing techniques.[1] Even within these loosely defined categories, it is clear that textile composites are 'advanced composites' by virtue of the manufacturing techniques required to produce the textile reinforcement. This chapter will be mostly concerned with textile-reinforced polymeric matrices. The reader should be aware that ceramic fibres in a textile format which reinforce ceramic matrices are also under investigation (e.g. Kuo and Chou,[5] Pryce and Smith[6]).

11.2 Textile reinforcement

11.2.1 Introduction

Textile-reinforced composites have been in service in engineering applications for many years in low profile, relatively low cost applications (e.g. woven glass-reinforced polymer hulls for minesweepers). While there has been a continual interest in textile reinforcement since around 1970, and increasingly in the 1980s, the recent desire to expand the envelope of composite usage has had a dramatic effect on global research into, and usage of, textile reinforcement. In addition to the possibility of a range of new applications for which textile reinforcement could replace current metal technology, textile reinforcement is also in competition with relatively mature composite technologies which use the more traditional methods of prepregging and autoclave manufacture. This is because TRCMs show potential for reduced manufacturing costs and enhanced processability, with more than adequate, or in some cases improved, mechanical properties. Those economic entities within which composite materials have been well developed, notably the European community (with about 30% of global composite usage), the USA (with about 30%) and Japan (with about 10%) have seen a growing interest in textile reinforcement in the 1990s, with China, Taiwan, Russia, South Korea, India, Israel and Australia being additional major contributors. In the last years of the 20th century, conferences devoted to composite materials had burgeoning sessions on textile reinforcement.

Of the available textile reinforcements (woven, braided, knitted, stitched), woven fabric reinforcement for polymer matrices can now be considered to be a mature application, but many textiles are still the subject of demonstrator projects. For example, a knitted glass fabric drawn over a mould and injected with a resin (using the RTM technique) has been used to manufacture a door component for a helicopter with the intention of replacing the current manufacturing route based on autoclave processing of carbon fibre/epoxy resin prepreg material.[7] Several textile techniques are likely to be combined for some applications. For example, a combination of braiding and knitting can be used to produce an I-shaped structure.[8]

For structural applications, the properties which are usually considered first are stiffness, strength and resistance to damage/crack growth. The range of textiles under development for composite reinforcement is indicated in the schematic diagram shown in Fig. 11.1 from Ramakrishna.[9] The intention of the following sections is to give an introduction to textile-reinforced composite materials employing woven, braided, knitted or stitched textile reinforcement. For more information, the reader is referred to the relevant cited papers in the first instance. However, before discussing textile-reinforced composites, it is necessary to provide an indication of the degree of complexity of the mechanical properties of the more traditional continuous fibre reinforcement of laminated composites. This discussion will also be useful when textile reinforcement is discussed subsequently.

11.2.2 Basic mechanics of composite reinforcement

11.2.2.1 Composites fabricated from continuous unidirectional fibres

It is important to recognise that the macroscopic elastic stress–strain relationships that are valid for isotropic materials are not valid for composite materials, except in rare cases when isotropy has been deliberately engineered (e.g. quasi-isotropic laminates loaded in-plane) or is a natural consequence of the material microstructure (e.g. transverse isotropy in the plane perpendicular to the fibre direction in a lamina). In composite materials texts, the basic mechanics always begin with continuous unidirectional fibres reinforcing a matrix, with the explicit (or implicit) assumption of a strong bond between matrix and fibre to enable good load transference from the matrix into the fibres (the detailed chemistry and properties of the 'interphase' region between fibre and bulk matrix is the subject of much research). This is both a logical and a practical starting point because much traditional composite fabrication uses sheets of reinforcing fibres preimpregnated with a resin which is partially cured to facilitate handling. These 'prepreg' sheets, which are usually about 0.125 mm thick, are stacked in appropriate orientations (depending on the expected loading) and cured, usually in an oven under load or applied pressure (autoclave processed), to produce the required component or part (Fig. 11.2).

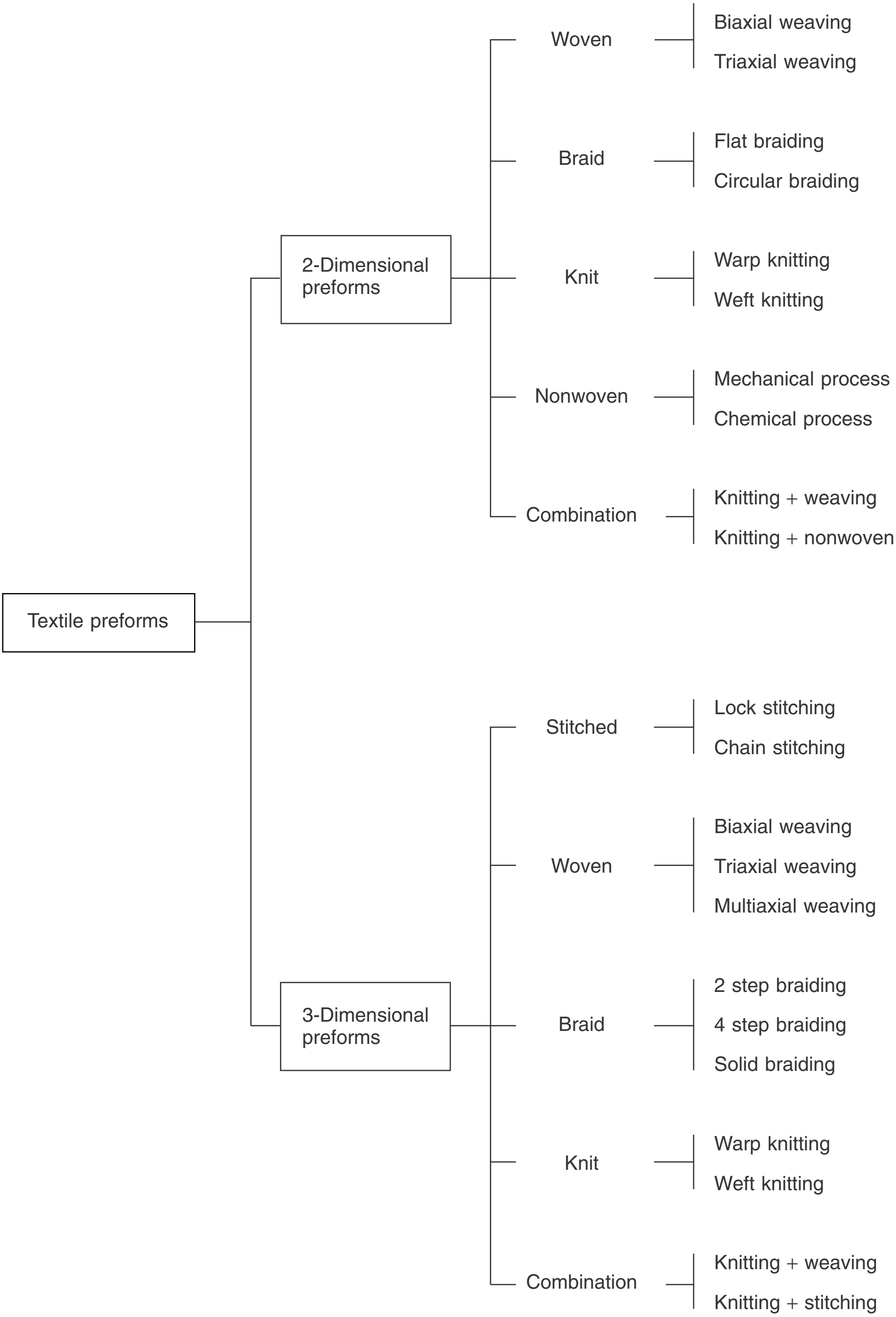
The Young's modulus of a composite lamina parallel to the fibres, E_1, is to a good approximation (which ignores the difference in Poisson's ratio between matrix and fibre) given by the 'rule of mixtures' expression (sometimes called the Voigt expression), which is:

$$E_1 = E_f V_f + (1 - V_f) E_m \tag{11.1}$$

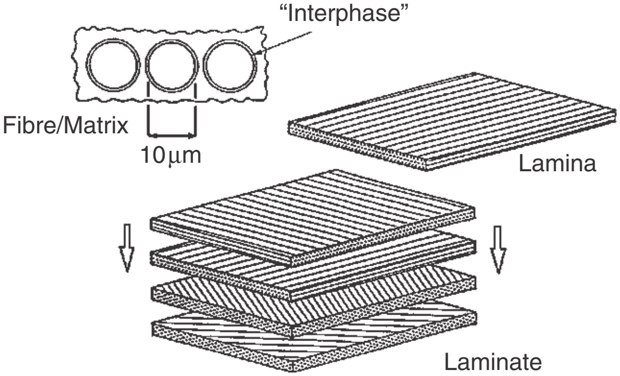
where, V_f is the fibre volume fraction in a void-free composite, and E_f and E_m are the fibre and matrix moduli, respectively. Perpendicular to the fibres, the modulus is given by:

$$E_2 = \frac{1}{\dfrac{V_f}{E_f} + \dfrac{1 - V_f}{E_m}} \tag{11.2}$$

which, for a given fibre volume fraction, is much lower than the rule of mixtures expression. This is because the longitudinal modulus is fibre dominated and the transverse modulus is matrix dominated.



11.1 Textile techniques under development for composite materials. Reprinted from S Ramakrishna, *Composites Sci. Technol.*, 1997, **57**, 1–22, with permission from Elsevier Science.[9]



11.2 Schematic of the interphase around a fibre, a lamina (or prepreg sheet, typical thickness 0.125 mm) and laminae stacked at different orientations to form a lamina. Reproduced courtesy of Bader.[1]

The longitudinal strength of a composite lamina is also described by rule of mixtures expressions, though the precise form depends on which of the strains to failure, matrix or fibres, is the larger. For example, if the strain to failure of the matrix is larger, and the fibre volume fraction is typical of the range of engineering composite materials (i.e. over 10% and up to about 70%), the composite strength, σ_c, is given by:

$$\sigma_c = \sigma_{fu} V_f \tag{11.3}$$

where σ_{fu} is the fibre strength.

Laminated composites will usually combine laminae with fibres at different orientations. To predict the laminate properties, the stress–strain relations are required for loading a lamina at an angle θ to the fibre direction, and for loading both in-plane and in bending. Composite mechanics for laminated composites is well developed and many textbooks deal with the subject (e.g. Jones,[10] Matthews and Rawlings,[2] Agarwal and Broutman[11]). For example, the modulus, E_x, of a ply loaded at an angle θ to the fibre direction is given by:

$$\frac{1}{E_x} = \frac{1}{E_1}\cos^4\theta + \left(\frac{1}{G_{12}} - \frac{2\nu_{12}}{E_1}\right)\sin^2\theta\cos^2\theta + \frac{1}{E^2}\sin^4\theta \tag{11.4}$$

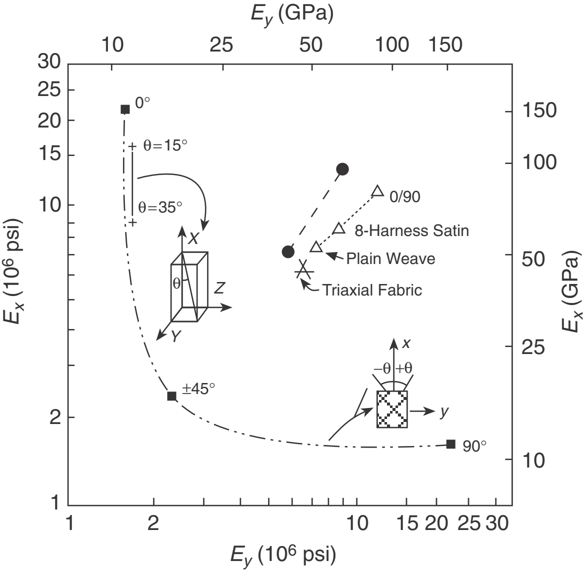
where E_1 and E_2 have been defined above, ν_{12} is the principal Poisson's ratio of the lamina (typically 0.3) and G_{12} is the in-plane shear modulus of the lamina. Unlike isotropic materials, which require two elastic constants to define their elastic stress–strain relationships, the anisotropy of a composite lamina (which is an orthotropic material, i.e. it has three mutually perpendicular planes of material symmetry) needs four elastic constants to be known in order to predict its in-plane behaviour. The stress–strain relationships for a laminate can be predicted using laminated plate theory (LPT), which sums the contributions from each layer in an appropriate way for both in-plane and out-of-plane loading. Laminated plate theory gives good agreement with measured laminate elastic properties for all types of composite material fabricated from continuous unidirectional prepreg layers (UD). Predicting laminate strengths, on the other hand, is much less reliable, except in some simple cases, and is still the subject of ongoing research. Because composite structures are usually designed to strains below the onset of the first type of visible damage in the structure (i.e. to design strains of about 0.3–0.4%), the lack of ability to predict the ultimate strength accurately is rarely a disadvantage.

Ply orientations in a laminate are taken with reference to a particular loading direction, usually taken to be the direction of the maximum applied load, which, more often than not, coincides with the fibre direction to sustain the maximum load, and this is defined as the 0° direction. In design it is usual to choose balanced symmetric laminates. A balanced laminate is one in which there are equal numbers of $+\theta$ and $-\theta$ plies; a symmetric laminate is one in which the plies are symmetric in terms of geometry and properties with respect to the laminate mid-plane. Hence a laminate with a stacking sequence 0/90/+45/–45/–45/+45/90/0, which is written $(0/90/\pm45)_s$ is both balanced and symmetric. Balanced symmetric laminates have a simple response. In contrast, an unbalanced asymmetric laminate will, in general, shear, bend and twist under a simple axial loading.

11.2.2.2 Overview of composite moduli for textile reinforcements

One of the simplest laminate configurations for continuous unidirectional fibre reinforced composites is the cross-ply laminate, for example $(0/90)_s$, which is 0/90/90/0. For such a laminate, the Young's moduli parallel to the 0° and 90° directions, E_x and E_y, are equal and, to a good approximation, are just the average of E_1 and E_2.

Yang and Chou[12] have shown schematically the change in these moduli, E_x and E_y, for a carbon fibre-reinforced epoxy laminate with a range of fibre architectures, but the same fibre volume fraction of 60% (see Fig. 11.3). This diagram provides a



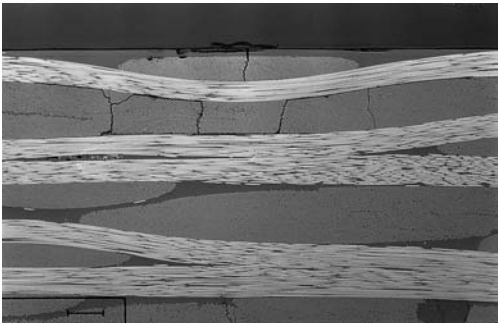
11.3 Predicted E_x and E_y moduli for a range of reinforcement architectures; ±θ angle ply (for θ = 0 to ±45 to 90), cross-ply (0/90), eight-harness satin and plain woven, triaxial woven fabric, braided (θ = 35° to 15°) and multiaxial warp knit (•--•), for the same fibre volume fraction of 60%. Reprinted, with minor changes, from Yang and Chou, *Proceedings of ICCM6/ECCM2*, ed. F L Matthews *et al.*, 1987, 5.579–5.588, with permission from Elsevier Science.[12]

good starting point for the discussion of textile-reinforced composites. The cross-ply composite has E_x and E_y moduli of about 75 GPa. In the biaxial weaves of the eight-harness satin and the plain weave, the moduli both fall to about 58 GPa and 50 GPa, respectively. These reductions reflect the crimps in the interlaced woven structure, with more crimps per unit length in the plain weave producing a smaller modulus. The triaxial fabric, with three sets of yarns interlaced at 60° angles, behaves similarly to a $(0/\pm60)_s$ angle-ply laminate. Such a configuration is quasi-isotropic for in-plane loading, that is, it has the same Young's modulus for any direction in the plane of the laminate. The triaxial fabric shows a further reduction in E_x and E_y to about 42 GPa, but this fabric benefits from a higher in-plane shear modulus (which is not shown in the diagram) than the biaxial fabrics. The anticipated range of properties for a multiaxial warp-knit fabric (or multilayer multidirectional warp-knit fabric) reinforced composite is also shown, lying somewhere between the triaxial fabric and above the cross-ply laminate (at least for the modulus E_x), depending on the precise geometry. Here warp, weft and bias yarns (usually ±45) are held together by 'through-the-thickness' chain or tricot stitching. Finally, a three-dimensional braided composite is shown, with braiding angles in the range 15° to 35°. This type of fibre architecture gives very anisotropic elastic properties as shown by the very high E_x moduli (which are fibre dominated) and the low E_y moduli (which are matrix dominated). In the following sections, the properties of these textile reinforcements (woven, braided, knitted, stitched) will be discussed in more detail.

11.3 Woven fabric-reinforced composites

11.3.1 Introduction

Woven fabrics, characterised by the interlacing of two or more yarn systems, are currently the most widely used textile reinforcement with glass, carbon and aramid reinforced woven composites being used in a wide variety of applications, including aerospace (Fig. 11.4). Woven reinforcement exhibits good stability in the warp and



11.4 Optical micrograph of an eight-harness woven CFRP laminate showing damage in the form of matrix cracks and associated delaminations. The laminate is viewed at a polished edge. The scale bar is 200 µm. Reprinted from F. Gao *et al.*, *Composites Sci. Technol.*, 1999, **59**, 123–136, 'Damage accumulation in woven fabric CFRP (carbon fibre-reinforced plastic) laminates under tensile loading: Part 1 – Observations of damage,' with permission from Elsevier Science.[15]

weft directions and offers the highest cover or yarn packing density in relation to fabric thickness.[13] The possibility of extending the useful range of woven fabrics was brought about by the development of carbon and aramid fibre fabrics with their increased stiffness relative to glass. Prepreg manufacturers were able, by the early 1980s, to supply woven fabrics in the prepreg form familiar to users of nonwoven material.[14]

There are a number of properties that make woven fabrics attractive compared to their nonwoven counterparts. They have very good drapability, allowing complex shapes to be formed with no gaps. Manufacturing costs are reduced since a single biaxial fabric replaces two nonwoven plies and the ease of handling lends itself more readily to automation. Woven fabric composites show an increased resistance to impact damage compared to nonwoven composites, with significant improvements in compressive strengths after impact. These advantages are gained, however, at the expense of lower stiffness and strength than equivalent nonwoven composites.

11.3.2 Mechanical behaviour

11.3.2.1 Mechanical properties

Bishop and Curtis[16] were amongst the first to demonstrate the potential advantages of woven fabrics for aerospace applications. Comparing a five-harness woven fabric (3k tows, which means 3000 carbon fibres per tow) with an equivalent nonwoven carbon/epoxy laminate, they showed that the modulus of the biaxial (0/90) woven laminate was slightly reduced compared to the nonwoven cross-ply laminate (50 GPa compared to 60 GPa, respectively). The compressive strength after a 7 J impact event was increased by over 30%. Similar results have been found by others. For example, Raju *et al.*[17] found a decreasing modulus for carbon/epoxy laminates moving from eight-harness (73 GPa) to five-harness (69 GPa) to plain weave (63 GPa). These results are in line with the moduli changes indicated in Fig. 11.3. The tensile strengths of woven composites are also slightly lower than the nonwoven equivalents. Bishop and Curtis[16] for example, found a 23% reduction in the tensile strength compared to UD equivalent laminates. Triaxial woven fabric composites, naturally, have further reduced longitudinal properties, as mentioned earlier. Fujita *et al.*[18] quote a Young's modulus and tensile strength of 30 GPa and 500 MPa, respectively, for a triaxial woven carbon/epoxy.

Glass-reinforced woven fabrics give rise naturally to composites with lower mechanical properties because of the much lower value of the glass fibre modulus compared to carbon. Amijima *et al.*[19] report Young's modulus and tensile strength values for a plain weave glass/polyester ($V_f = 33\%$) of 17 GPa and 233 MPa, respectively, while Boniface *et al.*[20] find comparable values for an eight-harness glass/epoxy composite, that is, 19 GPa and 319 MPa, respectively ($V_f = 37\%$).

Clearly, the mechanical properties of woven fabric-reinforced composites are dominated by the type of fibre used, the weaving parameters and the stacking and orientation of the various layers. However, there are additional subtleties which also affect composite performance. For example, some authors have noted the possibility of slightly altered mechanical properties depending on whether the yarns are twisted prior to weaving,[21] and work in this area has shown that damage accumulation under static and cyclic loading is different in laminates fabricated from twisted or untwisted yarn.[22]

11.3.2.2 Damage accumulation

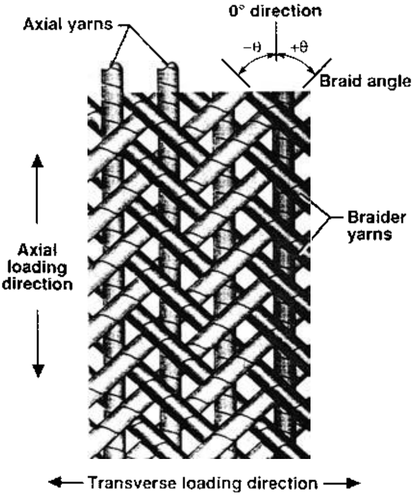
Damage under tensile loading in woven composites is characterised by the development of matrix cracking in the off-axis tows at strains well above about 0.3–0.4%. Most investigations of damage have considered biaxial fabrics loaded in the warp direction. Cracks initiate in the weft bundles and an increasing density of cracks develops with increasing load (or strain). The detailed crack morphology depends on whether the tows are twisted or untwisted. Twisted tows lead to fragmented matrix cracks; untwisted tows lead to matrix cracks, which strongly resemble the 90 ply cracks that develop in cross-ply laminates.[22,23] The accumulation of cracks is accompanied by a gradual decrease in the Young's modulus of the composite. In woven carbon systems, the matrix cracking can lead to considerable delamination in the region of the crimps in adjacent tows which further reduces the mechanical properties.[15] Damage modelling has been attempted using finite element methods (e.g. Kriz,[24] Kuo and Chou[5]) or closed-form models (e.g. Gao et al.[25]).

11.3.3 Analyses of woven composites

The majority of closed-form analyses of woven fabric composites have a substantial reliance on laminated plate theory. Numerical methods rely on the finite element method (FEM).

In a series of papers in the early 1980s by Chou, Ishikawa and co-workers (see Chou[26] for a comprehensive review) three models were presented to evaluate the thermomechanical properties of woven fabric composites. The mosaic model treats the woven composite as an assemblage of assymetric cross-ply laminates, ignoring the fibre continuity and undulation. The fibre undulation model takes these complexities into account by considering a slice of the crimped region and averaging the properties with the aid of LPT. This model is particularly appropriate for plain and twill weave composites. For five-harness and eight-harness satins, the fibre undulation model is broadened in the bridging model. These essentially one-dimensional models have been extended to two dimensions by Naik and co-workers (e.g. Naik and Shembekar[21]).

The finite element method is a powerful tool that makes use of a computer's ability to solve complex matrix calculations very quickly. When applied to analysing textile composites, the procedure consists of dividing the composite into a number of unit cells interconnected at nodal points. If the force-displacement characteristics of an individual unit cell are known, it is then possible to use FEM to evaluate the stress fields and macroscopic responses to deformation of the entire structure. The difficulty for FEM methods is that they are expensive and ideally need to be reapplied for even small changes in reinforcement architecture. For woven reinforcements in particular, where adjacent layers have a great degree of lateral freedom to move during fabrication, the results need to be treated with caution. Examples of this approach to investigation of the distribution of stresses and strain energy densities in woven fabric composites can be found in papers by Glaessgen and Griffin[27] and Woo and Whitcomb.[28]



11.5 Braided two-dimensional reinforcement; the pattern is a 2 × 2 braid. Reprinted from Naik *et al.*, *J. Composite Mater.*, 1994 **28**, 656–681, with permission from Technomic Publishing Co., Inc, copyright, 1994.[29]

11.4 Braided reinforcement

11.4.1 Introduction

Braided textiles for composites consist of intertwined two (or more) sets of yarns, one set of yarns being the axial yarns. In two-dimensional braiding, the braided yarns are introduced at ±θ directions and the intertwining is often in 1 × 1 or 2 × 2 patterns (see Fig. 11.5).[29,30] However, for significant improvements in through-the-thickness strength, three-dimensional braided reinforcement is an important category (e.g. Du *et al.*[31]). The braided architecture enables the composite to endure twisting, shearing and impact better than woven fabrics. Combined with low cost fabrication routes, such as resin transfer moulding, braided reinforcements are expected to become competitor materials for many aerospace applications (where they may replace carbon prepreg systems) or automobile applications (e.g. in energy absorbing structures), although realisation in practice is currently limited.

A variety of shapes can be fabricated for composite applications from hollow tubular (with in-laid, non-intertwined yarns) to solid sections, including I-beams. The stability or conformability of the braided structure depends on the detailed fibre architecture. With in-laid yarns, for example, stability in the 0° direction in tension is improved, though the axial compressive properties may be poor.[13] In general terms, the mechanical properties of composites fabricated using braided reinforcement depend on the braid parameters (braid architecture, yarn size and spacing, fibre volume fraction) and the mechanical properties of fibre and matrix.

11.4.2 Mechanical behaviour

In this section, two-dimensional braided reinforcement will be considered primarily, since it lends itself to direct comparison with laminated composites with a 0/±θ construction and such comparisons have been made by a number of authors. For example, Naik and co-workers[29] manufactured braided carbon fibre-reinforced epoxy resin composites with a number of fibre architectures while maintaining a constant fibre volume fraction ($V_f = 56\%$) overall. By keeping the axial yarn content constant, but varying the yarn size or braid angle, the effect of each variable on composite properties could be investigated. An insensitivity to yarn size was found (in the range of 6–75 k tow size), but the braid angle had a significant effect, as anticipated. A modest increase in longitudinal modulus (from 60–63 GPa) occurred in moving from a braid architecture of 0/±70 to 0/±45, with a much larger fall in transverse modulus (from 46–19 GPa).

The strengths of braided reinforced composites are lower than their prepregged counterparts. Norman *et al.*[32] compared the strengths of 0/±45 braided composites with an equivalent prepreg (UD) system, finding that the prepreg system had a tensile strength that was some 30% higher than the braided two-dimensional composite (849 MPa compared to 649 MPa). Similar results found by Herszberg *et al.* (1997) have been attributed to fibre damage during braiding. Norman *et al.*[32] also found the braided reinforcement to be notch insensitive for notch sizes up to 12 mm, whereas equivalent UD laminates showed a significant notch sensitivity in this range. Compression after impact tests also favour braided composites when normalised by the undamaged compression strengths, in comparison with UD systems. Indeed, the ability to tailor the braided reinforcement to have a high energy absorbing capability may make them of use in energy-absorbent structures for crash situations.[33] A review by Bibo and Hogg[34] discusses energy-absorbing mechanisms and postimpact compression behaviour of a wide range of reinforcement architectures, including braided reinforcement.

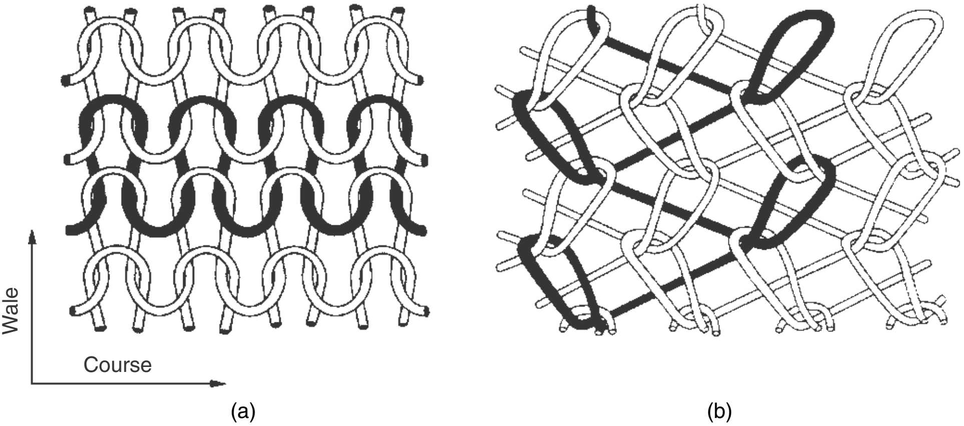
11.4.3 Analyses of braided reinforcement

The potential complexity of the braided structure, particularly the three-dimensional architectures, is such that the characterisation of structures is often taken to be a major first step in modelling the behaviour of the reinforced material. The desired outcome of this work is to present a three-dimensional visualisation of the structure (e.g. Pandey and Hahn[35]) or to develop models to describe the structural geometry (e.g. Du *et al.*[31]). Analytical models for predicting properties are frequently developments of the fibre-crimp model developed by Chou[26] and colleagues for woven reinforcements, extended in an appropriate way by treating a representative 'unit cell' of the braided reinforcement as an assemblage of inclined unidirectional laminae (e.g. Byun and Chou[36]). Micromechanics analyses incorporated into personal computer-based programs have also been developed (e.g. the Textile composite analysis for design, TEXCAD; see e.g. Naik[37]).

11.5 Knitted reinforcement

11.5.1 Introduction

The major advantages of knitted fabric-reinforced composites are the possibility of producing net shape/near net shape preforms, on the one hand, and the exceptional drapability/formability of the fabrics, which allows for forming over a shaped tool of complex shape, on the other. Both of these features follow from the interlooped



11.6 Schematic diagrams of (a) weft-knitted and (b) warp-knitted reinforcement. Reprinted from S Ramakrishna, *Composites Sci. Technol.*, 1997, **57** 1–22, with permission from Elsevier Science.[9]

nature of the reinforcing fibres/yarns which permits the fabric to have the stretchability to adapt to complex shapes without crimp (Fig. 11.6). However, the advantages which the knitted fibre architecture brings also lead to the disadvantages, which are the reduced in-plane stiffness and strength of the composites caused by the relatively poor use of the mechanical properties of the fibre (glass, carbon or aramid). Weft and warp knits can, however, be designed with enhanced properties in certain directions by the use of laid-in yarns.[13]

Both warp-knitted and weft-knitted reinforcements are under investigation. In general terms, the weft-knitted structures are preferred in developmental work owing to their superior formability (based on their less stable structure) and warp-knitted structures are preferred for large scale production (owing to the increased production rate allowed by the knitting of many yarns at one time).[7]

11.5.2 Mechanical behaviour

11.5.2.1 Mechanical properties

The tensile and compressive properties of the knitted fabrics are poor in comparison with the other types of fabric already discussed, but they are more likely to be chosen for their processability and energy-absorbing characteristics than their basic in-plane properties.

The detailed fibre architecture of knitted fabric reinforcement leads to in-plane properties which can either be surprisingly isotropic or very anisotropic. For example, Bannister and Herszberg[38] tested composites manufactured using both a full-milano and half-milano knitted glass-reinforced epoxy resin. The full-milano structure was significantly more random in its architecture than the half-milano, with the consequence that the tensile strengths in both the wale and the course directions were approximately the same. Typically, the stress–strain curve is approximately linear to a strain of about 0.6%,[39] followed by a sharp knee and pseudoplastic behaviour to failure. The tensile strengths were proportional to the fibre volume fraction (in a manner which is understandable based on a rule-of-mixtures prediction of composite strength; and see Section 5.3 below), with a typical value being about 145 MPa for a fibre volume fraction of 45%. However, the strains to failure were not only very large (in the range from about 2.8% for seven cloth layers to about 6.6% for 12 cloth layers) but also increased with number of layers/fibre volume fraction. The reasons for this variation are presumably related to the detailed manner in which the damage accumulates to produce failure in the composites. In contrast to the relatively isotropic full-milano reinforcement, the half-milano knitted architecture, which has a higher degree of fibre orientation, showed tensile strengths which varied by 50% in the two directions and difference in strains to failure which were even larger (about a factor of two).

Knitted carbon reinforcement has been investigated by Ramakrishna and Hull.[40] In general, the weft-knitted composites showed moduli which increased roughly linearly with fibre volume fraction, being typically 15 GPa when tested in the wale direction and 10 GPa when tested in the course direction, for a fibre volume fraction of about 20%. Tensile strengths also increase in a similar fashion for the wale direction (a typical value is 60 MPa for a 20% volume fraction), whereas the course direction strengths are reasonably constant with fibre volume fraction at around 34 MPa. These differences are related to the higher proportion of fibre bundles oriented in the wale direction.

In compression, the mechanical properties are even less favourable. For both the half-milano and full-milano glass-reinforced composites[39] the compression strengths showed features which are a consequence of the strong dominance of the matrix in compression arising from the highly curved fibre architecture. These features are manifest as compression strengths that were approximately the same in both wale and course directions and as a compression strength that only increased by about 15% as the fibre volume fraction increased from 29–50% (interestingly, the compression strengths were found to be consistently higher than the tensile strengths, by up to a factor of two). In the light of these results, it is not surprising that deforming the knitted fabric by strains of up to 45% prior to infiltration of the resin and consolidation of the composite has virtually no effect on the composite compressive strength.[41]

Similar findings have been reported by others. Wang *et al.*[42] tested a 1 × 1 rib-knit structure of weft-knitted glass-reinforced epoxy resin, finding compressive strengths which were almost twice as high as the tensile strengths. The relatively isotropic nature of this fibre architecture led to Young's modulus values and Poisson's ratio values which were also approximately the same for testing in both the wale and course direction.

11.5.2.2 Damage accumulation

There are a large number of potential sites for crack initiation in knitted composites. For example, observations on weft-knitted composites tested in the wale direction suggest that cracks initiate from debonds which form around the needle and sinker loops in the knitted architecture. Similarly, crack development in fabrics tested in tension in the course direction is believed to occur from the sides (or legs) of loops.[39,40] It appears likely that crack linking will occur more readily for cracks initiated along the legs of the loops (i.e. when the composite is loaded in the course direction) than when initiation occurs at the needle and sinker loops.

The damage tolerance of knitted fabrics compares favourably with other reinforcement architectures. For example, it has been found that a higher percentage of impact energy in the range 0–10 J is absorbed by a weft-knitted glass reinforced composite ($V_f = 50\%$) than was absorbed by an equivalent woven fabric. Observations indicated, in addition, that the damaged area was approximately six times larger for the knitted fabric than for the woven fabric, presumably reflecting the increased availability of crack initiation sites in the knitted architecture. Compression after impact (CAI) strengths were decreased by only 12% for the knitted fabric in this impact energy range, whereas the woven fabric CAI values fell by up to 40%.[38]

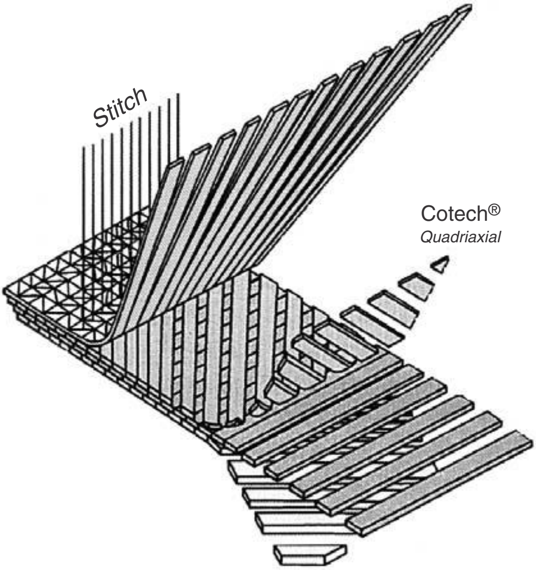
11.5.3 Analyses of knitted composites

Models for the elastic moduli and tensile strengths of knitted fabric reinforced composites have been developed (e.g. Ramakrishna,[9] Gommers *et al.*[43,44]). Ramakrishna, for example, divides a weft-knitted fabric architecture into a series of circular arcs with each yarn having a circular cross-section. It is then possible to derive an expression for the Young's modulus of the composite by integrating the expression for the variation in Young's modulus with angle (equation 11.4) along the required directions. Indeed, all the elastic moduli can be calculated in a similar fashion, although the predictions were about 20% higher than the experimental results. The predictions of tensile strength depend on the expression for the strength of an aligned fibre composite modified by terms which attempt to account for the average orientation of the yarns with respect to the loading direction and the statistical variation of the bundle strengths. The tensile strengths are predicted to scale in proportion to the fibre volume fractions in both the wale and course directions, which is exactly the result found by Leong *et al.*[39] Gommers *et al.*[43,44] use orientation tensors to represent fibre orientation variations in the fabric.

11.6 Stitched fabrics

11.6.1 Introduction

Stitching composites is seen as a direct approach to improving the through-the-thickness strength of the materials. This in turn will improve their damage tolerance, and particularly the CAI behaviour, where failure is usually triggered by microbuckling in the vicinity of a delamination. In its simplest form, stitching of composites adds one further production step with the use of a sewing machine to introduce lock stitches through the full thickness of the laminate. The stitching can be performed on unimpregnated fibres or fibres in the prepreg form, although the latter is usually to be avoided owing to excessive fibre damage. Stitching in this way can be carried out with carbon, glass or aramid fibre yarns. In its more sophisticated form, chain or tricot stitches are used to produce a fabric which consists of warp (0°), weft (90°) and (optionally) bias (±θ) yarns held together by the warp-knitted stitches, which usually consist of a light polyester yarn (Fig. 11.7). The resulting fabric is called a non-crimp fabric (NCF) or a multiaxial warp-knit fabric (MWK) (see e.g. Hogg *et al.*,[45] Du and Ko[46]). Whatever the terminology, the warp-knitted fabrics are highly drapable, highly aligned materials in which the tow crimp associated with woven fabrics has been removed almost completely (though some slight misalignment is inevitable). The fabric can be shaped easily and it remains stable when removed



11.7 Schematic of a quadriaxial non-crimp fabric (courtesy of BTI Europe Ltd).

from a tool owing to the ability of the stitching to allow sufficient relative movement of the tows.[47] With the potential for combining the fabric with low-cost fabrication routes (e.g. RTM), these fabrics are expected both to broaden the envelope of composite usage and to replace the more expensive prepregging route for many applications. The ability to interdisperse thermoplastic fibres amongst the reinforcing fibres also provides a potentially very attractive manufacturing route.[47] Hence, this brief introduction will concentrate on the warp-knitted materials. A comprehensive review of the effect of all types of stitching on delamination resistance has been published by Dransfield *et al.*[48]

11.6.2 Mechanical behaviour

11.6.2.1 Mechanical properties

The basic mechanical properties of NCFs are somewhat superior to the equivalent volume fraction of woven roving-reinforced material. For example, Hogg *et al.*[45] find the Young's modulus and tensile strength of a biaxial NCF glass-reinforced polyester, volume fraction 33%, to be 21 GPa and 264 MPa, respectively, which are values some 13 and 20% higher than those found for an equivalent volume fraction of plain woven-reinforced composite (see Section 11.3.2.1; Amijima *et al.*,[19]). Quadriaxial reinforcement of the same fibre volume fraction gave similar results (24 GPa and 286 MPa, respectively). The improvement in properties compared to woven-reinforced composites is emphasised by the work of Godbehere *et al.*[49] in tests on a carbon fibre-reinforced NCF epoxy resin and equivalent unidirectional (UD) laminates. All the composites had 0/±45 orientations. Although the NCF laminates had poorer properties than the UD laminates, the reduction was small (e.g. less than 7%) in the 0° direction. For example, the UD equivalent laminate gave values of Young's modulus and tensile strength of 58 GPa and

756 MPa, respectively, compared to NCF values of 56 GPa and 748 MPa (for fibre volume fractions of 56%).

The increases in through-the-thickness reinforcement achieved by NCFs have been demonstrated by a number of authors. For example, Backhouse *et al.*[50] compared the ease of delaminating polyester stitched 0/±45 carbon fibre NCF with equivalent carbon fibre/epoxy UD laminates. There were large increases, some 140%, in the measured parameters used to quantify resistance to delamination (the mode I and mode II toughness values) for the NCF fabrics compared to the UD material.

11.6.2.2 Damage accumulation

Owing to the fact that the fibres in each layer in an NCF-reinforced composite are parallel, it is to be expected that the damage accumulation behaviour is very similar to equivalent UD laminates. Indeed, Hogg *et al.*[45] found the matrix cracking in biaxial glass NCF to be very similar to matrix cracking in the 90° ply of cross-ply UD laminates. There are, however, microstructural features introduced because of the knitting yarn which do not have parallels in UD laminates. Local variations in fibre volume fraction, resin-rich pockets and fibre misalignment provide significant differences. In biaxial reinforced NCFs, for example, transverse cracks can initiate preferentially where the interloops of the knitted yarn intersect the transverse ply.[51]

11.6.3 Analyses of non-crimp fabrics

For in-plane properties of NCF composites, it is likely that there is sufficient similarity to UD materials to enable similar analyses to be used (although Hogg *et al.*[45] suggest that the properties of NCF composites may exceed the in-plane properties of UD equivalents). However, detailed models of the three-dimensional structure of NCF-based composites for manufacturing purposes (i.e. for determining process windows for maximum fibre volume fractions, for example) and for the prediction of mechanical properties, are being developed (e.g. Du and Ko[46]).

11.7 Conclusion

The 1990s saw a growing mood of cautious optimism within the composites community worldwide that textile-based composites will give rise to new composite material applications in a wide range of areas. Consequently, a wide range of textile-reinforced composites are under development/investigation or in production. Textile reinforcement is thus likely to provide major new areas of opportunity for composite materials in the future.

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12

Waterproof breathable fabrics

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12.1 What are waterproof breathable fabrics?

Waterproof breathable fabrics are designed for use in garments that provide protection from the weather, that is from wind, rain and loss of body heat. Clothing that provides protection from the weather has been used for thousands of years. The first material used for this purpose was probably leather but textile fabrics have also been used for a very long time. Waterproof fabric completely prevents the penetration and absorption of liquid water, in contrast to water-repellent (or, shower-resistant) fabric, which only delays the penetration of water. Traditionally, fabric was made waterproof by coating it with a continuous layer of impervious flexible material. The first coating materials used were animal fat, wax and hardened vegetable oils. Nowadays synthetic polymers such as polyvinylchloride (PVC) and polyurethane are used. Coated fabrics are considered to be more uncomfortable to wear than water-repellent fabric, as they are relatively stiff and do not allow the escape of perspiration vapour. Consequently they are now used for 'emergency' rainwear. Water-repellent fabric is more comfortable to wear but its water-resistant properties are short lived.

The term 'breathable' implies that the fabric is actively ventilated. This is not the case. Breathable fabrics passively allow water vapour to diffuse through them yet still prevent the penetration of liquid water.[1] Production of water vapour by the skin is essential for maintenance of body temperature. The normal body core temperature is 37 °C, and skin temperature is between 33 and 35 °C, depending on conditions. If the core temperature goes beyond critical limits of about 24 °C and 45 °C then death results. The narrower limits of 34 °C and 42 °C can cause adverse effects such as disorientation and convulsions. If the sufferer is engaged in a hazardous pastime or occupation then this could have disastrous consequences.

During physical activity the body provides cooling partly by producing insensible perspiration. If the water vapour cannot escape to the surrounding atmosphere the relative humidity of the microclimate inside the clothing increases causing a corresponding increased thermal conductivity of the insulating air, and the clothing

Table 12.1 Heat energy produced by various activities and corresponding perspiration rates[3]

Activity	Work rate (Watts)	Perspiration rate ($\mathrm{g\,day^{-1}}$)
Sleeping	60	2280
Sitting	100	3800
Gentle walking	200	7600
Active walking	300	11500
With light pack	400	15200
With heavy pack	500	19000
Mountain walking with heavy pack	600–800	22800–30400
Maximum work rate	1000–1200	38000–45600

becomes uncomfortable. In extreme cases hypothermia can result if the body loses heat more rapidly than it is able to produce it, for example when physical activity has stopped, causing a decrease in core temperature. If perspiration cannot evaporate and liquid sweat (sensible perspiration) is produced, the body is prevented from cooling at the same rate as heat is produced, for example during physical activity, and hyperthermia can result as the body core temperature increases. The heat energy produced during various activities and the perspiration required to provide adequate body temperature control have been published.[2,3] Table 12.1 shows this information for activities ranging from sleeping to maximum work rate.

If the body is to remain at the physiologically required temperature, clothing has to permit the passage of water vapour from perspiration at the rates under the activity conditions shown in Table 12.1. The ability of fabric to allow water vapour to penetrate is commonly known as breathability. This property should more scientifically be referred to as water vapour permeability. Although perspiration rates and water vapour permeability are usually quoted in units of grams per day and grams per square metre per day, respectively, the maximum work rate can only be endured for a very short time.

During rest, most surplus body heat is lost by conduction and radiation, whereas during physical activity, the dominant means of losing excess body heat is by evaporation of perspiration. It has been found that the length of time the body can endure arduous work decreases linearly with the decrease in fabric water vapour permeability. It has also been shown that the maximum performance of a subject wearing clothing with a vapour barrier is some 60% less than that of a subject wearing the same clothing but without a vapour barrier. Even with two sets of clothing that exhibit a small variation in water vapour permeability, the differences in the wearer's performance are significant.[4] One of the commonest causes of occupational deaths amongst firefighters is heart failure due to heat stress caused by loss of body fluid required to produce perspiration. According to the 1982 US fire death statistics, only 2.6% were due to burns alone whereas 46.1% were the result of heart attacks.[5] Firefighters can lose up to 4 litres (4000 g) of fluid per hour when in proximity to a fire.[6]

In 1991 Lomax reported that modern breathable waterproof fabrics were being claimed to be capable of transmitting more than $5000\,\mathrm{g\,m^{-2}\,day^{-1}}$ of water vapour.[2] By 1998 it was common to see claims of $10\,000\,\mathrm{g\,m^{-2}\,day^{-1}}$.

Thus, waterproof breathable fabrics prevent the penetration of liquid water from outside to inside the clothing yet permit the penetration of water vapour from inside

Table 12.2 Applications of waterproof breathable fabrics[2,7]

Leisure	Work
Heavy duty, foul weather clothing: Anoraks, cagoules, packs, over-trousers, hats, gloves, gaiters	Foul weather clothing: Survival suits, special military protective clothing, clean-room garments, surgical garments, hospital drapes, mattress and seat covers, specialised tarpaulins, packaging, wound dressings, filtration
Fashionable weather protection: Rainwear, skiwear, golf suits, walking boot linings, panels and inserts, sport footwear linings, panels and inserts	Domestic and transport: Non-allergic bedding, car covers, fire smoke curtains in ships, cargo wraps in aircraft
Tents	
Sleeping bag covers	

the clothing to the outside atmosphere. Examples of over 25 applications of waterproof breathable fabrics have been published.[2,7] Table 12.2 lists some examples of the applications of waterproof breathable fabrics with some additions by the author.

12.2 Types of waterproof breathable fabric

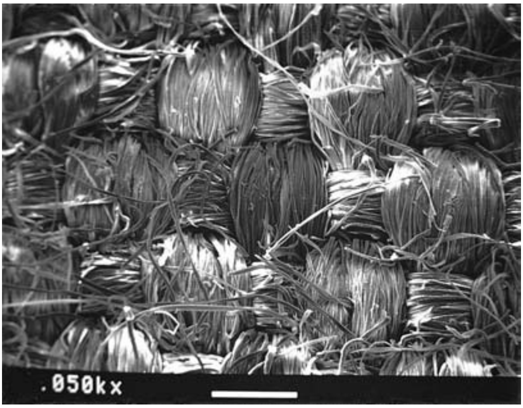
There are several methods which can be used to obtain fabrics which are both breathable and waterproof. These can be divided into three groups:

- densely woven fabrics
- membranes
- coatings.

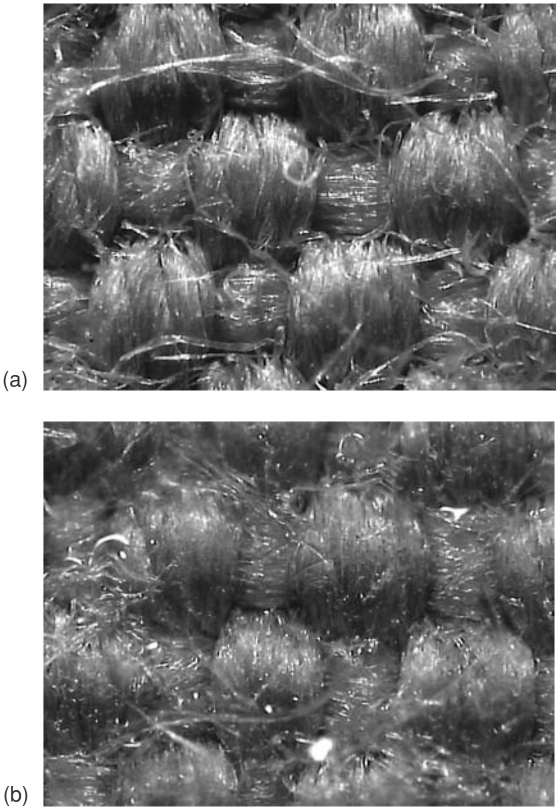
12.2.1 Densely woven fabrics

Probably the first effective waterproof breathable fabric was developed in the 1940s for military purposes and is known as Ventile (Fig. 12.1). The allied forces were losing aircrew that were shot down or had to ditch in the North Atlantic Ocean. This is a particularly hazardous environment, particularly in winter. A fabric was needed that would allow the personnel to be comfortable whilst carrying out their normal flying duties and prevent penetration of water if they were immersed in the sea. Ventile fabric was carefully engineered to make it effective.[8] The finest types of long staple cottons are selected so that there are very small spaces between the fibres. The cotton is processed into combed yarn, which is then plied. This improves regularity and ensures that the fibres are as parallel as possible to the yarn axis, and that there are no large pores where water can penetrate. The yarn is woven using an Oxford weave, which is a plain weave with two threads acting together in the warp. This gives minimum crimp in the weft, again ensuring that the fibres are as parallel as possible to the surface of the fabric.

When the fabric surface is wetted by water, the cotton fibres swell transversely reducing the size of the pores in the fabric and requiring very high pressure to cause

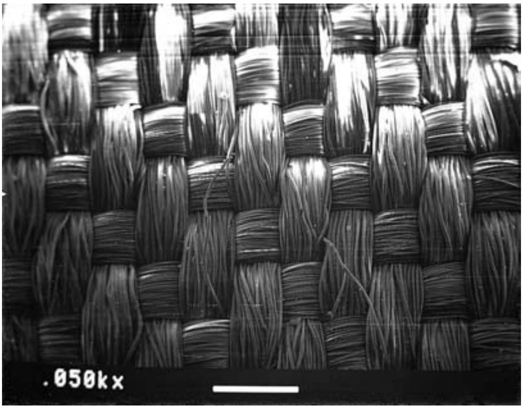


12.1 Scanning electron micrograph of Ventile fabric.



12.2 Photomicrograph of Ventile fabric, (a) dry, (b) wet.

penetration (Fig. 12.2). The fabric is thus rendered waterproof without the need for any water-repellent finishing treatment. It was first made for military applications but the manufacturers are now producing a range of variants to widen the market appeal.[9] The military variants use thread densities as high as 98 per cm. Fabric for



12.3 Scanning electron micrograph of mirofilament fabric.

other applications uses much lower thread densities, necessitating a water-repellent finish to achieve the waterproof properties.

Densely woven fabric can also be made from synthetic microfilament yarns. The individual filaments are less than 10 µm in diameter, so that fibres with very small pores can be engineered. Microfilaments are usually made from polyamide or polyester. The latter is particularly useful as it has inherent water-repellent properties. The water penetration resistance of the fabric is improved by application of silicone or fluorocarbon finish.

Although fabrics made from microfilaments have a soft handle many of them are windproof, but not truly waterproof as the synthetic filaments do not swell when wet (Fig. 12.3).

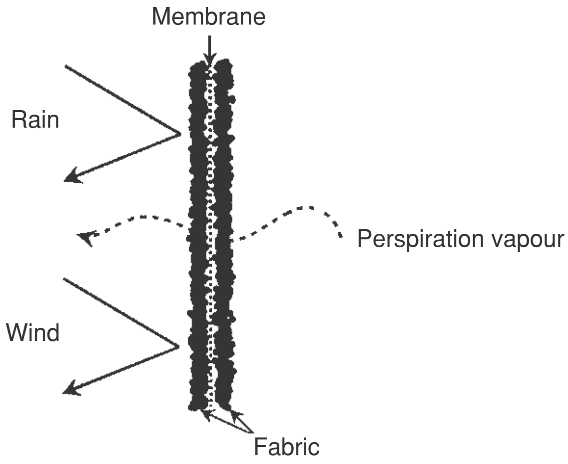
The use of very fine fibres and filaments and dense construction (sett) results in fabrics with very small pore size compared with conventional fabrics. Typical pore size for a waterproof fabric is about 10 µm compared with 60 µm for conventional fabric. Ventile fabric has a pore size of about 10 µm when dry and 3–4 µm when wet.[2] Fabric made from microfilaments is claimed to have up to 7000 filaments per centimetre. The author has estimated that the military variant of Ventile fabric has about 6000 fibres per centimetre.

12.2.2 Membranes

Membranes are extremely thin films made from polymeric material and engineered in such a way that they have a very high resistance to liquid water penetration, yet allow the passage of water vapour. A typical membrane is only about 10 µm thick and, therefore, is laminated to a conventional textile fabric to provide the necessary mechanical strength. They are of two types, microporous and hydrophilic.

12.2.2.1 Microporous membranes

The first and probably the best known microporous membrane, developed and introduced in 1976 by W Gore, is known as Gore-Tex (http://www.gorefabric.com). This is a thin film of expanded polytetrafluoroethylene (PTFE) polymer claimed to contain 1.4 billion tiny holes per square centimetre. These holes are much smaller



12.4 Schematic diagram of a typical membrane system.

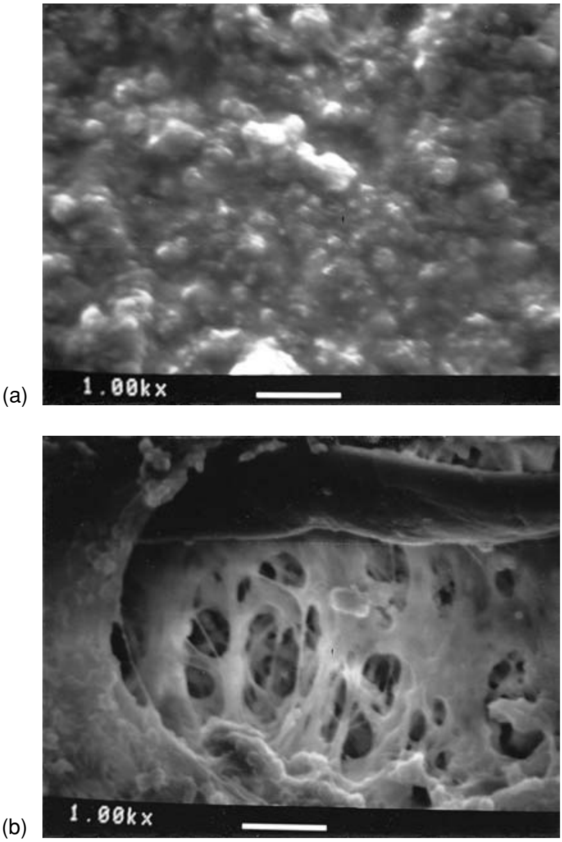
than the smallest raindrops (2–3 μm compared with 100 μm),[10] yet very much larger than a water vapour molecule (40×10^{-6} μm). Other manufacturers make similar membranes based on microporous polyvinylidene fluoride (PVDF) cast directly on to the fabric.[12] The hydrophobic nature of the polymer and small pore size requires very high pressure to cause water penetration. Contamination of the membrane by various materials including body oils, particulate dirt, pesticide residues, insect repellents, sun tan lotion, salt and residual detergent and surfactants used in cleaning have been suspected of reducing the waterproofing and permeability to water vapour of the membrane. For this reason microporous membranes usually have a layer of a hydrophilic polyurethane to reduce the effects of contamination.[11]

Figure 12.4 is a schematic diagram of a fabric incorporating a microporous membrane. Figure 12.5(a) is the polyurethane surface of the bicomponent microporous membrane and (b) shows the polyurethane layer partly removed to reveal the microporous fibrilar nature of the PTFE underneath.

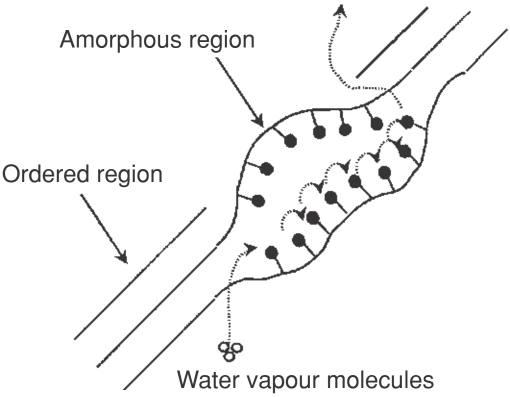
12.2.2.2 Hydrophilic membranes

Hydrophilic membranes are very thin films of chemically modified polyester or polyurethane containing no holes which, therefore, are sometimes referred to as non-poromeric. Water vapour from perspiration is able to diffuse through the membrane in relatively large quantities. The polyester or polyurethane polymer is modified by incorporating up to 40% by weight of poly(ethylene oxide).[2] The poly(ethylene oxide) constitutes the hydrophilic part of the membrane by forming part of the amorphous regions of the polyurethane polymer system. It has a low energy affinity for water molecules which is essential for rapid diffusion of water vapour.[1] These amorphous regions are described as acting like intermolecular ‘pores’ allowing water vapour molecules to pass through but preventing the penetration of liquid water owing to the solid nature of the membrane.

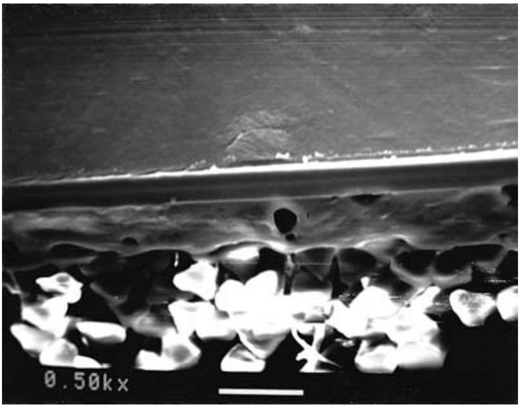
Figure 12.6 is a diagrammatic representation of the hydrophilic polymer vapour transport mechanism. Figure 12.7 is a scanning electron micrograph of a hydrophilic membrane.



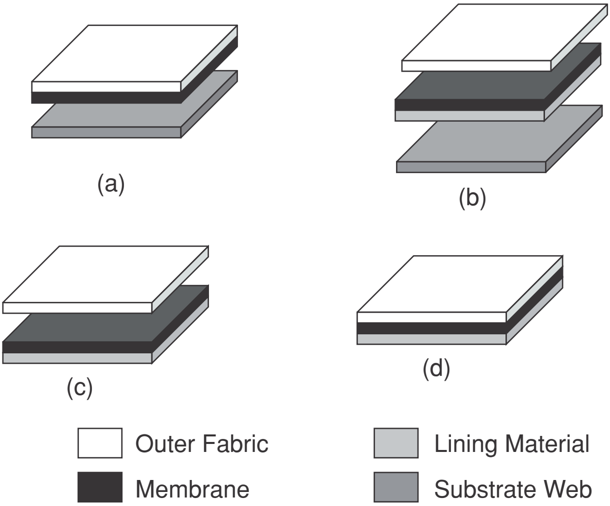
12.5 Scanning electron micrograph of microporous membrane. (a) Hydrophilic surface layer, (b) hydrophilic layer partly removed showing PTFE layer.



12.6 Schematic diagram of hydrophilic polymer mechanism.



12.7 Scanning electron micrograph of hydrophilic membrane.



12.8 Methods of incorporating membranes.

12.2.2.3 Methods of incorporation

Membranes have to be incorporated into textile products in such a way as to maximise the high-tech function without adversely affecting the classical textile properties of handle, drape and visual impression.[10] There are four main methods of incorporating membranes into textile articles. The method employed depends on cost, required function and processing conditions:[10]

1 Laminate of membrane and outer fabric (Fig. 12.8a) – The membrane is laminated to the underside of the outer fabric to produce a two-layer system. This method has the disadvantage of producing a rustling, paper-like handle with reduced aesthetic appeal but has the advantage of having very effective protective properties of wind resistance and waterproofing. This method is mainly used for making protective clothing.
2 Liner or insert processing (Fig. 12.8b) – The membrane is laminated to a light-

weight knitted material or web. The pieces are cut to shape from this material, sewn together and the seams rendered waterproof with special sealing tape. This structure is then loosely inserted between the outer fabric and the liner. The three materials (outer, laminate and lining) are joined together by concealed stitch seams. If high thermal insulation is required then the lightweight support for the membrane is replaced by a cotton, wool or wadding fabric. This method has the advantage of giving soft handle and good drape. The outer fabric can also be modified to suit fashion demands.

3 Laminate of membrane and lining fabric (Fig. 12.8c) – The laminate is attached to the right side of the lining material. The functional layer is incorporated into the garment as a separate layer independent of the outer fabric. This method has the advantage that the fashion aspects can be maximised.

4 Laminate of outer fabric, membrane and lining (Fig. 12.8d) – This produces a three-layer system, which gives a less attractive handle and drape than the other methods and, therefore, is not commonly used.

12.2.3 Coatings

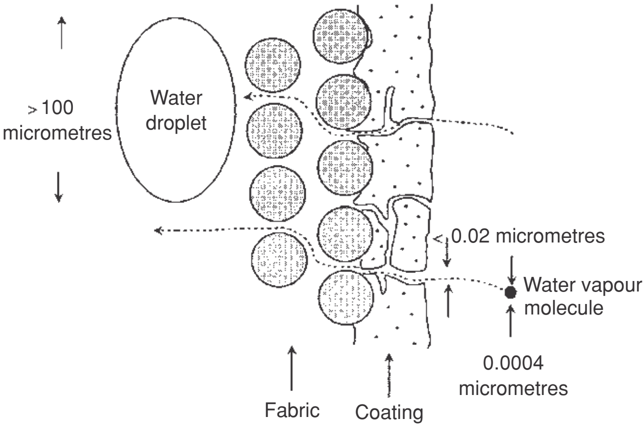
These consist of a layer of polymeric material applied to one surface of the fabric. Polyurethane is used as the coating material. Like membranes, the coatings are of two types; microporous and hydrophilic. These coatings are much thicker than membranes.

12.2.3.1 Microporous coatings

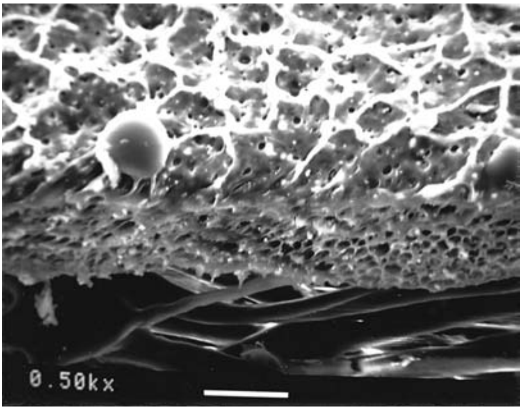
Microporous coatings have a similar structure to the microporous membranes. The coating contains very fine interconnected channels, much smaller than the finest raindrop but much larger than a water vapour molecule (Figs. 12.9 and 12.10).

Methods of production of microporous coatings have been described in differing detail in a number of publications.[2,10] Example recipes and processing conditions for producing microporous coatings have also been published.[10]

- *Wet coagulation*: Polyurethane polymer is dissolved in the organic solvent dimethyl formamide to produce a solution insoluble in water. This is then coated on to the fabric. The coated fabric is passed through a conditioning chamber containing water vapour. As the organic solvent is miscible with water, it is diluted and solid polyurethane precipitates. The fabric is then washed to remove the solvent, which leaves behind pores in the coating. Finally the coated fabric is mangled and dried. This method is not very popular as it requires high capital cost for machines and solvent recovery is expensive.
- *Thermocoagulation*: Polyurethane is dissolved in an organic solvent and the resulting solution mixed with water to produce an emulsion. The emulsion 'paste' is coated on to one side of the fabric. The coated fabric then goes through a two-stage drying process. The first stage employs a low temperature to remove the organic solvent, precipitating the polyurethane. The coating is now a mixture of solid polyurethane and water. The second stage employs a higher temperature to evaporate the water leaving behind pores in the coating.
- *Foam coating*: A mixture of polyurethane and polyurethane/polyacrylic acid esters are dispersed in water and then foamed. The foam is stabilised with the aid of additives. The foam is then coated on to one side of the fabric. The coated



12.9 Schematic diagram of a microporous coating.

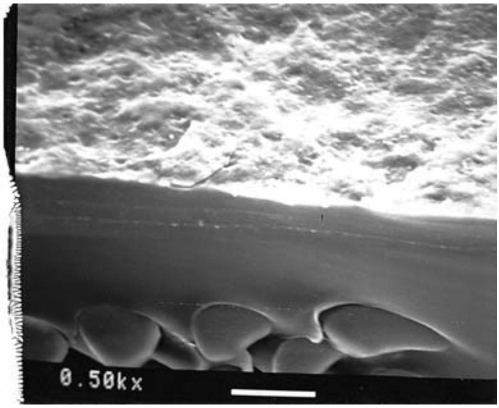


12.10 Scanning electron micrograph of a microporous coating.

fabric is dried to form a microporous coating. It is important that the foam is open cell to allow penetration of water vapour but with small enough cells to prevent liquid water penetration. The fabric is finally calendered under low pressure to compress the coating. As the foam cells are relatively large, a fluorocarbon polymer water-repellent finish is applied to improve the water-resistant properties. This type of coating production is environmentally friendly as no organic solvents are used.

12.2.3.2 Hydrophilic coatings

Hydrophilic coatings[11] (Fig. 12.11) use the same basic water vapour permeability mechanism as the hydrophilic membranes. The difference between microporous materials and hydrophilic materials is that with the former, water vapour passes through the permanent air-permeable structure whereas the latter transmit vapour by a molecular mechanism involving adsorption–diffusion and desorption.[11] These coatings are all based on polyurethane, which has been chemically modified by incorporating polyvinyl alcohols and polyethylene oxides. These have a chemical



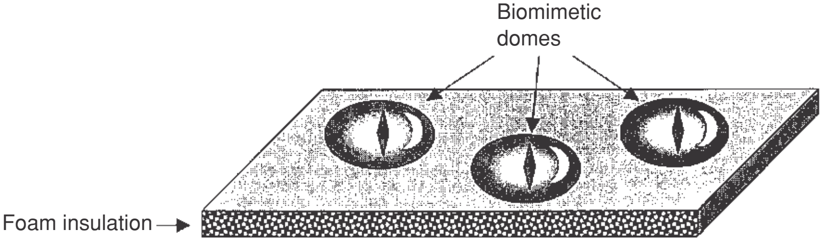
12.11 Scanning electron micrograph of a hydrophilic coating.

affinity for water vapour allowing the diffusion of water vapour through the amorphous regions of the polymer (see Fig. 12.5). The balance between hydrophilic and hydrophobic components of the polymer system has to be optimised to give acceptable vapour permeability, flexibility, durability and insolubility in water and dry cleaning solvents. Swelling of the membrane is encouraged to assist water vapour diffusion yet it also has to be restricted to prevent dissolution or breakdown in water or in the other solvents with which the polymer is likely to come into contact.[11] Poly(ether–urethane) coatings and membranes have excellent integrity. This can be conferred in two ways:

1 by a high degree of hydrogen bonding, principally between polar groups in the hydrophobic segments of adjacent polymer chains
2 by forming covalent crosslinks between adjacent polymer chains. The effective length and density of the crosslinks are variables affecting polymer swelling and thus vapour permeability.[11] Hydrophilic polyurethanes are discussed and formulations for the Witcoflex range of hydrophilic coatings are given by Lomax.[11]

12.2.3.3 Methods of applying coatings

The conventional method of applying coatings to fabric is to use direct application using the knife over roller technique.[10] The fabric is passed over a roller and liquid coating is poured over it. Excess liquid is held back by a 'doctor blade' set close to the surface of the fabric. The thickness of the coating is determined by the size of the gap between the blade and the surface of the fabric. The coated fabric is passed through a dryer to solidify the coating. Sometimes the coating is built up in several layers by a number of applications. In order to achieve thinner coatings and, therefore, more flexible fabric and to apply coating to warp knitted, nonwoven, open weave and elastic fabric, transfer coating is used. The liquid coating is first applied to a silicone release paper using the knife over roller technique. This is then passed through an oven to solidify the coating. A second coating is then applied and the textile fabric immediately applied to this. The second coating, therefore, acts as an adhesive. This assembly is passed through an oven to solidify the adhesive layer. The coated fabric is stripped from the release paper, which can be reused.



12.12 Stomatex biomimetic material.

12.2.4 Biomimetics

Biomimetics is the mimicking of biological mechanisms, with modification, to produce useful artificial items. The British Defence Clothing and Textile Agency instituted a three-year research programme to study natural systems which could be used to equip service personnel to survive a number of threats, one of which is weather and climate.[13] These workers consider that there is potential for improving the vapour permeability of fabric coatings by incorporating an analogue of the leaf stomata which opens when the plant needs to increase moisture vapour transpiration and closes when it needs to reduce it. They modelled an opening pore comprising flaps of two laminated materials with different moisture uptakes.

Biomimetics has now become a commercial reality. Akzo Nobel is marketing what they claim to be 'the most comfortable clothing and footwear systems in the world today', under the trade name of Stomatex.[14] This is closed foam insulating material made from neoprene incorporating a series of convex domes vented by a tiny aperture at the apex. These domes mimic the transpiration process that takes place within a leaf, providing a controlled release of water vapour to provide comfortable wear characteristics. Stomatex is claimed to respond to the level of activity by pumping faster as more heat is produced, returning to a more passive state when the wearer is at rest. Stomatex is used in conjunction with Sympatex, Akzo Nobel's waterproof breathable membrane, to produce a breathable waterproof insulating barrier for use in clothing and footwear (Fig. 12.12).

12.2.5 Market for waterproof breathable fabrics

In the UK alone there are about 800 000 climbers and walkers, many of whom require performance garments to protect them from the elements.[15] When Toray introduced Dermizax hydrophilic membrane laminated fabric in 1995 the initial sales volume was estimated as 300 000 m^2 rising to 1.2 million m^2 in three years.[16] Akzo state that 3 million jackets and coats were made from fabric containing Sympatex hydrophilic membrane in 1992.[17] D & K Consulting carried out a survey of the Western European market between November 1996 and July 1997.[18] The survey predicted that the market would grow to about 45 million linear metres per year by the year 2000. Since the beginning of the 1980s when the market started to expand rapidly almost 40 million m of waterproof breathable fabric have been used in Europe with a value of more than £270 million. Initially laminated fabrics dominated the market but coated fabrics had increased to 55% of the market by 1996. The UK market, accounting for more than 30% of the total European market, has been shown to be different from that of the rest of Europe. About 50% of the UK market is workwear/protective clothing and about 70% of fabrics are coated.

12.3 Assessment techniques

Assessment of the effectiveness of waterproof breathable fabrics requires measurement of three properties:

- resistance to penetration and absorption of liquid water
- wind resistance
- water vapour permeability.

12.3.1 Measurement of resistance to penetration and absorption of liquid water

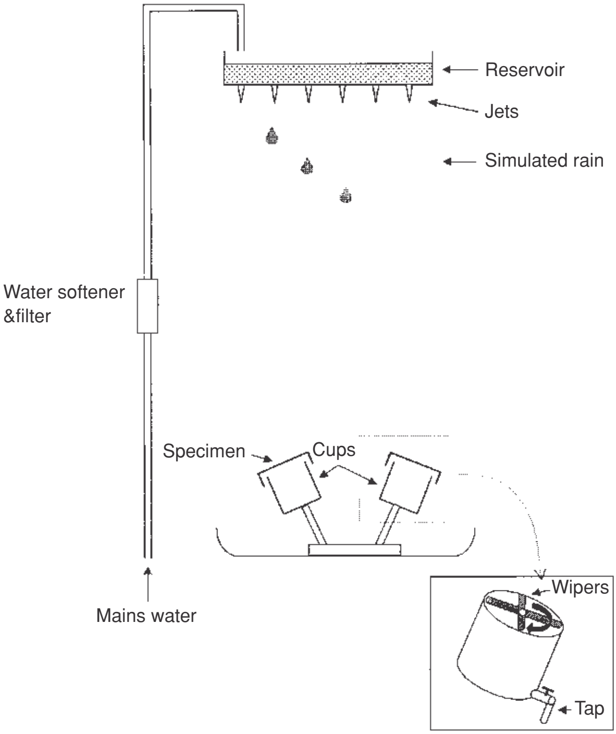
These measurements are conducted by two kinds of test, simulated rain tests and penetration pressure tests. The simulated rain tests include the Bundesmann rain tester, the WIRA shower test, the Credit Rain simulator and the AATC rain test. They simulate showers of rain, usually of relatively short duration, under controlled laboratory conditions.

12.3.1.1 Bundesmann rain tester

This apparatus and procedure was developed in 1935.[19] Water is fed from the mains through a filter and deioniser to an upper reservoir. The reservoir has a large number of jets of defined size in the base. The pressure of water in the reservoir causes water to flow out through the jets, which produce drops of simulated rain. Specimens of fabric are placed over four inclined cups and sealed at the edge. The cups contain rotating wipers, which rub the underside of the specimens, simulating the action of rubbing, which may occur in use due to the movement of the wearer. Any water penetrating the fabric collects in the cups which have taps so that the penetrated water can be run out and collected and its volume measured. The percentage of water retained by the fabric is also determined on a mass basis. The Bundesmann apparatus (Fig. 12.13) has been criticised on the grounds that it does not produce a realistic simulated shower.[20] Table 12.3 compares the drop sizes and velocities of the Bundesmann shower with different types of rain. It can be seen that the Bundesmann produces drops which have twice the diameter and, therefore, eight times the mass of drops in a cloudburst. The kinetic energy of the drops is 5.8 times the value for a cloudburst and 21 000 times the value of light rain. Owing to this criticism this apparatus fell into disuse but there has been sufficient renewed interest in it for it to be adopted for British, European and International standards.[21,22]

12.3.1.2 WIRA (Wool Industries Research Association) shower tester

A standard volume of water is placed in a funnel, which acts as a reservoir. The water flows slowly out of the funnel into a transparent reservoir with a perforated base made from PTFE. A filter paper is placed on top of the perforated base to slow down the flow of water through the perforations. The water then produces separate drops, which fall onto the fabric specimens placed a standard distance below the base of the reservoir. The fabric specimens are placed under tension over ribbed



12.13 Diagram of Bundesmann apparatus.

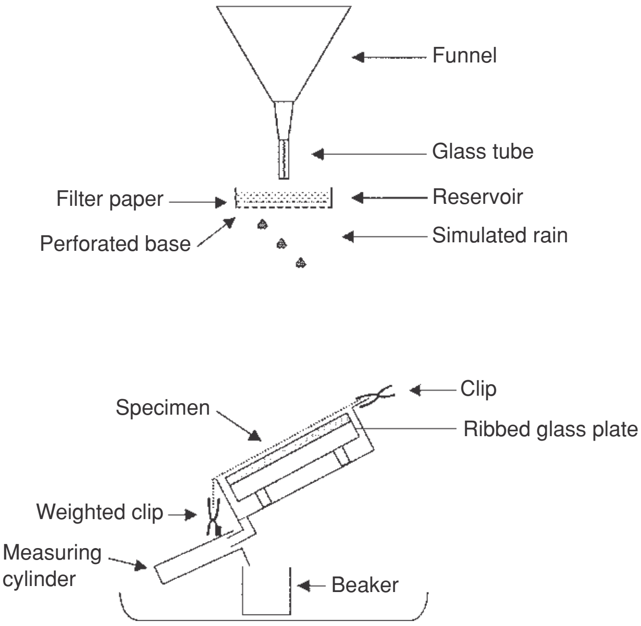
Table 12.3 Comparison of Bundesmann simulated shower and actual rain[20]

Type of drop	Diameter (mm)	Terminal velocity (cm s^{-1})	Kinetic energy (J × 10^{-6})
Cloud burst	0.30	700	346
Excessive rain	0.21	600	87
Heavy rain	0.15	500	22
Moderate rain	0.10	400	4.2
Light rain	0.045	20	0.095
Drizzle	0.02	75	0.0012
Bundesmann	0.64	540	2000

glass plates forming the top surface of an inclined box. Any water which penetrates the fabric runs down the ribbed plates into the box and then into a 10 cm^3 measuring cylinder. If the measuring cylinder becomes full it overflows into a beaker so that the total volume of penetrated water can be measured. The apparatus has been adopted as a British Standard[24] in which three results may be determined:

1 percentage absorption on a mass basis
2 the total volume of water that penetrates the fabric
3 the time taken for the first 10 cm^3 to penetrate.

Figure 12.14 is a diagram of the WIRA apparatus.



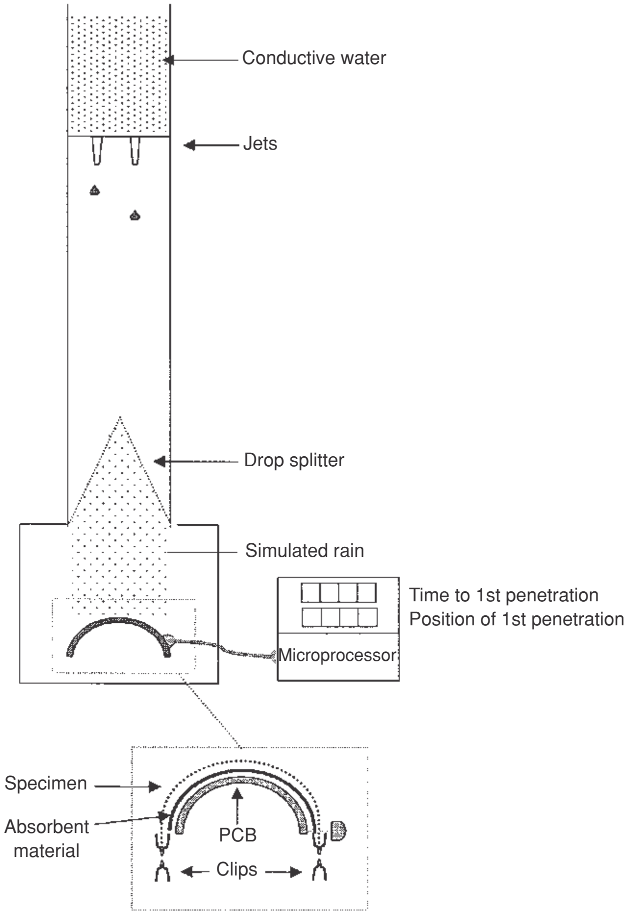
12.14 Diagram of WIRA simulated shower tester.

12.3.1.3 The Credit Rain Simulation tester

When waterproof fabric is made into garments, the seams can become the weak link unless properly constructed. The Credit Rain Simulator[24] was designed to test the effectiveness of seams. It consists of a small water reservoir, the base of which contains jets, which allow the water to flow out slowly forming drops of simulated rain. The drops hit a wire gauze 'drop splitter' which breaks the drops into random sized droplets. The seamed fabric specimen is placed over a semicylindrical printed circuit board (PCB) a standard distance below the base of the reservoir. The water is made electrically conductive by dissolving a small amount of mineral salt in it. Any water penetrating the seam completes an electrical circuit and a read-out indicates the elapsed time to penetration and locates the position of the penetration (Fig. 12.15).

12.3.1.4 AATCC (American Association of Textile Chemists and Colorists) rain test[25]

Many ASTM (American Society for Testing and Materials) fabric specifications[26] stipulate the use of this procedure for testing water penetration resistance. A column of water maintained at a constant height in a vertical glass tube is used to supply pressurised water to a horizontal spray nozzle containing a specified number of holes of specified size. The fabric specimen is placed vertically a specified distance in front of this nozzle backed by a slightly smaller piece of standard blotting paper. This specimen assembly is exposed to the standard spray for 5 min. The gain in mass of the blotting paper is an indication of the penetration of water through the fabric. The severity of the simulated rain can be altered by changing the height of the column of water to give pressures ranging from 60–240 cm water gauge. A complete overall picture of the performance of the fabric is obtained by determining:



12.15 Diagram of Credit Rain Simulator.

- the maximum pressure at which no penetration occurs
- the change in penetration with increasing pressure and
- the minimum pressure required to cause the penetration of more than 5 g of water, described as 'breakdown'.

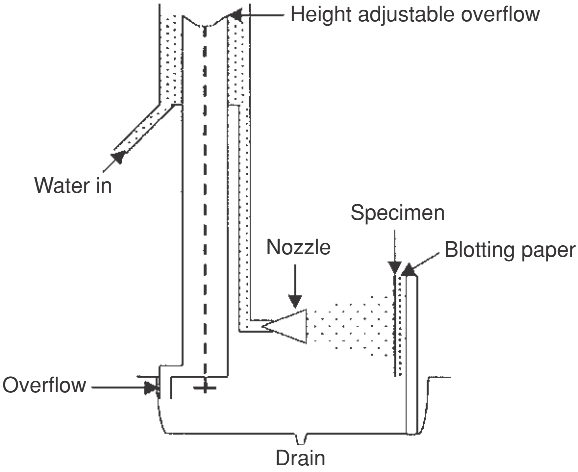
Figure 12.16 is a diagram of the AATCC rain test apparatus.

12.3.1.5 Penetration pressure tests

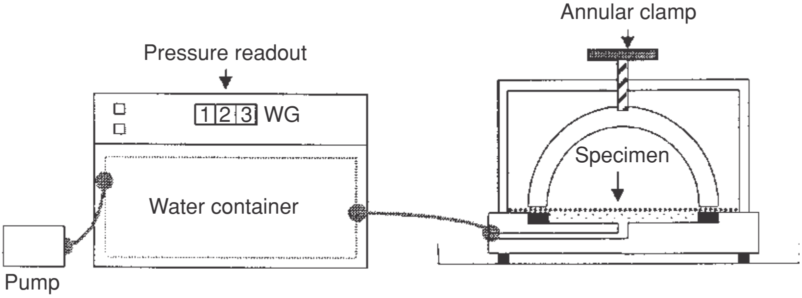
High performance waterproof fabrics are designed so that a high pressure of water is required to cause penetration and their effectiveness is usually measured on this basis. Tests can be carried out in two ways:[27]

- By subjecting fabric to water under pressure for a long period of time and noting if any penetration occurs
- By subjecting the fabric to increasing pressure and measuring the pressure required to cause penetration.

The British Standard[28] has adopted the second alternative. Fabric is placed over a recessed base filled with water so that the face exposed on the outside of the



12.16 Diagram of AATCC rain test apparatus.



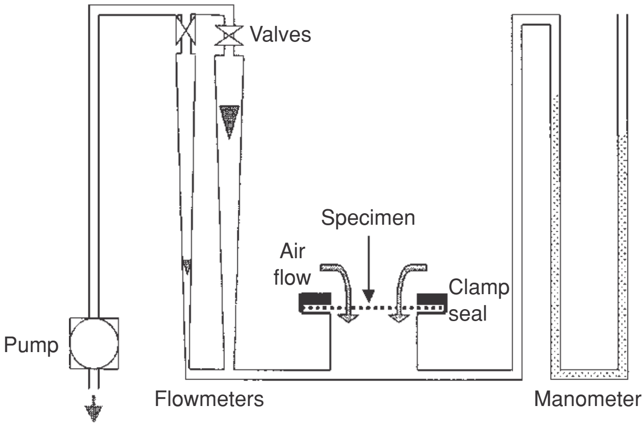
12.17 Diagram of hydrostatic head apparatus.

garment is in contact with the water. The fabric is clamped using an annular clamp. The recessed base is connected to a container of water. The pressure of the water is increased at a standard rate and the surface of the fabric is observed for signs of water penetration. Penetration pressure is determined as the pressure when the third penetration occurs, measured in centimetres water gauge.

Figure 12.17 shows a diagram of apparatus for determining penetration pressure.

12.3.2 Measurement of wind resistance

Before the development of modern waterproof breathable fabrics it was considered that vapour permeability was proportional to air permeability and could be used as a measure of breathability. This is not the case even for conventional woven fabrics. Also, theoretically, the air permeability of hydrophilic membranes and coatings should be zero. Wind resistance is usually assessed by measuring air permeability. This is the rate of air flow per unit area of fabric at a standard pressure difference across the faces of the fabric. Suitable apparatus consists of a pump to provide moving air, a manometer to establish standard pressure and flowmeters to measure



12.18 Typical air-permeability apparatus.

the rate of air flow. Several flowmeters with different ranges are usually incorporated to enable the instrument to deal with a wide range of fabrics (Fig. 12.18). The ASTM[29] procedure determines the volume rate of air flow per unit area of fabric in cubic centimetres per square centimetre per second. The British, European and International standard procedure[30] determines the velocity of air of standard area, pressure drop and time in millimetres per second. The velocity is calculated from measurements of volume rate of air flow. The standard pressure specified in the ASTM standard procedure is 125 Pa (12.7 mm water gauge) whereas that specified in the British Standard procedure is 100 Pa for apparel fabrics and 200 Pa for industrial fabrics. Results obtained using the two procedures are, therefore, not comparable. It must be pointed out that these are very low pressure differences and may not realistically simulate the pressure differences produced by actual wind.

12.3.3 Measurement of water vapour permeability

Techniques for measuring water vapour permeability can be divided into two types:

1. those which simulate sweating bodies and skin and which are mainly used for research work
2. those which are used for routine quality control, fabric development and marketing purposes.

Hong, Hollies and Spivak[31] consider that there are two approaches to measuring moisture vapour transfer:

1. Dynamic methods: these are concerned with moisture transfer prior to the time to reach equilibrium.
2. Equilibrium methods: these deal primarily with the moisture transfer after equilibrium has been established.

Hong *et al.* consider that short term dynamic moisture holds most promise for explaining wetness and moisture-related subject sensations in relation to the level of human comfort in clothing.

12.3.3.1 Research techniques

These are too large in number and too complex to review in detail here. They range from a thermoregulation model of the human skin for testing entire garments in which the microclimate in the vicinity of the skin can be reproduced,[32] through sweating hot plates with eight lines feeding water for simulated perspiration at different rates,[33] and the use of simulated skin made from wetted chamois leather,[31] to the adoption of highly sophisticated instrumental analysis techniques such as differential scanning calorimetry (DSC).[34]

Most research methods have been used to study ordinary non-waterproof woven and knitted apparel fabrics rather than waterproof breathable fabrics, although there is no reason why they cannot be used to study the latter. Similarly, standard routine methods have been used for research purposes.

12.3.3.2 Standard routine tests

The British and US standards all employ the same basic principle, which is an adaptation of the Canadian Turl Dish method.[35] A shallow impermeable dish is used to contain distilled water. The vapour evaporating from the surface of this water represents perspiration. The fabric specimen is placed over the mouth of the dish and sealed round the rim with a suitable impermeable, non-volatile material such as wax. An air gap is left between the surface of the water and the lower surface of the fabric to prevent them from coming into contact. It has been found that the size of this air gap has an influence on the results obtained below about 10–15 mm.[36] It is assumed that the relative humidity in the air space is 100%. The assembly is placed in a standard atmosphere for a length of time. A low-velocity current of air is passed over the upper surface of the fabric to remove the microclimate that develops as a consequence of water vapour passing through the fabric from inside the dish and that would otherwise suppress the passage of further vapour. The temperature of the water contained in the dish is the same as that of the atmosphere outside the dish. The loss in mass of the assembly after a certain time has elapsed is equal to the mass of water vapour that has passed through the fabric. Dolhan[36] compared several dish methods and concluded that none of them are appropriate for testing fabrics with hydrophilic coatings.

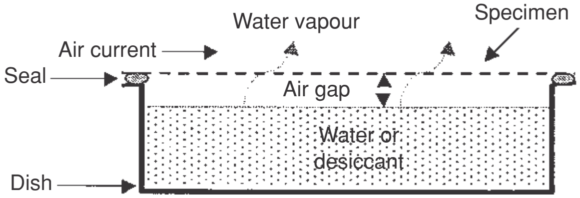
Figure 12.19 is a schematic diagram of the dish assembly.

12.3.3.2.1 ASTM methods

ASTM E96-80[37] is not specific to textile fabric. It is a standard for testing a range of materials where transmission of water vapour may be important. ASTM E96-80 includes two methods, one of which has two variants. The size and shape of the dish is not specified other than that it must have a minimum mouth area of 3000 mm^2.

In one method the dish is partly filled with desiccant, such as calcium chloride or silica gel so that the relative humidity inside the dish is very low. The specimen is placed over the mouth and sealed round the rim. The assembly is weighed at regular intervals until its mass has increased by a standard percentage. In this method, therefore, the water vapour is transmitted through the fabric from the outside atmosphere to inside the dish.

In the other method the dish is partly filled with distilled water, the fabric placed over the mouth and sealed round the rim. The assembly is weighed at regular intervals. Provision is made for the assembly to be inverted so that the water is in contact



12.19 British Standard and ASTM test assembly.

with the fabric during the test. This is intended for testing materials normally in contact with water during use. A graph is plotted of weight against elapsed time. The linear section of the graph represents nominally steady state conditions. The slope of this linear portion is used to calculate two results.

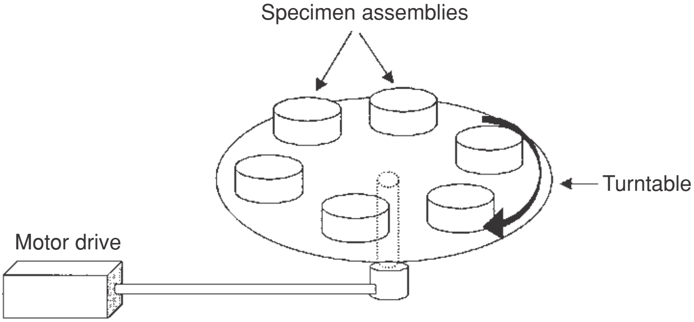
1 Water vapour transmission (WVT): this is the rate of water vapour transmission in grams per hour per square metre. It is an inherent property of the material tested (sic).
2 Permeance: this is the WVT rate per unit vapour pressure difference between the faces of the fabric in kilograms per pascal per second per square metre. It is a performance evaluation of the material and not an inherent property (sic).

As the standard allows for a wide range of test conditions such as dish shape and size, depth of water, depth of air space between water surface and fabric lower surface, atmospheric conditions, and so on, two laboratories will not necessarily obtain the same results for a given fabric sample. The only parameter specified is an atmospheric relative humidity of 50%. A temperature of 32.2 °C is recommended but not specified.

Many manufacturers quote the water vapour transmission rates of their products for marketing purposes but do not quote the test conditions employed. Therefore, it is difficult for customers to compare products from different manufacturers.

12.3.3.2.2 British Standard method

The British Standard[38] includes only one method and there is no choice of conditions as there is in the ASTM method. The impermeable dish of standard dimensions is partly filled with distilled water leaving a 10 mm gap between the surface of the water and the underside of the fabric. Sealant is placed on the rim of the dish and the fabric specimen is placed over it supported by wire to prevent it from sagging and touching the water. Several dishes are placed on a turntable rotating slowly to provide the air current which removes the microclimate above the fabric (Fig. 12.20). One hour is allowed for equilibrium conditions to develop and each assembly is weighed. The procedure is then continued for a period of at least 5 hours and the assemblies are reweighed. The procedure is carried out in a standard atmosphere of 20 +/− 2 °C and 65 +/− 2% relative humidity. From the mass loss of the specimen the WVP in grams per square metre per day is calculated. The WVP index is also determined. This is the WVP of the test fabric relative to the WVP of a standard reference fabric woven from high tenacity monofilament polyester and having a standard percentage open area.



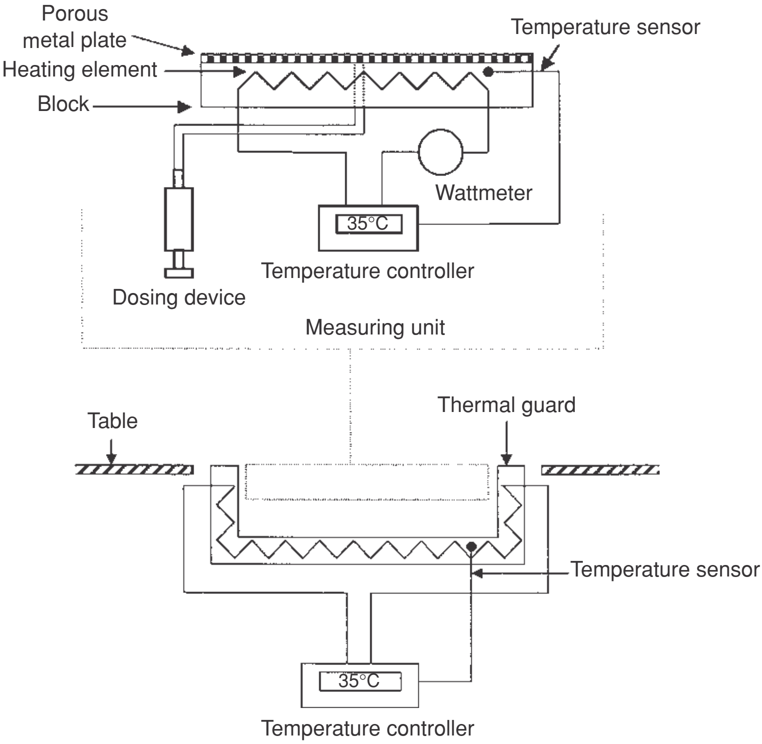
12.20 BS 7209 turntable system.

12.3.3.2.3 European and international standards

EN 31092[39] and ISO 11092[40] are identical. The apparatus and procedure are more complex than those used in the British and ASTM standards. The apparatus is described as a sweating guarded hotplate. In other words the apparatus simulates sweating skin. It consists of a two-layer metal block maintained at a temperature of 35 °C. The top layer of the heated block is porous and the top surface of the bottom layer contains channels allowing water to be fed into the porous layer. The upper face of the porous layer is covered in a cellophane membrane that is impervious to liquid water but permeable to water vapour. Water is fed to the porous plate and kept at a constant level by a controlled dosing device such as a motor driven burette. This maintains a constant rate of evaporation. The sides and bottom of the plate are surrounded by a heated guard allowing heat loss only from the top surface of the plate. The apparatus is used in an enclosure with the atmosphere controlled at 20 °C and 40% relative humidity. A current of turbulent air is passed over the top surface of the apparatus. The electrical power required to maintain the plate at 35 °C is measured (Fig. 12.21).

Two measurements of power consumption are made after steady state conditions have been obtained, one with and one without a fabric specimen covering the top surface of the plate. The difference between these two measurements is the heat loss from the fabric, which is also equal to the heat required to evaporate the water producing the vapour that passes through the fabric. As the latent heat of vaporisation of water is known, this equates to the mass of water vapour transmitted by the fabric. The two measurements are used to calculate three values related to water vapour transmission properties:

1 Water vapour resistance: this is the water vapour pressure difference across the two faces of the fabric divided by the heat flux per unit area, measured in square metres pascal per watt. As standard plate temperature and atmosphere temperature and relative humidity are used, the vapour pressure difference has a standard value.
2 WVP: this is the mass of water vapour passing through the fabric per unit area unit time, unit vapour pressure difference, measured in grams per square metre per hour per pascal
3 WVP index: this is the ratio of dry thermal resistance to water vapour resistance. A value of zero implies that the fabric is impermeable to water vapour and a



12.21 EN and ISO water vapour resistance apparatus.

value of one indicates that it has the same thermal and water vapour resistance of a layer of air of the same thickness. This WVP index is not the same as the index determined by the British Standard method.[38]

The apparatus can also be used to determine water vapour permeability characteristics under transient conditions and under different wear and environmental conditions but the standard only relates to steady state conditions.

Alternative definitions and explanations of water vapour transmission rate, water vapour resistance and resistance to evaporative heat flow have been given by Lomax.[11] The measurement of water vapour resistance in thickness units (mm) is explained. This is the thickness of a still air layer having the same resistance as the fabric. The use of thickness units facilitates the calculations of resistance values for clothing assemblies comprising textile and air layers.

12.4 Performance of waterproof breathable fabrics

Several research workers have compared the performance characteristics of different types of waterproof breathable fabrics. As Salz[41] points out,

> When it comes to waterproofing and comfort, an objective comparison is almost impossible. Many fabrics can withstand a hydrostatic head of 100 cm (9800 Pa) which makes them seem more than adequate for all but the most severe conditions. But are they? The vapour transmission rates are often difficult to

Table 12.4 Typical water vapour resistance of fabrics[11]

Fabric	WVR (mm still air)
Outer (shell) material	
Neoprene, rubber or PVC coated	1000–1200
Conventional PVC coated	300–400
Waxed cotton	1000+
Wool overcoating	6–13
Leather	7–8
Woven microfibre	3–5
Closely woven cotton	2–4
Ventile L28	3.5
Other Ventiles	1–3
Two-layer PTFE laminates	2–3
Three-layer laminates (PTFE, polyester)	3–6
Microporous polyurethane (various types)	3–14
Open pores	3–5
Closed pores	6–14
Hydrophilic coated, e.g.	
Witcoflex Staycool	
on nylon, polyester	9–16
on cotton/polyester	5–10
Superdry	6–14
on cotton, polyester/cotton	4–7
on liner fabric	3–4
Waterproof, breathable liners (coated and laminated)	2–4
Inner clothing	
Vests (cotton, wool)	1.5–3
Shirtings (cotton, wool)	0.8–3
Pullover (lightweight wool)	3–5

compare because of the variety of the test methods, but also because the conditions during the tests do not even remotely reflect the conditions of rainy weather for which the fabrics are designed.

Lomax[11] quotes the example of a two-layer PTFE laminate having a water vapour permeability of only 500 $g\,m^{-2}\,day^{-1}$ by one recognised method, whereas exactly the same test specimen can have a permeability of 20 000 $g\,m^{-2}\,day^{-1}$ by another method. This large difference is due to the difference in test conditions.

In standard water vapour permeability tests the inside of the cup is at the same temperature as the outside laboratory atmosphere (e.g. 20 °C), whereas in use, conditions inside the clothing will be at a temperature approaching 37 °C. When it is raining the outside relative humidity is likely to be near saturation rather than 50 or 65% as used in standards. Some water vapour resistance data on different types of outerwear fabrics obtained using a dish method are presented in Table 12.4 and compared with typical values for normal clothing layers.[11] The conditions under which the tests were carried out are not stated but the data are still useful for comparison purposes. In general the following conclusions can be drawn:

- Breathable materials are very much better than fabrics coated with conventional waterproof materials.

Table 12.5 Water vapour transport (WVT) through rainwear fabrics under different conditions[41]

Material	WVT ($g\,h^{-1}\,m^{-2}$)	
	Dry	Rain
Microporous PU coated fabric A	142	34
Microporous PU coated fabric B	206	72
Two-layer PTFE laminate	205	269
Three-layer PTFE laminate	174	141
Hydrophilic PU laminate	119	23
Microporous AC coated fabric	143	17
Microfibre fabric	190	50
PU coated fabric	18	4

- Breathable fabrics have a higher resistance to vapour transport than ordinary woven and knitted apparel fabrics but in some cases this difference is not very large.
- In a limited number of cases waterproof breathable fabrics have a lower vapour resistance than some ordinary apparel fabrics.
- The vapour resistance of breathable membranes and coatings is influenced by the fabric substrate to which they are applied.

Attempts have also been made to study performance under simulated 'actual' weather conditions rather than standard conditions.

Saltz[41] developed a laboratory method by using a heated cup method in combination with an artificial rain installation. The simulated rain tester combined mechanical action and wicking effects. The water in the cup was maintained at 36 °C and the water for the shower at 20 °C. The shower duration was one hour, much longer than standard simulated rain tests. A series of fabrics including two- and three-layer PTFE laminates, normal and microporous coated, hydrophilic polyurethane laminated, Ventile and microfibre, were tested under dry and rain conditions. The water vapour transport results are presented in Table 12.5.[41]

The authors make no attempt to carry out a general comparison of the various fabrics but it can be seen that the microporous coatings and laminates have higher vapour transport properties than the hydrophilic laminate. All are significantly higher than the normal coated fabric. The microfibre fabric has one of the highest values. It is concluded that rain has a major influence on vapour transport. In most cases wetting by rain reduces the vapour transmission rate. The two-layer PTFE laminate was an exception to this general rule, showing an increase in vapour transport when exposed to rain. This increase is claimed to be caused by the condensation of escaping water vapour on the reverse side of the fabric caused by the cooling effect of the rain. Thus, the air layer, which forms a vapour resistance in the dry test, is bridged in rain conditions. It is assumed that vapour transport in rain is influenced by the following factors:

- Microporous fabrics can become virtually impermeable in rain owing to blocking of the micropores by water.
- If the pores in the fabric are very small and highly hydrophobic, then blocking will not occur.

- Saturation of hydrophilic membranes with rain water can prevent the absorption of water vapour from the heated cup.

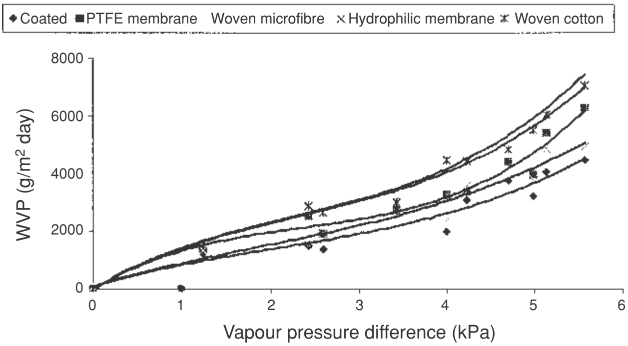
Although the best fabrics studies allowed water vapour transport of up to 200 $\text{g m}^{-2}\text{h}^{-1}$ in dry conditions, rain reduced the value of most fabrics to a maximum of 50 $\text{g m}^{-2}\text{h}^{-1}$. This may prove to be insufficient, particularly for persons working in strenuous conditions. The cooling effect of rain can cause condensation of the escaping vapour causing the wearer to become wet owing to backward wicking. Mechanical action, such as movement of limbs, was found to reduce the rain resistance of some microporous fabrics owing to the pumping action and wicking. Some fabrics requiring very high water penetration pressure when tested using a standard hydrostatic pressure test had a poor resistance rating compared with the other fabrics when exposed to simulated rain under mechanical action.

Holmes, Grundy and Rowe[42] studied the effect of atmospheric conditions on the water vapour permeability characteristics of various types of waterproof breathable fabrics. A modification of the BS 7209 was used. The water in the cups was maintained at a temperature of 37 °C by partial immersion in a water bath whose temperature was controlled by heating and cooling circuits. The whole assembly was placed in an environmental chamber to control the atmosphere outside the fabric at a range of temperatures and relative humidities. In general it was concluded that the fabrics could be ranked in decreasing order of vapour permeability as follows:

- Tightly woven:
  tightly woven synthetic microfilament
  tightly woven cotton
- Membranes:
  microporous membrane
  hydrophilic membrane
- Coatings:
  hydrophilic coating.

This rank agrees with Ruckman's rank[43] and the order in which Salz's results can be ranked.[41] It was found that atmospheric conditions have a considerable effect on vapour permeability, which can be much less than that measured under standard conditions. In fact, at high temperatures and relative humidities the vapour can pass from the outside atmosphere to the inside of the fabric. Water vapour permeability is a function of the vapour pressure difference between the two faces of the fabric. Vapour pressure is, in turn, a function of both temperature and relative humidity. The relationship between vapour permeability and vapour pressure difference is complex. The best fit is given by a third degree polynomial (i.e. $\text{WVP} = ax + bx^2 + cx^3 + C$, where a, b, and c are constants and x is the vapour pressure difference). The graphs of vapour permeability against vapour pressure differences are presented in Fig. 12.22.

The regression equations presented in Table 12.6 were used to predict the permeabilities of two fabrics at opposite ends of the performance spectrum under 'realistic' conditions. Such conditions are represented by the atmosphere inside the clothing at 37 °C and saturated with vapour, and the outside atmosphere relatively cold and also saturated, as may be found during rain, and at virtually zero as may be found at subzero temperatures. The total breathability of a suit made from



12.22 Water vapour permeability plotted against vapour pressure difference.

Table 12.6 Regression equations and correlation coefficients[42]

Fabric type	Regression equation	Correlation coefficient
Densely woven cotton	$Y = 1788x - 4401x^2 + 62.0x^3 - 25$	0.9876
Woven polyamide Hydrophilic PU coating	$Y = 929x - 194x^2 + 30.4x^3 + 58$	0.9325
Two-layer: woven polyamide Hydrophilic polyester membrane	$Y = 928x - 148x^2 + 25.5x^3 + 78$	0.9434
Three-layer: knitted polyamide Microporous PTFE membrane	$Y = 1856x - 580x^2 + 81.9x^3 - 38$	0.9703
Woven polyester microfilament	$Y = 1835x - 473x^2 + 68.8x^3 - 11$	0.9877

Y = water vapour permeability ($\mathrm{g\,m^{-2}\,day^{-1}}$); x = vapour pressure difference (kPa)

breathable fabric was estimated. The results are presented in Table 12.7. Comparing this data with published perspiration rates, it was concluded that the best fabric could not cope with activity beyond active walking with a light pack and the worst could not cope with activity beyond gentle walking.

Ruckman has published a series of investigations into water vapour transfer in waterproof breathable fabrics under steady state, rainy, windy, and rainy and windy conditions.[43–45] Twenty-nine samples of microfibre, cotton Ventile, PTFE laminated, hydrophilic laminated, polyurethane-coated and poromeric polyurethane-coated fabrics of differing weights per unit area and thickness were studied. A dish method was used in which the water in the dish was controlled at a temperature of 33 °C to simulate body temperature and with ambient temperatures ranging from –20 to +20 °C. It was found that water vapour permeability was influenced by ambient temperature, the permeability reducing as the ambient temperature decreased. There is very little difference between the various fabrics at low ambient temperatures although there is, in fact, a factor of about four between the lowest and highest. It is shown that the effect is caused by differences in vapour pressure difference between the faces of the fabric. Graphs of water vapour transmission (water vapour permeability per unit vapour pressure difference) show very complex behaviour possibly due to condensation on the inner surface of the fabric at ambient temperatures below 0 °C.

Table 12.7 Water vapour permeability under 'realistic' conditions[42]

	Temperature (°C)	Relative humidity (%)	Vapour pressure (kPa)	
Inside	37	100	6.28	
Outside	0	0	0.56	
	6	100		0.93
Vapour pressure difference between inside and outside atmospheres (kPa)			5.84	5.33
			Water vapour permeability (WVP) (g m^{-2} day^{-1})	
Vapour pressure difference (kPa)			5.33	5.84
Woven cotton fabric			6300	7080
Hydrophilic coated fabric			4200	4530
			Calculated Total WVP (g day^{-1})	
Woven cotton suit			15000	17000
Hydrophilic coated suit			10000	10900

The effect of windy conditions was studied by using a fan to produce a low turbulence current of air parallel to the face of the fabric.[44] Experiments were carried out using wind velocities between zero and 10.0 m s^{-1} and air temperatures between zero and 20 °C. It was found that wind increases the vapour permeability of the fabric by causing an increase in the vapour pressure difference across the fabric. The effect is greatest with the microfibre and cotton Ventile fabrics and increases as air temperature decreases. Condensation of water vapour at low temperatures reduces the rate of vapour transfer. It is suggested that careful consideration should be given to the suitability for intended end-use when selecting waterproof breathable fabrics for manufacture into sportswear and foul weather garments, especially garments to be used under windy conditions. In particular it should be taken into account that different types of product behave differently under windy conditions in terms of formation of condensation.

The effect of rainy and windy conditions was studied using the dish method, modified so that the specimen was held at an angle that allowed rain to run off but did not affect the hot plate controlling the water temperature.[45] Simulated rain at various temperatures was provided by a set of shower heads complying with the requirements of the AATCC standard rain test.[25] Experiments were carried out in rain, wind driven rain and prolonged rain. All fabrics continued to breathe under rainy conditions except microfibre fabrics which ceased to breathe in less than 24 hours of rain. Although no rain penetrated the fabrics, the cooling effect of rain caused condensation on the inner surface of the fabrics. This effect was the least with PTFE laminated fabrics.

The following conclusions were drawn:

1 Water vapour transfer in waterproof breathable fabrics decreases as rain temperature increases.
2 Waterproof breathable fabrics continue to breathe under rainy conditions. However, the breathability of most of them ultimately ceases after long exposure to prolonged severe rainy conditions.

The time of cessation of breathability can be ranked in the following increasing order:
- microfibre
- cotton Ventile
- poromeric polyurethane laminate
- PTFE laminate
- polyurethane coated
- hydrophilic laminate.

3 More condensation occurs on all fabrics under rainy conditions than under dry conditions except for PTFE laminated fabric.

4 The water vapour transfer rate is reduced under wind driven rainy conditions compared to that under rainy conditions for all fabrics owing to the effect of both rain and condensation.

Ruckman draws general conclusions from her extensive studies discussed above.[45] These are that water vapour transfer of breathable fabrics depends very much on atmospheric conditions. In general, wind increases and rain decreases the water vapour transfer rate of fabric, giving in descending order of water vapour transfer performance: windy, dry, wind driven rainy, rainy. The findings suggest that careful consideration should be given when choosing the appropriate waterproof breathable fabric for manufacture of sportswear and foul weather garments. The end-use envisaged for the garment and the environment it will be used in should always be taken into account.

The effect of subzero temperatures on the water vapour transfer properties of breathable fabrics has been studied by Oszevski[46] but was limited to the hydrophilic component of Gore-Tex II. The experiment was designed to simulate diffusion of water vapour through a clothing shell from a coating of ice on its inner surfaces as can occur when the fabric is used in very cold weather conditions. A procedure similar to the ASTM desiccant method[37] was used with one face of the fabric specimen in contact with or close to a block of ice. The experiments were carried out in an environmental chamber at various temperatures as low as –24 °C. It was found that the water vapour diffusion resistance increased exponentially as temperature decreased because the vapour pressure over ice has a very low value, thus creating a very low vapour pressure difference across the fabric. It is predicted that the diffusive flux of water vapour through the fabric at –10 °C will only be about 4% of its value at room temperature. It is speculated that the same is probably true of any hydrophilic rainwear fabric although high-tech waterproof materials should dry more quickly than non-breathable materials.

The effect of other garment layers and condensation in clothes systems incorporating waterproof breathable fabric has been studied by Gretton and co-workers.[47,48] Samples of every type of breathable fabric were used with a standard clothing system comprising a polyester lining fabric, a polyester fleece and a cotton jersey T-shirt fabric. A heated evaporative dish procedure based on BS 7209[38] was employed with ambient temperatures ranging from 5–20 °C and a constant relative humidity. The results obtained were confirmed by the use of field trials. It was found that condensation occurred at ambient temperatures below 10 °C. There are several mechanisms of condensation formation and dispersal within clothing systems. The mechanism involved depends on the type of breathable fabric, and fabric layers underneath also interact with the condensation and alter the transport properties of the clothing system.

A large amount of condensation accumulates in microporous coatings significantly impeding the transport of water vapour. Condensation cannot be removed easily from such coatings because the liquid water cannot travel through the pore network of the polymer. Hydrophilic coatings accumulate less condensation than the microporous coatings because liquid water is absorbed into and transported through the hydrophilic polymer without the need for re-evaporation. The high water content of the polymer caused by condensation plasticises and swells the polymer improving the water vapour transport at relatively high temperatures. However, low temperatures offset the benefits of plasticisation.

Condensation can occur within the pore structure of microporous PTFE membranes but the hydrophilic layer in the bicomponent versions reduces this to a small value and also prevents condensation forming on the surface. However, once condensation has occurred it is slow to re-evaporate. Laminated fabrics were found to perform better than coated fabrics under cold ambient conditions, transmitting more water vapour and preventing condensation from forming for a longer period of time.

The presence of a lining fabric was found to influence the manner in which the waterproof breathable fabric dealt with condensation. Lining fabrics actively drawing condensation away from microporous polymers improve the vapour transport properties, whereas linings not drawing condensation away provide an improvement in vapour transport of hydrophilic polymers.

The incorporation of other clothing layers reduced the vapour transport properties of the breathable layer. This is claimed to be because the additional insulation maintains the inner layer of the breathable at a relatively low temperature, reducing the vapour driving force across it and the mobility of its polymer molecules. During physical activity that produces sensible perspiration, removal of an insulating layer, such as a fleece garment, should improve the comfort of the clothing system by increasing the temperature of the breathable layer, improving its vapour transport and reducing condensation. The use of a laminated fleece (presumably meaning the wind-resistant type) promoted the formation of condensation on the fleece and the waterproof breathable layer owing to restriction of ventilation within the clothing system. This severely reduced the thermal insulation of the fleece. It was found possible for a fleece fabric to deal effectively with condensation if the pile is worn facing inwards towards the body so that condensation was transported away from the body into the knitted backing of the fleece fabric. Like other research workers,[45] Gretton[48] concludes that assessment of waterproof breathable fabrics in isolation using standard test methods does not give a true indication of their performance in actual wear situations. It is important to assess the transport properties of performance clothing systems as a whole entity under the range of ambient conditions the garments are likely to experience in use.

Gretton *et al.*[49] also carried out a study of simulated clothing systems using a wider range of under layer fabrics than the 'standard' described above. The full range of under layer fabrics was: woven lining, double-sided fleece, lightweight double-sided fleece, single-sided fleece, laminated fleece, honeycomb knitted under layer and single jersey T-shirt fabric. The fibre content was 100% polyester except for the T-shirt, which was cotton. The 'standard' clothing layer reduced the moisture vapour transmission rate of the breathable outer layer samples by 14%. The effect

Table 12.8 Water vapour permeabilities of membranes under different conditions[51]

Membrane type	Water vapour permeability ($g\,m^{-2}\,day^{-1}$)	
	dry	wet
Microporous PTFE	4000	3200
Hydrophilic	4400	4300

was the same on microporous and hydrophilic polymers. It was found possible to predict the water permeability index of a multiple layer clothing assembly from the indices of the individual layers using Equation (1):

$$\text{Multiple layer \% MVP} = \frac{\text{T-shirt \% MVP}}{100} \times \frac{\text{fleece \% MVP}}{100} \times \frac{\text{lining \% MVP}}{100} \times \text{outer fabric \% MVP} \qquad (1)$$

where MVP is the moisture vapour permeability.

Marxmeier[50] carried out a limited study on the effects of wetting on breathable materials. Only two membranes were used, a microporous PTFE type and a hydrophilic type. Tests were carried out on the membranes alone so as to exclude the influence of textile fabric and lamination method. A dish method was employed with the water at a temperature of 37 °C and the ambient atmosphere at 25 °C and 50% relative humidity. Two experiments were carried out, one with the membrane dry and the other with the membrane covered in a continuous film of water. This was achieved by covering the membranes with porous water absorptive polyester fabric with its ends dipped into reservoirs of water at 25 °C. The results obtained are presented in Table 12.8.

Under dry conditions there is little difference between the permeabilities of the membranes. However, under wet conditions the permeabilities of the membranes were reduced, that of the hydrophilic type by only a small amount, but that of the microporous type was reduced dramatically. The difference in behaviour is explained with reference to the mechanism of vapour transport. The water swells the hydrophilic membrane, increasing its diffusion coefficient, whereas the PTFE microporous membrane is hydrophobic. The swelling compensates for the reduction in partial vapour pressure difference across the fabric caused by the presence of water. It is concluded that hydrophilic membranes have an advantage over microporous membranes under aggravated conditions. It is also stated that hydrophilic membranes have advantages in terms of after care (dry cleaning) and durability (abrasion resistance).

Water penetration can occur at points on garments subjected to pressure loading (for example, at knees or elbows, by rucksack straps, carrying handles and so on). In adverse circumstances pressures of 10 bar can occur. This is particularly important when the membrane material is to be used in gloves and footwear. In footwear especially, high loading is a necessary consequence of a good fit. Creases at the toe and heel are a problem. Uedelhoven and Braun[51] built a modified hydrostatic head apparatus enabling them to test breathable materials under pressure loading. They tested 24 materials including PTFE and polyester membranes alone and in two- and three-layer constructions, as well as polyurethane coatings. It was found that the microporous PTFE membranes had the highest pressure resistance of over 20 bar and the polyurethane materials had the lowest at only 0.5 bar. It was also found that repeated pressure loading reduced the water penetration pressure of all the materials significantly. The general conclusion drawn was that hydrostatic penetration resistance depends, not only on the membrane material, but also especially on the construction of the finished garment. Apart from better protection from damage, lamination onto woven or knitted fabric enables hydrostatic pressure resistance to be significantly improved. Inappropriate laminate construction can have an adverse influence on hydrostatic pressure resistance, especially with repeated cycles of pressure loading.

Most studies on the performance of waterproof breathable fabrics concentrate on the vapour permeability characteristics. Weder[52] carried out an extensive study of the performance of breathable rainwear materials with respect to protection, physiology, and durability. Twenty-three samples of waterproof breathable fabrics from the following categories were tested:

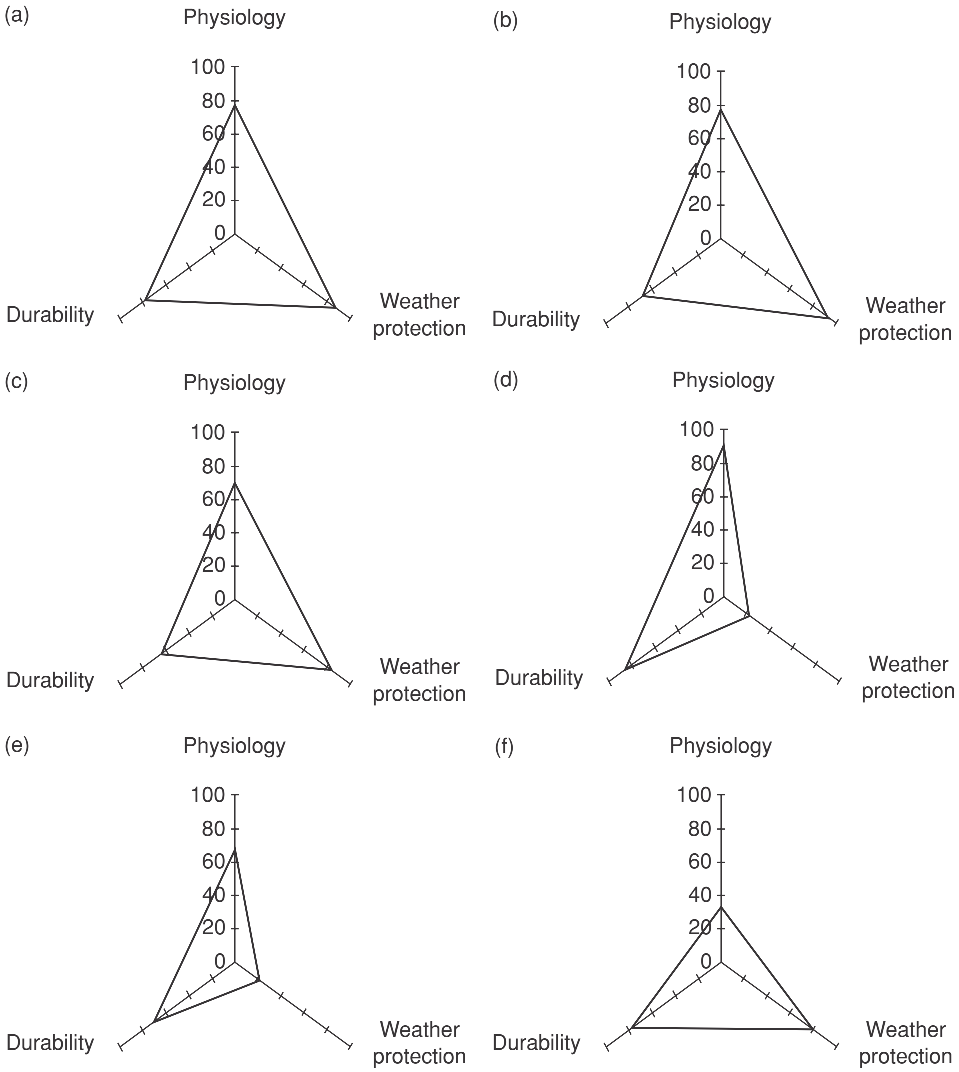
- PU coatings
- PTFE membranes
- PES membranes
- cotton Ventile

A non-breathable PVC-coated fabric and an ordinary polyester apparel fabric were included for comparison. The samples were subjected to a large number of simulated performance tests including:

- vapour permeability
- rain resistance
- water pressure resistance
- wind resistance
- mechanical strength
- abrasion resistance
- effect of mechanical pressure
- effect of wind on water penetration resistance
- effect of laundering
- effect of diagonal pulling
- effect of weathering
- effect of flexing
- effect of low temperatures
- occurrence of condensation
- effect of thorn pricking
- drying behaviour
- complete jacket tests.

Not every possible combination of sample and test was discussed in detail. The various categories of sample were compared by constructing three-dimensional plots of weather protection, physiology and durability to give what is described as 'cobweb diagrams' (radar diagrams). These are reproduced in Fig. 12.23.

It is concluded that:



12.23 Attributes of different types of breathable and conventional fabrics.[52] (a) PTFE laminate, (b) PES laminate, (c) PU coating, (d) PES/cotton blend, (e) Ventile, (f) PVC coating.

1 There was no significant overall difference between the various categories of breathable fabric.
2 The main parameter contributing to durability is the outer material to which the waterproof polymer is attached.
3 It makes no sense to design leisurewear that is used only occasionally to meet the same rigorous standards as professional clothing.
4 Polyurethane coatings have better resistance to mechanical damage than PTFE and PES laminates.
5 Almost all the samples had sufficient to good vapour transport properties but ventilation openings in garments are important because the vapour perme-

ability capabilities of the fabrics are not sufficient for moderate physical activity.

6 Correct manufacture of the final product is as important as the properties of the fabric for water penetration resistance.

7 The question 'which product performs the best' cannot be answered. The conditions of application and corresponding requirements imposed on a product are quite different.

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