

6.1 Introduction

6.1.1 Historical perspective

The drawing of glass into fine filaments is an ancient technology, older than the technology of glass blowing. Winding coarse glass fibres onto a clay mandrel was used as an early manufacturing route for a vessel. With the advent of glass blowing, similar fibre technologies were used to decorate goblets.

In the 1700s, Réaumur recognised that glass could be finely spun into fibre that was sufficiently pliable to be woven into textiles. Napoleon's funeral coffin was decorated with glass fibre textiles. By the 1800s, luxury brocades were manufactured by co-weaving glass with silk, and at the Columbia Exhibition of 1893, Edward Libbey of Toledo exhibited dresses, ties and lamp-shades woven from glass fibre.

The scientific basis for the development of the modern reinforcing glass fibre stems from the work of Griffiths,¹ who used fibre formation to validate his theories on the strength of solids.

Glass fibres are used in a number of applications which can be divided into four basic categories: (a) insulations, (b) filtration media, (c) reinforcements, and (d) optical fibres.

6.1.2 Fibreglass for insulation and filtration

For insulation, the thermal conductivity or sound transmission ability of a fibrous 'wool' is of the most importance. Clearly, the thermal performance will be directly related to the low thermal conductivity of the glass itself but also to the density of the material. In other words, the entrapped air provides the insulating properties but the fibres provide the supporting structure. The efficiency of air entrapment is determined by the fibre diameter and its configuration, which is a function of the fibre spinning technique.

Table 6.1 Typical compositions (in weight %) for glass fibres used for thermal and acoustic insulation¹

	Typical mineral or slag wool	Typical fibre glass insulation	Typical high- temperature grade
SiO ₂	50	63	50
Al ₂ O ₃	10	} 6	} 40
Fe ₂ O ₃	1		
CaO	25	7	6
MgO	14	3	4
Na ₂ O	—	14	—
K ₂ O	—	1	—
B ₂ O ₃	—	6	—
F ₂	—	0.7	—

For filtration, the surface area of the fibres and the size of the spaces between them are the important factors. A number of spinning techniques have been developed, to produce fibres with a range of diameters from 0.05–25 µm. The finest diameter fibres provide the most insulation and filtration effectiveness² as a result of the pore size of the mat.

Fibre spinning for insulation and filtration materials can be achieved by flame attenuation, developed by Owens-Corning Fiberglass in the late 1940s, and the improved Toration process. Steam fiberisation was the basis of the mineral wool process which operated in the 1930s in Toledo, Ohio. This was adapted for glass, in the steam-blown process, which uses high-pressure steam jets below a tank of molten glass to attenuate the glass drops falling from the bushing into fibres. Subsequent techniques involve the free fall of a glass melt onto a fiberising roller (spinning process), air jet (rotary process), or spinning drum (Schuller). In all of these, the fibres are bound into a ‘wool’ or mat with a phenolic resin binder. The glass source can be a cupola or tank of glass melt above a bushing (in later techniques) or precast marbles, which are melted directly above the bushing. These historical developments are discussed in detail by Mohr and Rowe.²

The formulations for the glasses are shown in Table 6.1.

6.1.3 Reinforcing fibres

For reinforcements, it was recognised by Griffiths¹ that the strength of any material was determined by the presence of flaws of critical dimension. Glass was an obvious material for demonstrating that increasing the surface to volume ratio would lead to increased strength, by reducing the number of flaws of critical dimension. Thus, high strength materials will be filamentary of fine diameter.³

Furthermore, within a bundle of fibres, the individual filaments will have differing strengths, giving rise to progressive failure that can be harnessed in the formation of a composite material. The Young's modulus of inorganic glass is about 20 times that of the polymer resin that holds the fibres together as a composite (originally referred to simply as 'fibreglass' or glass fibre-reinforced plastic). The development of so-called advanced composites occurred with the discovery of high-strength and high-modulus carbon fibres in 1965.⁴ However, reinforced materials had been known since biblical times. The best way of comparing the performance of differing fibres (and of their composites) is through their specific stiffness and strength E_f/ρ and σ_{fu}/ρ , where E_f is the Young's modulus of the fibre, σ_{fu} the strength of the fibre and ρ the density. As shown in Table 6.2, the specific strength of glass fibres is significantly higher than that of conventional bulk materials. However, even after dilution with a resin to give composites of fibre volume fraction 35–60% there is still an advantage in specific strength and specific stiffness for structural applications, especially where low weight, high strength and high stiffness are critical design parameters.⁵ Another advantage is their corrosion resistance.⁶ This chapter will describe their fabrication, properties, applications and performance.

6.1.4 Optical fibres^{7,8}

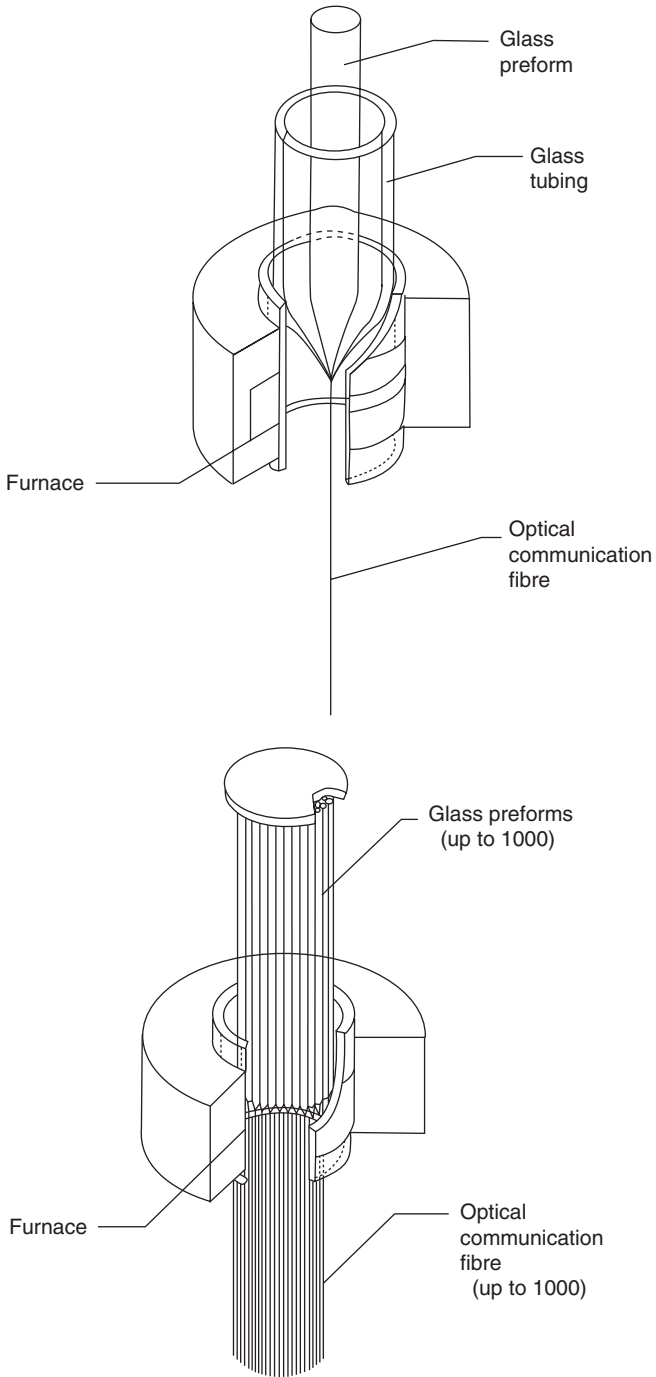
Optical fibres can be made from polymeric (e.g. polymethyl methacrylate) and inorganic glasses. The latter have initiated a revolution in information technology, because they are an effective means of transmitting digitalised data as an electromagnetic wave. Clad optical fibres allow transmission over many kilometres without the need for signal boosting. The high frequency of optical signals allows a bandwidth of 10^5 MHz, permitting significantly higher data capacity than conventional copper cables, while appropriate fibre design allows signal dispersion to be minimised.

Most commercial optical fibres consist of a silica glass core-clad structure, made as a bulk preform and drawn down into an optical fibre of diameter 125 μm , as shown in Fig. 6.1. Ge, P and B are introduced as dopants to give the required refractive index profile, *viz* a core of approximately 8 μm diameter with a refractive index enhancement of 0.001 to give a monomode fibre. The efficiency of light transmission depends on the wavelength of light employed. Pure fused silica has low loss windows at 1.3 and 1.5 μm with transmissions down to 0.2 dB km⁻¹ and possible transmission distances of hundreds of kilometres. In the near-UV, this increases to >10 dB km⁻¹. Chemical vapour deposition (CVD) techniques allow the manufacture of preforms with the required refractive index profile and purity levels of better than 0.1 ppb for critical absorbing transition metal impurities. Wide

Table 6.2 Specific properties of glass and other fibres in comparison to other materials

	E (GPa)	σ_u (GPa)	ρ (g/cm ³)	E/ρ (M/m)	σ_{tu}/ρ (km)	ϵ_u (%)	d_f (μm)
E-glass fibre	72	1.5-3.0	2.55	2.8-4.8	58-117	1.8-3.2	10-20
S-glass fibre	87	3.5	2.5	3.5	140	4.0	12
S2-glass fibre	86	4.0	2.49	3.5	161	5.4	10
Carbon fibre	220-350	2.3-3.7	1.8-2.0	12-18	130-190	0.7-1.7	7
High-performance polymer fibres:	60-180	2.65-3.45	1.44-1.47	4.0-12.2	180-235	4-1.9	12
Aramid	250	2.4	1.5	17.0	160	1.0	20
PBT	60-120	1-3	1.0	6-12	100-300	—	—
PE	210	0.34-2.1	7.8	2.7	4.3-27	—	—
Steel	70	0.14-0.62	2.7	2.6	5-22	—	—
Aluminium	60	0.05-0.07	2.6	2.3	1.9-2.7	0.08-0.12	—
Bulk glass	2-3.5	0.05-0.09	1.2	0.16-0.29	4-7.5	1.5-6	—
Resins (epoxy)	1.3	0.027	0.96	0.135	2.8	—	—
High-density polyethylene (PE)							

E = Young's modulus, σ_u = tensile strength, ρ = density, E/ρ = specific modulus, σ_u/ρ = specific strength, ϵ_u = failure strain, d_f = fibre diameter.



6.1 Schematic of single and multimode optical fibre forming (after Mohr and Rowe²).

core, multimode optical fibres have been developed where fibres of high numerical aperture are needed, such as for image transmission in medicine. The latter fibres are unsuitable for telecommunications because of the signal dispersion that arises from the many possible light paths.

Recent advances have concentrated on rare earth doping to produce fibre lasers for optical amplification, fibres with Bragg reflection gratings built into their core for signal multiplexing, and both fluoride and chalcogenide glasses that have extended infrared transmission and enhanced amplification characteristics.

6.2 Glass for fibres

6.2.1 Formulations

These inorganic glasses are all based on silica, because it is an excellent glass former. Polymerisation means that $(\text{SiO}_{4/2})_n$ three-dimensional networks form which do not have a sharp melting point and which start to soften at 1200 °C but are not fluid enough for spinning as fibres until they reach 2000 °C. When silica crystallises, it forms networks made up of cyclic groups such as $(\text{Si}_6\text{O}_{18})^{12-}$ containing 6 SiO_4 tetrahedra, sharing corners, and as embodied in crystalline forms of SiO_2 such as tridymite and cristobalite. Smaller rings occur in various silicate minerals and probably contribute to the disorder present in vitreous silica. Further additives are introduced to reduce the melting temperatures needed for these glasses. Al_2O_3 and B_2O_3 are present in significant concentrations and act as network formers, i.e. are built into the silica network as tetrahedra, as found, for example, in the mineral albite, $\text{NaAlSi}_3\text{O}_8$. These oxides are oxygen deficient compared with silica. Consequently, there will be some oxygen ions in the network with unsatisfied charges. Neutrality can be achieved by incorporating so-called network modifiers such as CaO , BaO , Na_2O or K_2O . Such modifier ions are located near the unsatisfied oxygen ions in the interstices in the network. At higher concentrations they can also start to break up the network, forming non-bridging oxygens. Such alkali boroaluminosilicate glasses can form stable glasses that can be spun at temperatures between 1300 and 1600 °C and have high chemical durability.

Intermediate oxides such as MgO and TiO_2 can be found in both locations described above, i.e. as network formers or modifiers. This is a brief description of glass chemistry and the reader is referred to a fundamental text.⁹

Na^+ and K^+ are relatively mobile and therefore will contribute to the electrical conductivity of the glass. Only at high temperatures is the bulk conductivity significant, but surface conductivity can occur at ambient conditions. The volume resistivity of A-glass, which is an alkali glass, is $10^{10} \Omega\text{m}$. E-glass was developed principally for its good electrical properties

Table 6.3 Typical fibre-forming E-glass compositions¹⁰

Constituent	Weight %
SiO ₂	52–56
Al ₂ O ₃	12–16
B ₂ O ₃	5–10
TiO ₂	0–1.5
MgO	0–5
CaO	16–25
Na ₂ O + K ₂ O	0–2
Fe ₂ O ₃	0–0.8
F ₂	0–1

(10¹⁵ Ωm) but it has become the universal glass for fibre reinforcement as a consequence of its excellent chemical durability.

More than 99% of continuous glass fibres are spun from an E-glass formulation. A typical range of formulations is given in Table 6.3. A-glass is an economically attractive alternative because it utilises plate glass scrap, made in a remelt process rather than the direct melt process, but the fibres only have half the strength of E-glass. However, E-glass is not resistant to acid or alkalis, and a chemically-resistant C-glass is available for use in applications where acidic environments are met. C-glass is also used as an alternative to E-glass in the reinforcement of bitumen for roofing mat. In practice, E-glass dominates because of the scale of manufacture.¹⁰

The range of compositions of other specialist glasses is given in Table 6.4. For high-strength composites, S-glass (Owens-Corning Fiberglass) and R-glass (Vetrotex), which have similar compositions, are used. However, the high cost of manufacture means that they are only used where this can be justified, e.g. in aerospace, military components and specialist sports equipment.

*Cemfil*¹¹ and *AR*¹² glass are alkali resistant and were developed for the reinforcement of cement and related products. *Cemfil* was originally developed from the glass composition identified by Majumdar¹¹ and commercialised by Pilkington Fibreglass. This has now been transferred to Vetrotex who have also utilised the acid-resistance of the *AR* glass formulation to spin a universal chemically-resistant fibre glass called *Chem Glass*, principally to compete with the chemically resistant E-glass (*ECR*) developed by Owens-Corning. *ECR* glass was a result of the continued developments in formulations for E-glass fibre given in Table 6.5. Commercialisation was prompted by the observation of environmental-stress corrosion cracking of GRP (glass fibre-reinforced plastic) in late 1970s, when demanding corrosion-resistant applications (such as chemical plant and sewer pipes) were being explored.

Table 6.4 Compositions (in weight %) of typical glasses for fibres, with some properties (after Loewenstein¹⁰ and Jones⁵)

Constituent or property	E	ECR	C	A	S	R	Cemfil ¹¹	AR ¹²	AR
SiO ₂	55.2	58.4	65	71.8	65.0	60	71	60.7	61
Al ₂ O ₃	14.8	11.0	4	1.0	25.0	25	1	—	0.5
B ₂ O ₃	7.3	0.09	5	—	—	—	—	—	—
ZrO ₂	—	—	—	—	—	—	16	21.5	13.0
MgO	3.3	2.2	3	3.8	10.0	6	—	—	0.05
CaO	18.7	22.0	14	8.8	—	9	—	—	5.0
ZnO	—	3.0	—	—	—	—	—	—	—
TiO ₂	—	2.1	—	—	—	—	—	—	5.5
Na ₂ O	0.3	—	8.5	13.6	—	—	11	14.5	—
K ₂ O	0.2	0.9	—	0.6	—	—	—	2.0	14.0
Li ₂ O	—	—	—	—	—	—	—	1.3	—
Fe ₂ O ₃	—	0.3	0.26	0.3	tr	—	tr	—	—
F ₂	0.3	—	—	—	—	—	—	—	—
Liquidus temp. ^a (°C)	1140	—	—	1010	—	—	1201	1172	—
Fiberising temp. ^b (°C)	1200	—	—	1280	4.7	4.5	1470	1290	—
Single fibre tensile strength at 25°C, (GPa)	3.7	3.4	3.4	3.1	—	—	2.9	—	2.5
Single fibre tensile modulus (GPa)	76.0	73.0	—	72.0	86.0	85.0	—	—	80
Density, (g/cm ³)	2.53	2.6	2.49	2.46	2.48	2.55	—	2.74	2.74
Refractive index <i>n_D</i>	1.550	—	—	1.541	1.523	—	—	—	1.561
Coefficient of linear thermal expansion (10 K)	5.0	—	7.1	9	2.85	4.10	—	—	—
Volume resistivity (Ωcm)	10 ¹⁵	—	—	10 ¹⁰	10 ¹⁶	—	—	—	—
Dielectric constant at 25°C and 10 ¹⁰ Hz	6.11	—	—	—	—	—	—	—	—
Loss tangent at 25°C and 10 ¹⁰ Hz (10 ⁻³)	3.9	—	—	—	—	—	—	—	—

^a The liquidus temperature is the highest temperature at which a glass, if held there sufficiently long, will develop crystals. The greater the difference between this and fiberising temperature, the more stable the fibre-forming process.

^b Indicates temperature at which the viscosity of the glass is 10³ P.

^c Measured at 10⁶ Hz.

Table 6.5 E-glass compositions 1940–1990 (weight %) (after Loewenstein¹⁰)

	Original E glass ¹⁶	'Improved' E glass ¹⁷	621 glass ¹⁸	MgO-free glass	816 glass ²⁰	F-free glass ²¹	B&F-free glass ²²	Low n_D glass ²³
SiO ₂	60	54.0	54.0	54.3	58.0	55.3	59	55.8
Al ₂ O ₃	9	14.0	14.0	15.1	11.0	13.9	12.1	14.8
B ₂ O ₃	—	10.0	10.0	7.4	—	6.8	—	5.2
TiO ₂	—	—	—	—	2.4	0.2	1.5	—
MgO	4	4.5	—	0.1	2.6	1.8	3.4	—
CaO	27	17.5	22.0	22.1	22.5	21.4	22.6	21.0
ZnO	—	—	—	—	2.6	—	—	—
Na ₂ O/K ₂ O	—	1.0	1.0	0.4	1.0	0.4	0.9	1.4
Fe ₂ O ₃	—	trace	trace	0.2	0.1	0.2	0.2	n.d.
F ₂	—	0.5	0.5	0.6	0.01	—	—	0.5

Table 6.6 Compositions (in weight %) for dielectric glass (D-glass) (after Loewenstein¹⁰)

Constituent/properties	Japan ¹³	USA	Europe (Vetrotex)
SiO ₂	45–65	75.5	72–75
Al ₂ O ₃	9–20	0.5	—
B ₂ O ₃	13–30	20.0	20–23
CaO	—	0.5	—
MgO	—	0.5	—
CaO + MgO + ZnO	4–10	—	—
Li ₂ O + Na ₂ O + K ₂ O	0–5	3.0	1 (max)
Other	—	—	4 (max)
Dielectric constant at 10 ¹⁰ Hz	4.3–4.9	3.8	3.85
Loss tangent at 10 ¹⁰ Hz (10 ⁻³)	—	—	0.5

To meet the requirements of fast-response electronic circuit boards, D-glass with lower dielectric constant than E-glass has been introduced over the last decade. Typical compositions are given in Table 6.6. A further discussion of other aspects is given in Section 6.8.2.

6.2.2 E-glass

E-glass is basically a calcium aluminoborosilicate glass containing less than 1% alkali calculated as Na₂O. Actual content varies, as do the presence of trace elements, with the choice of minerals, which will mainly be locally sourced. Most contain a small quantity of fluoride to assist dissolution of raw materials and to lower the liquidus temperature (the liquidus temperature is the highest temperature at which a glass would develop crystals if held there for a long time). Crystal formation is disastrous for glass fibre manufacture because submicroscopic particles will behave like strength-reducing flaws and cause problems in fibre spinning. Fluoride-free E-glass has been developed by optimising the MgO content at 1.8%, when the liquidus temperature is at a minimum of 1083 °C and the fibre-forming temperature is lower than for traditional E-glass (1212 °C). Fe₂O₃ is an adventitious component that increases the rate of heat loss through infrared radiation when the molten glass leaves the bushing and can assist fibre forming. However, Fe in the glass may be involved in acidic degradation reactions.^{14,15}

Fluoride is one of the components in the glass composition that presents a pollution hazard since it volatilises as fluorosilicic acid, hydrofluoric acid and fluoroborates.

As shown in Table 6.5, the composition has moved in the direction of boron- and fluoride-free. The ‘original’ composition represents the early attempt to find an alkali-free formulation.¹⁶ The ‘improved’ composition

has a lower liquidus temperature¹⁷ as discussed above. '621' glass¹⁸ has MgO eliminated through replacement by CaO. Of importance was its ability to accommodate ZrO₂ from refractory dissolution without devitrification.¹⁹ Developments in refractory technology have led to significant improvements in corrosion resistance, so that higher temperatures can be used in the process with the reduction or elimination of B₂O₃ from the compositions – '816' glass.²⁰ Fluoride-free composition is a Japanese glass²¹ whereas the boron and fluoride free (B&F free) composition is American.²² However, according to Loewenstein¹⁰ the extent of use of these boron-free glasses in the USA is uncertain since most manufacturers have used pollution control rather than composition refinement to meet legislative requirements.

A special glass of low refractive index designed for translucent sheeting²³ falls just outside the E-glass definition.

6.3 Fibre manufacture

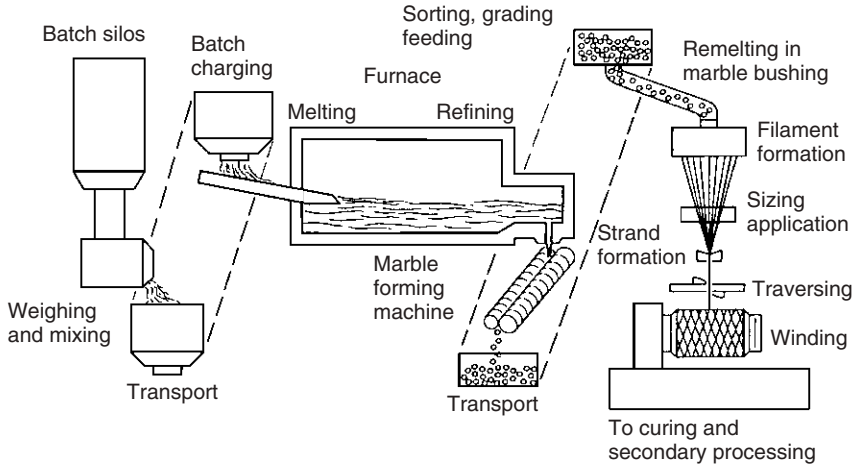
The fibre manufacturing process has effectively two variants. One involves the preparation of marbles, which are remelted in the fiberisation stage. The other uses the direct melting route, in which a furnace is continuously charged with raw materials which are melted and refined as that glass reaches the forehearth above a set of platinum–rhodium bushings from which the fibres are drawn. The two processes are described in Figures 6.2 and 6.3.² Glass fibres are produced by rapid attenuation of the molten glass exuding through nozzles under gravity. The glass melt has to have a narrow range of viscosity between 600 and 1000P. The rate of fibre production at the nozzle is a function of the rate of flow of glass, not the rate of attenuation, which only determines final diameter of the fibre.

The flow of molten glass through a nozzle can be described by the Poiseuille's equation:

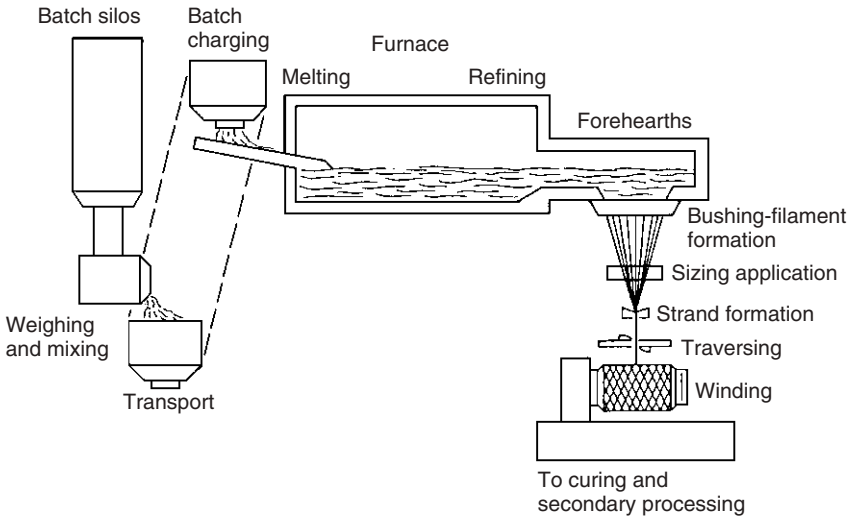
$$F \propto \frac{r^4 h}{l \eta}$$

where F is the rate of flow, r is the radius of the nozzle at its narrowest cylindrical section, l is the length of the cylindrical section, h is the height of the glass above the nozzle and η is the viscosity of the glass. Modified equations for nozzles of different geometry are given by Loewenstein.¹⁰ As the melt cools, it increases in viscosity, which varies along the nozzle making exact predictions of the flow rate difficult. Iterative procedures can be used to determine the dimensions of a nozzle of a selected design. Direct melt spinning is more predictable because of the complexities introduced by remelting preformed marbles.

The bushing is made from typically 87 Pt/13 Rh to 90 Pt/10 Rh alloys. The rhodium additions increase the hardness and stiffness of the alloy, which significantly enhances the lifetime of the bushing by reducing creep



6.2 Schematic of marble melt process for continuous filament (after Mohr and Rowe²).



6.3 Schematic of direct melt process for production of continuous filaments (after Mohr and Rowe²).

at the high temperatures employed. An additional benefit is the increased contact angle with the molten E-glass.

With a soft alloy, the size of bushing and hence of the number of holes is limited. Thus, the standard bushing is used to produce 200–204 fibres. However, as the number of fibres is increased, the stiffness of the bushing

Table 6.7 Typical commercial fibre strands (after Loewenstein¹⁰)

USA ^a	Strand designation		Number of filaments per strand	Average filament diameter (µm)
		Metric ^b		
D	1800	EC5 2.75	50	5.33
D	900	EC5 5.5	100	5.33
D	450	EC5 11	200	5.33
D-E	150	EC6 33	400	6.35
E	300	EC6 16.5	200	6.35
E	450	EC7 11	100	7.32
E	225	EC7 22	200	7.32
G	150	EC9 33	200	9.14
G	130	EC9 38	200	9.65
G	75	EC9 66	400	9.14
H	110	EC11 45	200	10.67
H	55	EC11 90	400	10.67
J	90	EC12 55	200	11.75
J	45	EC12 110	400	11.75
J	23	EC12 220	80	11.75
K	31	EC14 160	400	14.19
K	16	EC14 320	800	14.19
K	10	EC14 480	1200	14.19
K	8	EC14 640	1600	14.19
M	6	EC16 800	1600	15.86
M	5	EC16 1000	2000	15.86
N	4	EC17 1200	2000	17.38
N	2	EC17 2400	4000	17.38
T	2	EC24 2200	2000	23.52
T	1	EC24 4400	4000	23.52

^aFilament designation and count.

^bE = E glass, C = continuous, then nominal filament diameter and tex.

needs to be increased. This is being achieved by using composite alloys containing dispersed zirconia, yttria, or thoria.^{24,25} 4000 filaments can now be spun at one bushing and 6000 filaments are planned.¹⁰

The collected bundle of fibres is known in the industry as roving, which is commonly produced by assembling multiples of 200 filaments into the required size of roving as a separate operation. However, with the development 2–4000 nozzle bushings, direct rovings can be formed into a final package immediately.

A typical haul-off rate of 2500 m/min is employed to attenuate the fibre to the required diameter. The fibres are immediately cooled by sprayed water at the bushing, coated with a size, assembled into a 'strand' and wound onto a culet to produce a cake, as shown in Fig. 6.3.

In the metric system, rovings are defined by the fibre diameter and the

number of filaments per strand, which defines the total linear density (tex) of the roving. Tex is the number of grams per kilometre (1 tex = g/1000 m) and is preferred to the older textile unit of denier (g/9000 m). In the American system, a standard alphabetic letter followed by the 'count', which is the number of hundred yards per pound, is used.

$$\text{Count} = 4961/\text{tex}$$

Thus, in the metric system EC14 160 refers to E-glass continuous roving with fibres of nominal diameter 14 µm of tex 160. The American designation is K 31. It contains 400 filaments per strand. A list of typical roving definitions is given in Table 6.7.

The fibre diameter, d_f (in µm) can be computed from roving tex according to the equation:

$$d_f = 15.8 \left(\frac{T}{0.4961N} \right)^2$$

where T = tex and N is the number of filaments per strand.

The term tow is used to define the smallest unitary element of the strand and represents the number of filaments drawn from a single bushing, which was commonly equal to 200 or 204. The number of fibres in a strand is made up from multiples of the bushing number. However, rovings (other than direct rovings) are reassembled from a number of strand-cakes in a separate operation. A typical roving could have a tex of 2300 and consist of 30 strands.

6.4 Fibre finish

6.4.1 Sizes and finishes

Immediately after cooling with water the fibres are coated with an aqueous size (usually an emulsion) in contact with a rubber roller. Typical designs for sizing applicators are given in the literature.¹⁰ The size (or finish) is crucial to the handleability of the fibres and their compatibility with the matrix. The size is chosen to suit the application or further processing. For example, for chopped fibres (see Section 6.6), strand integrity may be a particular requirement. As a result, the number of formulations is extensive. An additional binder would be used to hold chopped or continuous fibres in a mat (see Section 6.6). The 'finish' therefore may consist of:

- (i) an adhesion promoter or coupling agent,
- (ii) a protective polymeric size or film former,
- (iii) lubricant(s),
- (iv) surfactant(s),
- (v) antistatic agent(s), and
- (vi) an optional polymeric binder (emulsion or powder) used for fibre mats.

The solids content of the emulsion employed for sizing will be of the order 10% of which 0.3–0.6% will be the coupling agent. The film former is a polymer that may contain a plasticiser (a high-boiling compound such as dibutyl phthalate). The lubricant, surfactant and antistat are usually present in the emulsion at 0–0.3%, 0–0.5% and 0–0.3% respectively. There is some confusion over the use of the term ‘size’. It is often used to refer to the film former including all of the additives (including coupling agent) in an aqueous base. Others use the term to refer to the solids deposited on to the fibres at the bushing, whilst it can also mean the compounded film former without coupling agent. The term ‘finish’ universally refers to the deposited solids including any optional binder, used for mats.

6.4.2 Film former

Items (ii)–(vi) in the list in Section 6.4.1 impart good handleability and controlled wet-out kinetics with matrix resins in composites and are therefore chosen for compatibility with the fabrication process. For specialist applications such as environmental resistance, the chemical nature of the film former in the size and the binder are crucial and are selected accordingly. Good economical design can be achieved by combining fibres with differing finishes in different laminae. Typical film formers and binding resins are given in Table 6.8.

The film former is chosen for one or more of the following criteria:

- compatibility with coupling agents and other components
- stability of the emulsion during application
- handling characteristics after drying
- unwind potential for repackaging
- wet-out rate in the resin matrix
- dry and wet properties of the composites.

These emulsions clearly contain emulsifying agents (surfactants) that contribute to the complexity of the deposit on the fibre. A typical surfactant is polyoxyethylene monophenyl ether. Commercial emulsions of film formers are not always used. Often in specialist applications, the manufacturer will prepare their own emulsion.

6.4.3 Lubricants and antistatic agents

Typical lubricants are based on fatty acid amides, which, in the presence of the acetic acid used to adjust the pH of the sizing emulsion to approximately 4, will be protonated. Cationic quaternary ammonium sites are positively charged and will have an affinity to the negatively charged glass surface. Polyalkylene glycols are also used and often a complex blend is required to give the correct requirements.

Table 6.8 Typical sizing resins and binders for glass fibres (after Jones⁵)

Glass type	Polymeric size	Polymeric binder	Application
E	PVAc	—	General purpose roving
E	PVAc	PVAc emulsion	General purpose CSM
E	Polyester	—	Environmentally resistant GRP
ECR	Polyester	—	Environmentally resistant GRP
E,ECR,S,R	Epoxy	—	High-performance composites
E	Epoxy/ polyester copolymer	—	High-performance composites with wide range of compatibility
E,ECR	Polyester	Various powder	CSM, environmental resistant GRP CSM processing with controlled wet-out, CRM
E	Polyurethane	—	Roving for thermoplastics – short fibre moulding compounds (e.g. nylon)
C		Polyacrylate Polystyrene	Reinforcing veils for gel coats, chemically resistant barrier layers

PVAc = polyvinyl acetate, CSM = chopped strand mat, CRM = continuous random mat.

Since glass is a non-conductor, static electricity can build-up during the use of the rovings at the high speeds used in the manufacturing process. Antistatic agents such as alkyl trimethyl ammonium chloride (*Arquad S50*) and quaternary ammonium methyl sulphate (*Neoxil AO 5620*) are used to impart surface conductivity.

6.4.4 Sizings for yarns and fabrics

A yarn is an assembled roving in which a twist has been imparted onto the strands. These are used for weaving or knitting. In most applications, such as braiding for wire insulation, a starch size including a vegetable oil and surfactants is used. For composites the woven fabric would be desized and resized before use. Similarly for rubber reinforcement in tyres, heavy cord is manufactured and desized prior to being given an appropriate finish.

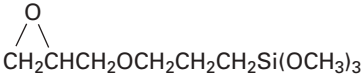
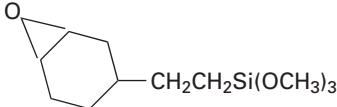
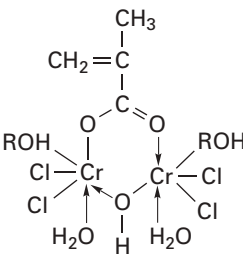
6.4.5 Silane and other coupling agents

Adhesion promoters are added to the sizing emulsion to provide the glass with compatibility and potential coupling of the glass surface to the matrix resin. The role is the following:

- (i) Displace adsorbed water on the glass surface.
- (ii) Create a hydrophobic surface of the correct thermodynamic characteristics for complete wetting by the matrix resin.
- (iii) Develop strong interfacial bonds between the fibre and resin. These may involve covalent bonding or, in the case of thermoplastics, long compatible molecular chains that are completely solubilised into the polymer, in analogy to graft and block copolymers employed in polymer blends.

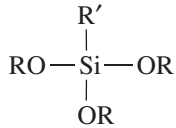
Typical adhesion promoters or coupling agents are given in Table 6.9. The chrome complex was one of the original ones. It is still used in some applications, for example it improves the abrasion and flexure resistance of

Table 6.9 Typical coupling agents for glass fibre-resin adhesion (after Jones⁵)

Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$
Epoxy	
Methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Primary amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Mercapto	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Cationic styryl	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3\text{HCl}$
Cationic methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_2\text{CH}_2-\text{N}(\text{Me}_2)^+\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3\text{Cl}^-$
Cycloaliphatic epoxide	
Titanate	$[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}]_3\text{TiOCH}(\text{CH}_3)_2$
Chrome complex	

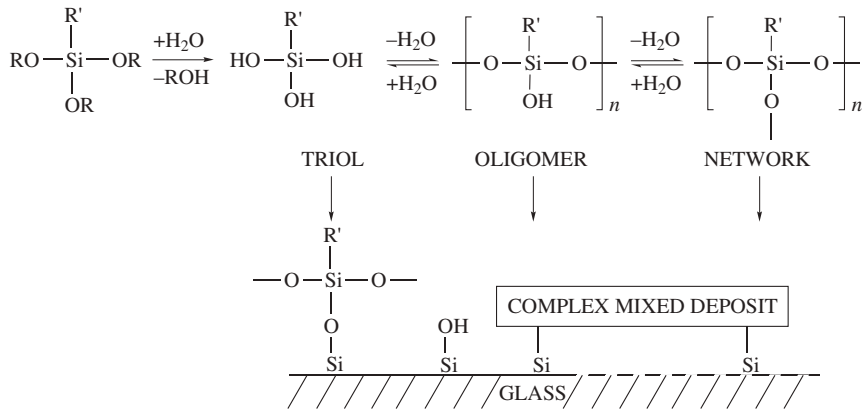
'starch' sized fibres used in yarns and fabrics,²⁸ but it has been largely replaced now by the alternative silanes.^{26,27}

The silanes given in Table 6.9 all have the following structure:



Where R' is a polymer-compatible or -reactable organic group. R is either ethyl or methyl.

In aqueous solution and usually in the presence of acetic acid which is used to adjust the pH (of the sizing emulsion) to approximately 4, the alkoxy (RO) groups are hydrolysed and can polymerise to give linear and branched poly (hydroxy siloxane).



This equilibrium polymerisation is strongly dependent on the nature of R' so that the concentration at which only the silane triol exists in aqueous solution (in the absence of the film former) varies. For example with γ -aminopropyltriethoxysilane (γ -APS), the triol will only exist at concentrations below 0.15%.²⁹ For most sizings, the concentration is closer to 0.5% so that it is expected that the hydrolysed 'silane' will be a mixture of monomeric triol and oligomers of differing degrees of polycondensation. The further away from the floor concentration, the more polymeric is the hydrolysed silane. The extent of this varies from silane to silane.

Examination of Table 6.10 shows that the glass fibre surface is silica-rich and that aluminium tends also to be enriched.^{5,30} The calcium on the other hand is depleted relative to the bulk. Since the glass is made in the presence of water, the silicon at the surface will have hydroxyl groups attached. Therefore, the hydrolysed silane will be in competition for condensation with silanols on the glass surface or through self-condensation.

Table 6.10 Typical bulk (ICP) and surface (XPS) percentage elemental composition for heat-cleaned polished E-glass plate* and as-received non-treated, water-sized fibres† (after Jones⁵)

Element	Uncoated plate		Uncoated fibre	
	Bulk	Surface	Bulk	Surface
Si	22.3	25.1	22.8	22.4
Al	7.4	8.4	7.0	8.5
Ca	16.4	9.6	17.6	8.6
O	49.6	56.9	50.4	60.5
Mg	0.4	—	0.5	—
B	2.1	—	1.4	—
Fe	0.6	—	0.3	—

— Below the detectable limit of X-ray photoelectron spectroscopy (XPS).

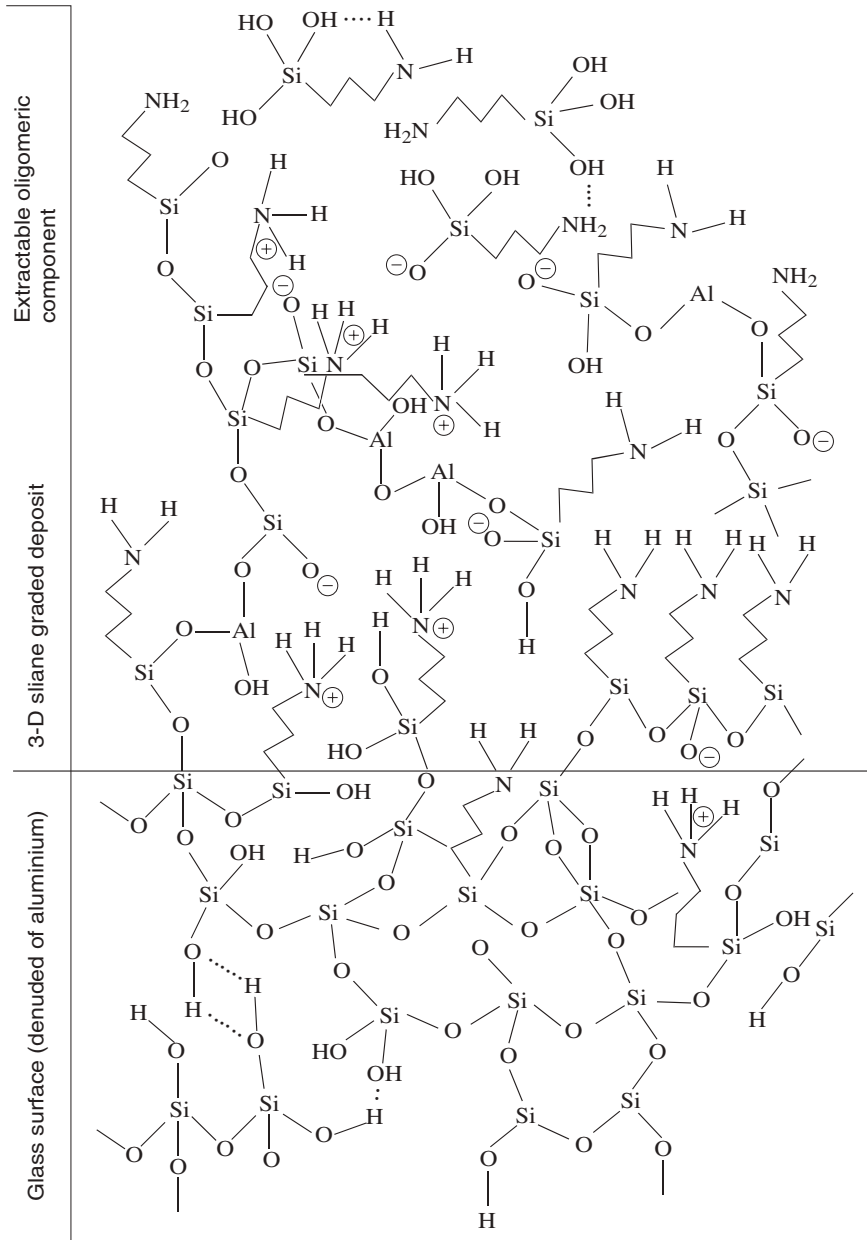
* Cast from E-glass marbles.

† Commercial fibres treated only with water during manufacture.

ICP = Inductively coupled plasma technique.

The important factor, therefore, is to differentiate between the potential for polycondensation or adsorption of the 'silane' at the surface. For strongly active surfaces, such as silicate minerals, the triol will tend to be adsorbed. For example, with γ -APS, additional internal hydrogen bonding stabilises the adsorbate, forming a monolayer. However, with glass surfaces, multilayers are deposited. Typically, more than 100 molecular layers might be deposited, of which 90% would readily be extracted in water at 50°C. Approximately three to six molecular layers remain after more rigorous hydrolytic extraction at 80–100°C. This leaves a deposit that is highly hydrolytically-resistant.^{29–38} These components or layers have been referred to respectively as: (i) the physisorbed layers, (ii) the loosely chemisorbed layer, (iii) the strongly chemisorbed layer. Wang and Jones^{30,33,34} confirmed the presence of differing components using changes in the mass of the secondary ions sputtered from the silanised surfaces in the time-of-flight surface ionisation mass spectroscopy (ToF SIMS) spectra. In this way they demonstrated that the deposit was a graded network of higher density at the fibre surface. They also found that the concentration of aluminium was enhanced at the fibre surface which led them through thermodynamic argument to suggest that the strongly chemisorbed material was a copolymer with aluminium hydroxide extracted from the fibre surface.³⁴

The graded network model had further confirmation in the observation that phenolic resins of higher molecular weight penetrated less efficiently into the hydrolysed γ -APS deposit.³⁵ They also demonstrated that the amino group was ionised to an extent of 40%. This led to a modification of the

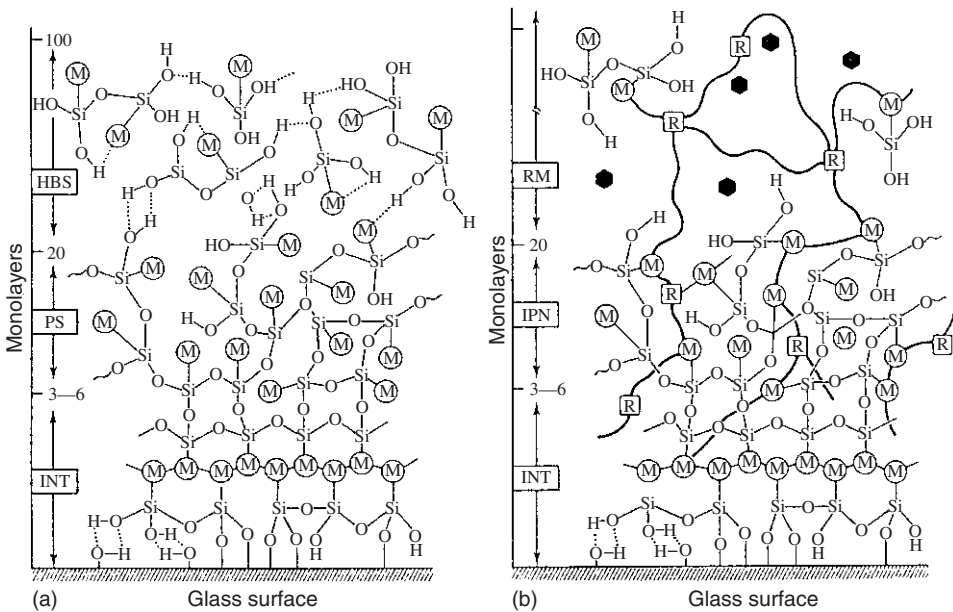


6.4 Schematic of the structure of hydrolysed γ -APS on E-glass, showing the presence of the denuded glass surface and quaternary ammonium ions.³⁵ (Reproduced with permission of VSP International Science Publishers.)

structure of hydrolysed γ -APS previously reported.³⁵ The latest schematic diagram, given in Fig. 6.4, also proposes that the silane can penetrate the denuded glass surface to provide a rather diffuse 'interphase' region.

The above model has been derived from studies on γ -APS because the nitrogen atom enables a detailed surface analysis with XPS and to some extent SIMS.

Other common silanes such as γ -methacryloxypropyl trimethoxysilane (γ -MPS) and vinyltrimethoxysilane have received less attention, but Fourier transform infrared (FTIR) studies have proved valuable. These two silanes behave differently from each other on hydrolysis. γ -MPS behaves very similarly to γ -APS with a deposit consisting of about 200 molecular layers that can be readily desorbed at 80°C to leave a deposit of about 7–20 molecular layers thick, which is hydrolytically stable. Ishida and Koenig³⁶ also observed that polymerisation through the methacrylate group may have occurred at the glass fibre interface. In the ToF SIMS Analysis of commercially silanised fibres (without film former),³⁹ evidence for this mechanism was also observed.



6.5 Schematic of γ -methacryloxypropyl triethoxysilane deposit on (a) glass fibre surface showing presence of oligomeric hydrogen bonded silane (HBS) and graded polysiloxane 3D deposit (PS), (b) after impregnation with resin (R) and dissolution of sizing (black hexagons). IPN is the semi-interpenetrating network between resin and silane; RM is the copolymer of silane oligomer and resin.

Jones⁴⁰ interpreted this data in the form of a schematic diagram of the deposit (Fig. 6.5a) and its interaction with resins as shown in Fig. 6.5b.⁵ Recent work³⁵ suggests that the interface between the glass and silane is more diffuse, as shown in Fig. 6.4.

Vinyltrimethoxysilane (VTS) on the other hand behaves completely differently. Ishida and Koenig³⁷ showed that the deposit was much more hydrolytically resistant. Thus, it is concluded that the hydrolysed VTS deposit was one of a crosslinked network with only limited oligomers present.

6.4.6 Structure of the interphase

The previous section discusses the structure of the hydrolysed silane on the glass surface in the absence of the film former. The presence of the film former will influence the nature of the deposit. Thomason^{41,42} has studied these aspects using extraction procedures, thermal analysis and surface analysis techniques. It is generally accepted that the silane is partitioned at the glass surface leaving the film former to diffuse to differing degrees into the matrix during fabrication of the composite.⁴³ Add to this that there will be an oligomeric component to the silane that will also be mobile, and it is clear that a complex interphase will form at the interface between fibre and matrix. Fig. 6.5(b) gives a schematic of how the interphase might be configured. Briefly, on embedding in a liquid resin, the soluble components of the sizing on the fibre will diffuse into the resin to a varying degree, depending on the thermodynamic compatibility of the 'blend' and the rate of diffusion which will also be a function of molecular weight of each component. Since the silane oligomers are likely to be mobile, the chemisorbed 'silane' will, in effect, be rather like a molecular sponge with molecular pores that can accept the resin molecules. Therefore, the best representation of this structure is one of a bonded semi-interpenetrating network.

6.4.7 Mechanisms of adhesion

Several theories of adhesion were identified by Erickson and Plueddemann,⁴⁴ viz:

- (i) chemical bonding
- (ii) deformable layer hypothesis
- (iii) surface wettability hypothesis
- (iv) restrained layer hypothesis
- (v) reversible hydrolytic bonding mechanism.

Chemical bonding (i) invokes the simplistic formation of chemical coupling between the components. This would produce a distinct interface, which from the forgoing is difficult to justify. The deformable layer theory (ii)

recognises the presence of an interphase where stress relaxation can occur and is probably one of the most important contributing factors. The restrained layer hypothesis (iv) is effectively equivalent except that the interphase exhibits a higher modulus than the matrix, through a higher degree of crosslinking. Surface wetting (iii) alone is unsatisfactory, but in order to achieve a strong interface this aspect must be satisfied. The reversible hydrolytic bonding theory (v) was favoured by E P Plueddemann^{26,44} to explain the reduction in wet strength and its recovery on drying, by reformation of hydrolysed siloxane bonds. With recent knowledge, it is clear that it is not necessary to invoke chemical bond hydrolysis to explain the reversibility of transverse strength because we now know that the stress transfer between fibre and resin is strongly influenced by the presence of a thin interphase.^{45,46} With differential plasticisation of the interphase and matrix, the effect of water can be explained.

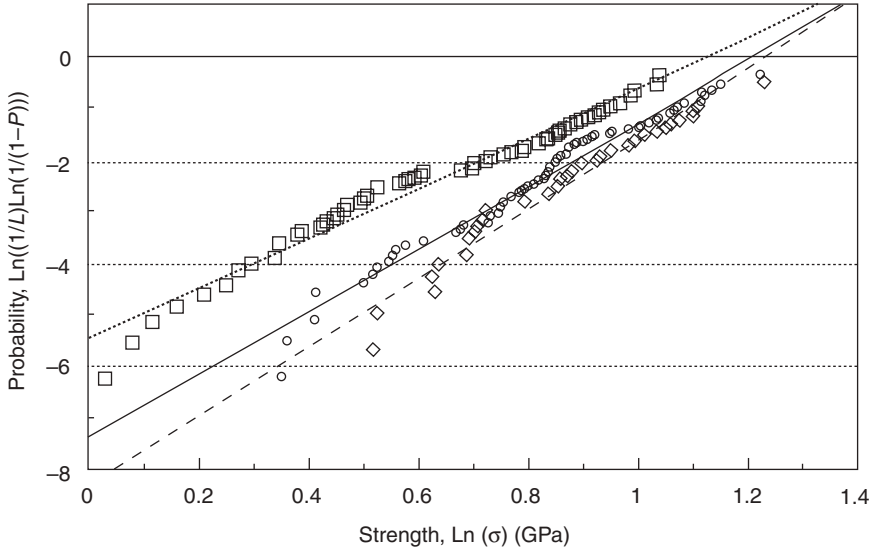
6.4.8 Characterisation of the interface/interphase

The assessment of interfacial response is an essential aspect of sizing development. Most commercial work generally involves simple composites such as impregnated bundles. Optimisation therefore involves relevant tests such as tensile or interlaminar strength. For short-fibre reinforced materials, other specific tests such as impact strength may be utilised. Attempts have been made to assess performance using single filament tests such as pull-out, microdebond, push-in and fragmentation. The test methods have been reviewed recently.⁴⁷ Problems arise from the complexity of interfacial response under shear, which was also reviewed.⁴⁸ Certainly for sized glass fibres, debonding is not always observed so that yield of an interphasal region limits the stress transfer at the interface. As a consequence, without full knowledge of the interphase properties it is often difficult to interpret single filament test data. It is, however, clear that careful study illustrates that 'sizing' formulations influence composite micromechanics.⁴⁵

6.5 Glass fibre properties

6.5.1 Strength and stiffness

The mechanical properties of glass fibres are shown in Table 6.2. The modulus is very much dominated by the chemical forces operating within the amorphous inorganic glass and has a value of around 70–80 GPa. Higher modulus can be achieved only with crystallisation into a glass-ceramic or ceramic. The strength of any solid is dominated by the presence of flaws that grow under stress. At a critical size given by the Griffith equation,^{1,3} rapid fracture occurs. The population of flaws and their size therefore deter-



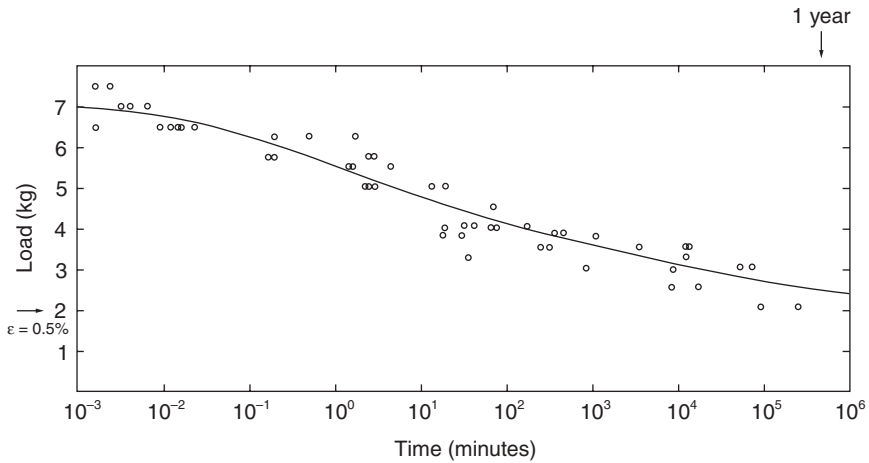
6.6 Weibull plots for three laboratory coated E-glass fibres showing differing protective abilities. □ = Pure γ -APS (Sigma Chemicals); ○ = commercial γ -APS (A1100); ◇ = polydimethyl siloxane. The values of the Weibull parameter m and the characteristic strength σ_0 are, respectively 4.88, 3.1 GPa; 6.1, 2.4 GPa; 6.7, 3.4 GPa. L = gauge length of fibres tested (= 6.35 mm); P = probability of failure.

mines the failure of the material, so a fine filament, which will have a lower density of critical flaws, will be stronger than the bulk solid. Furthermore, the strength of a fibre will therefore be gauge dependent and a bundle of fibres will fail progressively because each individual filament will have a different strength.

As a rule of thumb, the theoretical strength will be approximately $E/10$. For glass this will be about 7 GPa, but the practical strength would be significantly less at about 0.07 GPa. Filaments provide a method of realising a significant fraction of the ideal strength. A typical E-glass fibre can have a strength of 3 GPa. However, the introduction of surface flaws during manufacture and storage can reduce the fibre strength significantly. Hence, the 'finish' is applied to the fibres at the bushing immediately after spinning to provide maximum protection.

As-drawn glass fibres have been shown to exhibit three populations of flaws both by Bartenev⁴⁹ and Metcalfe and Schmitz.⁵⁰ In a statistical analysis, the latter authors concluded that the population of fibres with:

- (i) average strength of 3 GPa could be attributed to severe surface flaws of 20 mm spacing;
- (ii) average strength of 3–5 GPa could be attributed to mild surface flaws



6.7 Static fatigue of E-glass strands in distilled water (after Aveston *et al.*⁵²). Reproduced with permission.

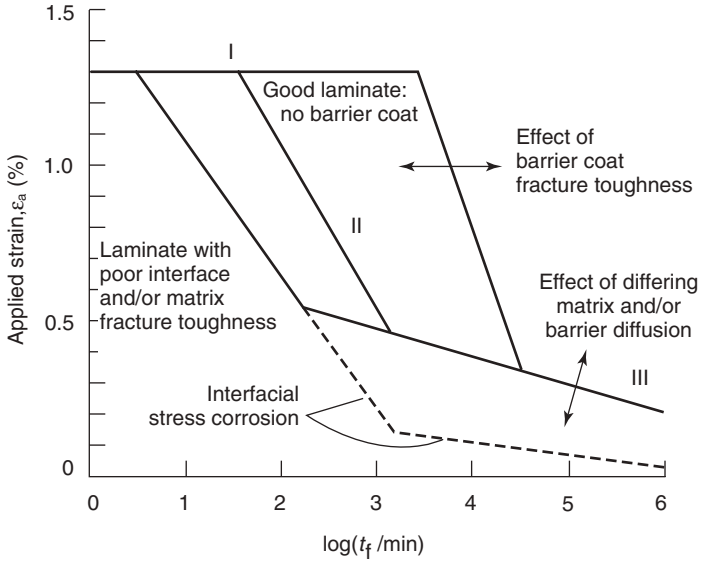
- of 0.1 mm spacing associated with a tempered layer 10 nm thick which is fractured to expose an inner core whose strength is determinant;
- (iii) average strength of 5 GPa could be attributed to internal defects of 10^{-4} mm spacing, characteristic of defect-free filaments with an uninterrupted surface layer.

Bartenev, however, attributed (ii) to internal defects. Despite this, the presence of a tempered surface is generally accepted.

The Griffith flaws have been associated with the structure of the glass network.⁵¹ In the analysis of commercial fibres it is generally assumed that one population exists and a single parameter Weibull distribution is used. Figure 6.6 gives a typical set of strength data for a glass fibre with a Weibull analysis. From the Weibull parameter, m , and the characteristic strength, σ_0 , it is possible to predict the strength of fibres of differing length. This approach is commonly employed in the analysis of fragmentation test data for adhesion assessment.⁴⁸ It can also be shown by these studies that the 'finish' on glass fibres is an effective protective coating for strength retention (Fig. 6.6).

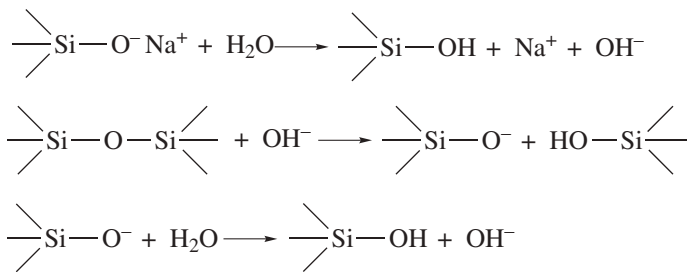
6.5.2 Static fatigue

Glass fibres are subject to static fatigue, which is the time-dependent fracture of a material under a constant load, as opposed to a conventional fatigue test where a cyclic load is employed. This phenomenon is illustrated in Fig. 6.7⁵² where the failure times of fibre bundles under stress in distilled



6.8 Schematic failure map for a unidirectional E-glass fibre composite under acidic environmental stress corrosion conditions, illustrating the three stages of failure I, II, and III and the influence of composite variables.

water are given. The same trend is found for immersion in air. Generally, it is considered that there is no time-dependence of strength in a vacuum,⁴⁹ so that the reduction in strength is a stress corrosion mechanism in the presence of water and not creep rupture as in polymer fibres. The reactions are:



Thus the Na^+ acts as a catalyst for the degradation of the silica network which is propagated by the OH^- ion.

The stress versus time curve has the general form shown in Fig. 6.7 (this is illustrated in Fig. 6.8 for a 0° composite in an acidic environment where these effects are amplified) in which three stages are seen.⁵³

I *Stress dominated region* at high stresses, where crack propagation is more rapid than the corrosion at the crack or flaw tip. Here the

rate of diffusion of Na^+ to the surface is considered to be rate determining.

- II *Stress corrosion cracking* region, where the rate of corrosion is similar to the rate of crack propagation. Here the crack remains sharp and propagates into a weakened glass.
- III *Stress-assisted corrosion* region, where the effect of stress on the failure time is much less significant because the rate of hydrolysis of the silica network is higher than the rate of crack growth: the chemistry at the crack tip causes a rounding of the crack tip and a reduction in potential to propagate according to the well-known equation

$$\alpha_{\max} = 2\sigma_a (x/\rho)^{1/2}$$

where σ_{\max} stress at the crack tip, σ_a = applied stress, x and ρ are the flaw depth and radius, respectively.

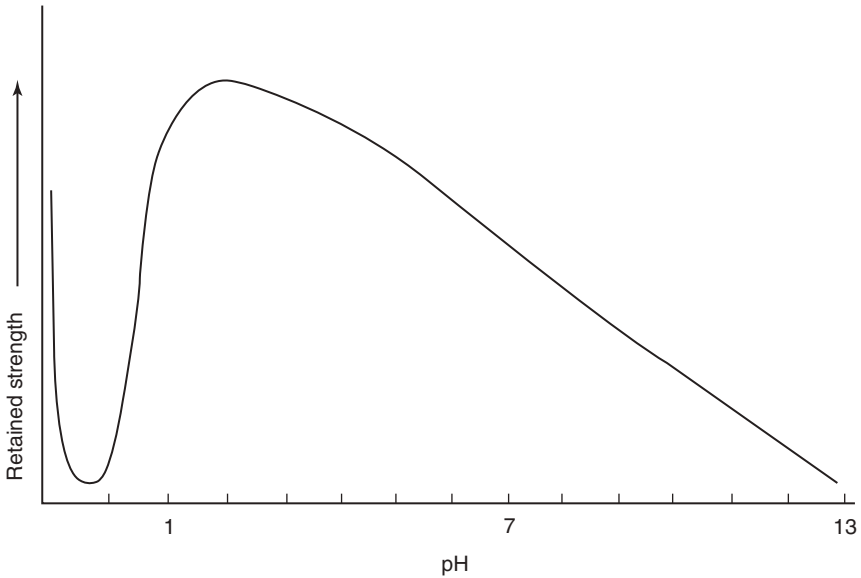
The static fatigue of the glass fibres is clearly determinant of the minimum life of a structural composite under load. Thus, the rate of moisture diffusion, even from humid air, can determine the protective effectiveness of a well-bonded matrix. This can also explain the need for a good interfacial bond, otherwise rapid ingress from an environment could reduce the durability to the minimum for a composite under load in service.

Typically a bundle of E-glass fibres can have a lifetime of 10^7 mins (19 years) at a typical strain of 0.5%, providing the minimum for a composite (see Fig. 6.7).

6.5.3 Environmental stress corrosion cracking (ESCC)

As shown in the previous section, E-glass fibres have a reduced lifetime under load and this is more severe in an acidic environment. This is generally referred to as environmental stress corrosion cracking or ESCC. Here, a synergism between stress and chemistry occurs as described in the previous section under II. At low loads and in alkaline environments, chemical corrosion dominates but is stress assisted. Figure 6.8 illustrates this effect, where the left-hand line approximates to the fibres. Corrosion of the glass is clearly pH dependent, with the network modifiers becoming involved. It is well established that leaching of Ca^{2+} , Al^{3+} , Fe^{3+} , Na^+ , K^+ and other residuals leaves a weakened sheaf. It is now possible to explain ESCC in an analogous mechanism to that given previously for static fatigue.

Leaching also leads to spiral cracking of unstressed fibres after storage in aqueous acid for a short period. It is not clear whether the crack forms prior to optical or SEM examination or after removal from the environment. The latter is favoured and the spiral or multiple cracks form when the hydrated sheaf dries out. However, not all of the fibres in a bundle suffer from this phenomenon. This would appear to confirm that the leaching of the network modifiers is also stress dependent and that variable residual



6.9 Illustration of the retained strength of unloaded E-glass in environments of differing acidity and alkalinity (after Cockram⁵⁵). Reproduced with permission of The Society of Glass Technology.

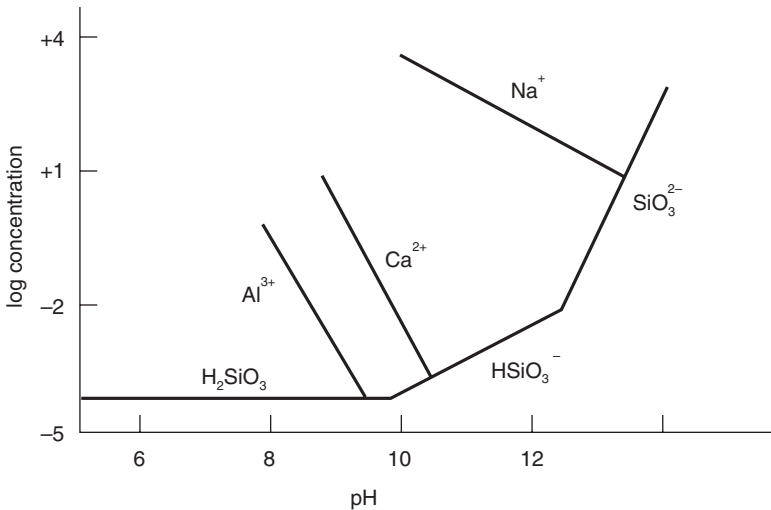
stresses are built into the fibres as a result of the water-cooling regimes employed in manufacture. This is further complicated by the complexation of leachable ions such as Fe(III) in the aqueous solution, which promotes the process. This may be the mechanism by which ultraviolet illumination can accelerate ESCC of E-glass filaments.^{15,54}

6.5.3.1 Corrosion of E-glass fibres

As shown in Fig. 6.9, the retained strength of the filaments is strongly dependent on the pH of the environment.⁵⁵ Of note is the lowest durability at a pH of 0.2. This can be explained by the thermodynamics of the glass/aqueous solutions interaction. Fig. 6.10 shows how the solubility of different glass modifiers varies with pH. For example, $\text{Ca}(\text{OH})_2$ can be precipitated above a pH of 10,⁵⁶ thereby explaining the dominance of ESCC in acids and corrosion in alkalis. The rate of corrosion in the latter is so high that zirconia glasses are preferred.

6.5.3.2 ESCC of E-glass fibres

Most studies have been conducted in acidic environments, when rapid failure occurs. But studies on composites confirm that the effect of pH on



6.10 Thermodynamic calculations of the aqueous solubility of differing glass components at differing pH (after Fox⁵⁶).

ESCC of E-glass fibres shows a similar trend to Fig. 6.9. For example, corrosion appears to dominate at high pH whereas at low pH, ESCC dominates. However, *AR* glass and *ECR* glass fibres show improved resistance to stress corrosion cracking in aqueous acidic environments. This phenomenon can be applied to the design of glass fibre composites with resistance to ESCC (see Section 6.8.3).

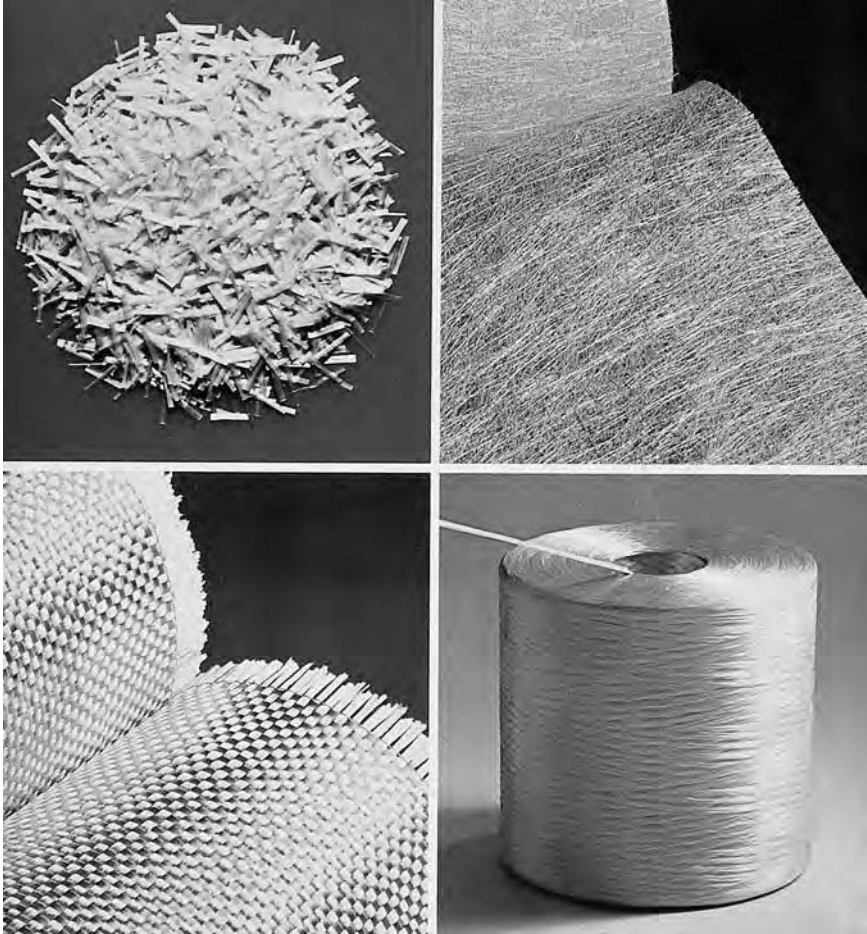
6.6 Fibre assemblies

6.6.1 A variety of types

As shown in Fig. 6.11(a) and (b), the form of fibres used for composite manufacture is quite varied. As discussed in Section 6.4, the strands can be compiled at the bushing to make direct rovings that, when unreel, do not have a twist and are ideal for advanced composites made from prepreg, or by filament winding and pultrusion. Alternatively, the fibres are collected on a culet, where they are dried and sent for further packaging.

6.6.2 Mats

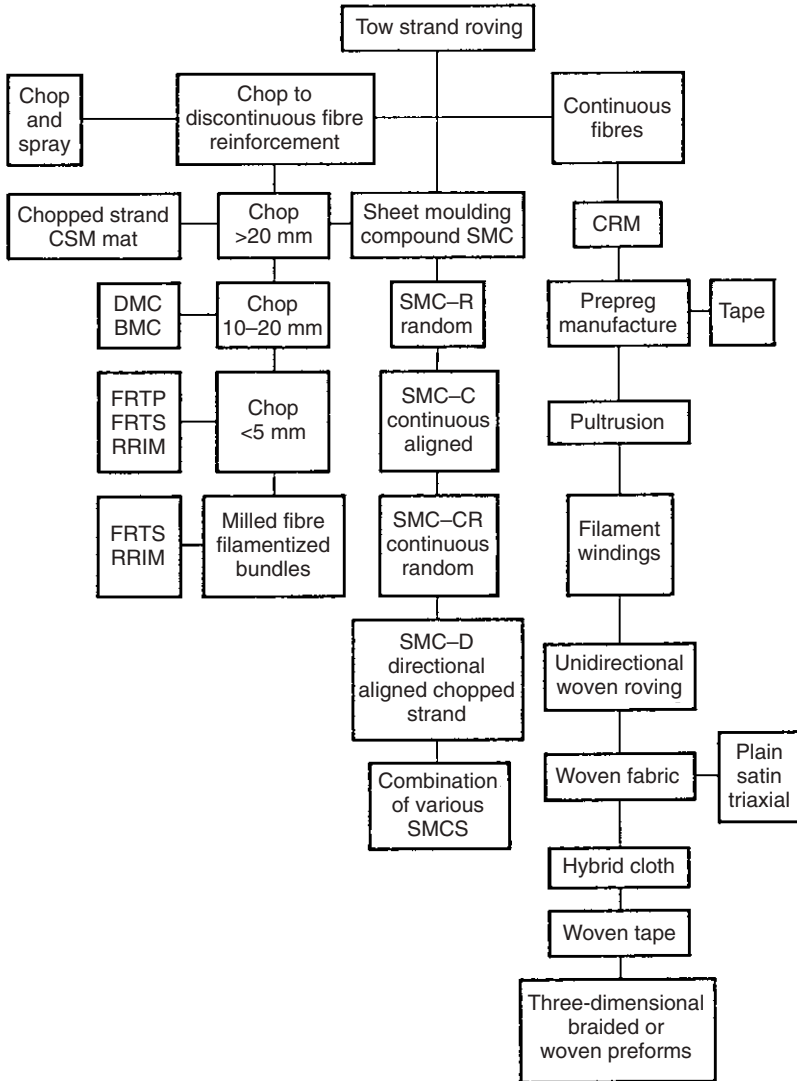
Chopped strand mat (CSM) is a non-woven fabric that is formed by chopping the rovings into strands of 20–50 mm in length, compacting them in a random orientation on a foraminous moving belt and binding them



6.11 (a) Photograph of differing forms of glass fibres as reinforcements.

together with either an aqueous polymer emulsion or a fused powder binder. These mats are used in hand lay-up or related fabrication techniques.

Continuous random mat (CRM) is analogous to chopped strand mat but *unchopped* strands are assembled into an interlocked spiral and bound together with a powder binder or needled to provide a proportion of through-thickness fibres that mechanically bond the assembly. The benefit of the former is in its drape onto a mould surface combined with good surface finish. The needled CRM is used for thermoplastic sheet product where mechanical stability during melt impregnation is crucial.



Types and forms of glass fibre products. R = random; D = directional; C = continuous; CR = continuous random, CRM = continuous (filament) random mat, CSM = chopped strand mat, DMC = dough moulding compound, BMC = bulk moulding compound, SMC = sheet moulding compound, FRTP = fibre reinforced thermoplastics, FRTS = fibre reinforced thermosets, RRIM = reinforced resin injection moulding (after Jones⁵).

6.11 (b) Schematic of fibre forms and composite fabrication routes.

Fine continuous random mats are used as surfacing *tissue* for resin-rich liners or gel-coats. *Overlay mat* is a heavier grade where more robust handling is encountered, as in press moulding.

Roofing mat or *tissue* is a CSM with binders specific to bitumen or similar matrices used in building products, or for a reinforcement of PVC flooring.

Needled mat consists of chopped fibres as strands, bonded to a glass fabric by needling.

6.6.3 Continuous roving

A typical roving is an assembly of parallel strands (typically 30 at a tex of 2300) for unwinding during fabrication to give a non-twist product. Often these are unwound from the inside of the package and care is needed to ensure that the numbers of twists in the final composite is low. They can be subsequently processed into unidirectional reinforced composites through filament winding or pultrusion (see Section 6.7), woven into various fabrics (see Fig. 6.12), or chopped into short lengths for spraying directly into a mould with the resin or deposition with the resin into a secondary moulding product such as dough or bulk moulding compound (DMC or BMC) or sheet moulding compound (SMC).

Direct rovings are assembled at the bushing. These are generally used for advanced composites where the memory of the tows is a distinct disadvantage and where twists need to be absent.

6.6.4 Woven rovings

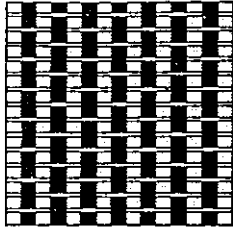
Rovings can be woven in a variety of fabrics of differing configurations as shown in Fig. 6.12. For example, satin weaves are chosen where drape onto a mould surface without distortion of the fibre orientation is required and therefore are often used in advanced composites in the form of a prepreg. The weave pattern can be chosen to ensure appropriate fibre orientation in the moulding. The properties of a fibre composite are dominated by the alignment of the fibres to the principal stress axes.

6.6.5 Combination mats

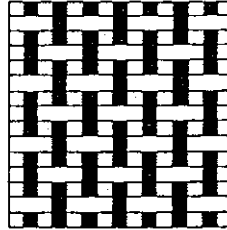
These combine CSM and woven rovings, or needled mat and woven rovings to provide specialist products for specific applications.

6.6.6 Yarns

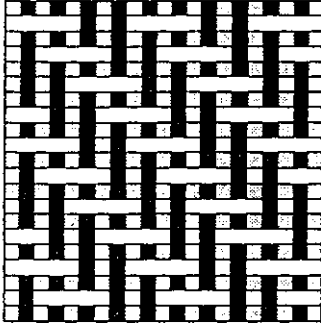
Glass fibre yarns are analogous to other textile fibres in which a twist is incorporated into the rovings and doubled for weaving of glass fabrics.



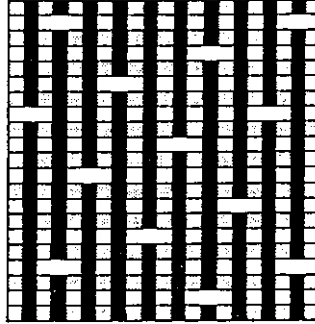
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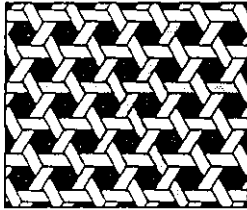
Plain



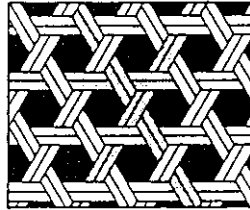
Twill 2.2



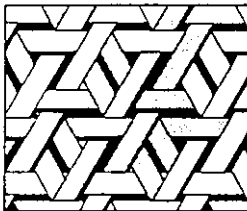
Satin 8



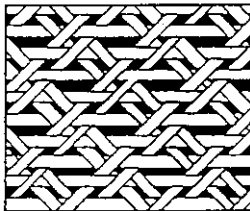
Basic (triaxial) weave



Basic basket weave



Bi-plain weave
(filling 60° to warp)



Bi-plain weave
(filling 45° to warp)

6.12 Schematic of glass fibre fabric weaves (after Jones⁵).

Typical examples are heavy cords for reinforcing elastomers, electrical insulation laminates for electrical circuit boards, and fireproof curtains.

6.6.7 Chopped strands

These are fibres which have been chopped to lengths of 1.5 to 50 mm, depending on the application. These are combined with thermoplastic or thermosetting resins for moulding compounds. Chopped strands are either soft- or hard-sized, depending on the moulding application. Optimum impact strength is often achieved by energy absorption from bundle disintegration so that the glass finish is designed to keep the chopped bundles intact. Alternatively, for most applications (such as thermoplastic injection moulding granules) soft sizings are used which diffuse efficiently giving finely dispersed filaments.

6.6.8 Milled fibres

These are made by milling chopped strands to filamentise the bundle and provide a reinforcement without maintenance of bundle integrity, to give good dispersion. Fibre length is also degraded during milling but fortunately, with complete dispersion, the reinforcing efficiency can be maintained because it is the length-to-diameter ratio of the reinforcing element which is critical. These fibres are often used in reinforced reaction injection moulding (RRIM), where the fibres are dispersed in one of the reacting components (the polyol in a polyurethane) for mixing with the other component at a rapid mixing head. They are also used in short-fibre reinforced phenolic and related fibre-reinforced thermoset mouldings (FRTS).

6.6.9 Knitted reinforcements

Knitted fabrics are now being used for composite fabrication, especially by resin infusion on transfer. These present an opportunity for manufacture of 3D structural preforms. Knitted structures based on fibrous glass yarn are fast becoming a technological solution to the fabrication of one-piece complex shapes such as a T-joints and flanges. The interlooped nature of the reinforcement leads to relatively poor reinforcement efficiency so that attempts to include planar elements are being researched.

6.7 Composites

6.7.1 Fabrication

The fabrication of composite materials, of which glass fibre reinforced plastics form a major part, is the main application of E-glass and other fibres.

Glass fibres are used to reinforce rubber for conveyor belts and some tyres. AR glass fibres are used for the reinforcement of cementitious products such as spun pipe. This is essentially analogous to the centrifugal casting process used in the plastics industry. Sprayed chopped strands are also used in other reinforced concrete processes for more complex shapes such as ovoid sewers. Bundle integrity appears to be an important aspect and sizes are chosen accordingly.

The range of fabrication routes to glass fibre reinforced plastics is extensive. Those described here illustrate the basic principles, but for detailed discussions of each technique the reader is referred to other texts.^{5,57}

The fabrication routes can be discussed in terms of primary or direct routes, where the artefact is fabricated from its component fibres and resins, and secondary or indirect routes, where the fibres are preimpregnated to form a moulding material prior to the moulding stage.

6.7.2 Direct or primary impregnation methods

6.7.2.1 *Hand lay-up*

This is the 'original' manufacturing route to so-called 'fibreglass', where E-glass fibres in the form of CSM (woven rovings and combination mats can improve the product stiffness) are placed into a mould that had been pre-coated with a layer of gelled resin or gel-coat. Depending on the requirements, the gel-coat is generally an unfilled resin with relevant properties, but it may be reinforced with a fine glass veil or scrim. Glass fibre mat is then placed upon it and impregnated with catalysed liquid resin, using a paint brush, and consolidated with a roller. The resin 'cold' cures in a specified time. The resins employed are generally from the family of styrenated unsaturated polyester resins which are cured with a peroxide catalyst (e.g. methylethylketone peroxide) and redox accelerator, such as cobalt octoate. Other resins are used for special purposes or to improve consolidation. Variations, which improve consolidation, combine hand-lay with application of pressure to the impregnated glass through a plastic film, using a positive gas pressure or evacuation through the tooling. Hand-lay moulding is rather labour intensive but provides an economic flexible manufacturing route for large mouldings from low cost tooling.

6.7.2.2 *Spray-up*

This process is a semi-automated version of the hand-lay process, where the rovings are chopped and sprayed directly into the mould with the liquid resin. However, consolidation routes are generally the same as in hand-lay.

6.7.2.3 *Centrifugal casting*

In this related technique to spray-up, the chopped fibres and resin are introduced into a rotatable cylindrical moulding to manufacture a pipe. The fibre volume fraction can be adjusted by varying the speed at which the mould is rotated. Alternate layers of sand reinforcement can be readily included for rigidity. Furthermore, the matrix resin properties can be graded to provide high fracture toughness at the surface in contact with the environment.

6.7.2.4 *Pultrusion*

This technique is used to fabricate continuous lengths of product at constant cross-section. These are usually linear but a degree of curvature can be introduced by placing the impregnated fibres onto a large diameter wheel prior to completion of the cure. Clearly, arcs of a circle can be cut from the product. In this simple process the fibrous reinforcement is impregnated with thermosetting resin (unsaturated polyester and related resins, epoxy or phenolic resins) and pulled through a heated die that shapes the section and initiates the curing chemistry. The major difficulty is in controlling the curing kinetics of the resin to ensure that the shape introduced at the die is stabilised after full resin impregnation. The partially cured resin needs to have good mechanical properties and release from the tooling to provide a good finish to the product. Normally, unidirectionally reinforced pultrudates of high stiffness and flexural strength, which rely on aligned fibre properties, are manufactured. However, for improved transverse properties, a CRM can be incorporated as a surface layer. The proportion of unidirectional rovings will determine the balance of properties. Typical applications are tension members such as supports for optical fibre cables.

6.7.2.5 *Filament winding*

There are two variants: wet and dry filament winding. In the former, the fibres are impregnated by pulling them through a resin bath, similar to pultrusion, onto a rotating mandrel. The tension on the fibres determines the consolidation and fibre volume fraction. Generally, a winding angle of 53° is used, with several passes to manufacture an angle plied material and optimise the properties of the pipe. Hoop winding can also be used, providing a principally circumferentially reinforced pipe. In practice, the angle will be approximately 8° . These are often referred to as flexible pipes. However, to achieve axial stiffness and strength, unidirectional woven rovings can be applied to provide fibres in the axial direction. In applications such as sewer pipes, fillers can be added to provide stiffness at eco-

conomic cost. Chemical plant and other containers are often manufactured from filament wound pipes onto which hand-layed bases and tops (dished-ends) are adhered, using overwind technology.

Dry filament winding is commonly employed to provide fibre orientation at various angles on complex-shaped mandrels. (For enclosed artefacts such as a sphere, the mandrel would be a foamed polymer which can be left *in situ* after manufacture.) Because of the practical difficulties of wet winding, these are dry wound into a preform and impregnated with resin in a separate procedure, such as resin transfer moulding. Planetary whirling arm, or tumble winders, are often used in combination with a robot to secure the fibres to a mandrel of complex curvature with adhesive, in the manufacture of complex-shaped preforms, with controlled reinforcement angle.

6.7.2.6 Resin transfer moulding (RTM)

Resin infusion or impregnation of a preform of fibres is usually carried out in a process called RTM (the term resin injection is reserved for the related RIM process (see Section 6.7.2.7)). In the RTM process, the preform is placed into a mould which is closed, and the catalysed liquid resin is pumped into it. The resin usually cold-cures so that the artefact can be demoulded. In a variation, the infusion is done under vacuum assist. This technique is referred to as vacuum assisted resin injection (VARI) or vacuum assisted resin transfer moulding (VARTM). The SCRIMP process employs a stitched preform with angle ply configuration. The clamping pressures in the mould are low because of the low viscosity of the resins used in the process and, as a consequence, the tooling requirements are relatively low in cost, providing economic manufacture of large structural components such as car bodies of low volume production cars (e.g. the *Lotus Elan*). Reactive processing (fast curing monomers replacing the resin) can be used to increase the rate of production and this is referred to as structural reaction injection moulding (SRIM).

6.7.2.7 Reinforced reaction injection moulding (RRIM)

RRIM refers to the technique of reactive processing where monomer(s) are polymerised immediately after injection into the mould cavity. Reaction injection moulding (RIM) was developed from the rapid polymerisation of ϵ -caprolactam into nylon 6. However, a range of polyurethane materials which are formed by rapid reaction of a polyol with di-isocyanate at a fast mixing head are the most common matrices employed. Demoulding can be achieved in less than 20s. In RRIM, short fibres (often milled glass fibres) are included in the polyol monomer stream (rather than in the isocyanate because of its sensitivity to residual water on the glass surface). A common

application has been for the manufacture of large, medium-volume production body components for automobiles, with high impact performance. In structural reaction injection moulding, SRIM, a fibre preform is placed in the mould cavity prior to injection of rapidly mixed reactants. Fast curing epoxy resins have also been used in the manufacture of structural composites by these methods.

6.7.3 Indirect impregnation

These manufacturing processes employ resin or polymer preimpregnated glass fibres or compounded moulding material.

6.7.3.1 *Prepreg*

Prepreg (or preimpregnated fibres) is commonly used in the aerospace industry where high-performance or advanced composites are employed. The advantage of this approach is the ease with which laminates of differing configurations can be manufactured, by stacking plies of unidirectional prepreg at appropriate angles for consolidation.

Prepreg is manufactured by either hot-melt or solution impregnation. In both, a liquid film of the resin including latent hardeners is cast onto a roller and brought into contact with the fibres, in the form of unidirectional or woven rovings, at the nip of additional rollers. Recently hot-melt impregnation has tended to replace the use of solvents, which have to be removed carefully, otherwise voidage can be created in the cured laminate. However, since the resins are designed to be heat cured, they have to be carefully formulated for hot-melt casting otherwise partial cure of the resin can lead to a variable viscosity and problems during consolidation of the laminae.

Epoxies, bismaleimides, cyanate ester and related resins can be impregnated in this way to provide a feedstock for the lamination industry. Thermoplastics can also be used as matrices for prepreg but these are mostly manufactured by a hot-melt pultrusion technique. Thermoplastic prepreps employing glass fibres are mostly based on polypropylene.

6.7.3.2 *Sheet moulding compound (SMC)*

The unsaturated polyesters and related resins are unsuitable for prepregging because of their low viscosity and cure mechanisms which involve a reactive solvent. As a result, for equivalent preimpregnated fibres, thickening agents and particulate fillers are employed. Thus chopped random, continuous random, discontinuous and continuous aligned fibres are impregnated with a filled resin between release films. Magnesium oxide is incorporated into the resin, which chain extends the unsaturated polyester

through ionomer bond formation with the end-groups to increase the viscosity of the resin during maturing, to give a practical preimpregnated sheet material for hot-press moulding. Typical recipes are given elsewhere.⁵ The fibres are mostly arranged in plane. Hard-sized (resin insoluble) strands are used so that bundle integrity is maintained in the final moulding.

6.7.3.3 *Dough or bulk moulding compounds (DMC, BMC)*

These are formulated similarly to SMC except they do not contain the thickening agent, have a higher proportion of mineral fillers (such as chalk) and are prepared into a dough which can be compression or injection moulded.⁵ The fibre length is shorter than for SMC and is typically about 6mm in length, compared to 25–50mm in SMC. Again, hard sizing is employed. Both terms DMC and BMC are employed for the same material but BMC tends to infer longer glass fibres.

6.7.3.4 *Long glass fibre thermoplastic sheet (RTS)*

These are the analogous thermoplastic sheets for thermal processing (hot stamping) or compression moulding. The preimpregnation process can be through lamination of extruded polymer films and random continuous fibre mat, but an alternative process involves the *in situ* consolidation of the glass rovings and particulate thermoplastic powder into an impregnated mat. These are referred to as glass mat reinforced thermoplastic sheet (GMT). Structural thermoplastic composites (STC) are random short-fibre sheets that have been manufactured by the wet slurry process, which was developed from traditional paper making technology and uses an aqueous dispersion of polymer particles and chopped fibres.⁵

6.7.3.5 *Moulding granules*

These are generally made by compounding chopped fibres into either short-fibre thermoplastics (SFRTTP) or short-fibre thermosets (SFRTS) to produce granules for moulding by compression, injection or extrusion processing. The fibres can be incorporated in a number of mixing techniques, passed through an extruder and chopped into granules. The extrusion process introduces some alignment into the fibre orientation but the fibre length is generally extremely low (e.g. ~0.2mm). Long-fibre thermoplastic moulding granules (fibre length typically ~10mm) are made by pultrusion impregnation followed by chopping, to give an aligned discontinuous fibre granule. This is generally referred to as the Vertron process. With this, after injection moulding, the artefact contains fibres with higher average fibre length, and consequently improved strength.

6.7.4 Consolidation or moulding techniques

6.7.4.1 *Vacuum bag moulding*

This composite fabrication employs prepreg to manufacture advanced structural components. Prepreg is stored between release film in a freezer (to maintain the life of the latent hardened resin) and has to be brought to room temperature before unwrapping, to avoid excess moisture absorption. After stacking on the tooling at an appropriate angular configuration, the prepreg is covered in a porous release layer, resin absorber, breather cloth (to equalise the pressure) and a membrane which forms the vacuum-bag when vacuum is applied through a valve. On application of the vacuum, the bag conforms to the tooling and places the prepreg stack under 1 atm pressure, where consolidation and curing can take place in an oven.

6.7.4.2 *Autoclave moulding*

This is the standard fabrication route for advanced composites and involves the procedures of Section 6.7.4.1 except that the ‘bagged-up’ component is placed in the pressure chamber where it can be connected to the vacuum. In this way vacuum pressure and gas pressures of >1 MPa can be applied at appropriate times during the heating schedule in order to optimise the consolidation process and minimise void formation, while maintaining precise fibre angles in the structural composite. The tooling used is often manufactured from composite materials, in order to match the thermal expansion/contraction of the tooling to the component. The prepregs used for tooling may be cured at low temperatures followed by free-standing post-curing after manufacture to appropriate temperatures to ensure their thermal stability during component manufacture.

6.7.4.3 *Compression moulding*

This is a standard moulding technique where a weighed charge is placed into a heated, matched die mould and subjected to mechanically applied pressure. The artefact can be removed after a defined curing schedule (fusion and cooling in the case of a thermoplastic).

6.7.4.4 *Injection moulding*

In this standard plastics process the granules are plasticised in a screw and barrel and then metered into a closed mould. For thermoplastics, homogenisation in the barrel is followed by cooling in the mould. For thermosets, such as DMC or short fibre-reinforced phenolics (SFRTS), the resins have

to cure within the heated tooling after injection. The barrel temperatures are chosen to provide plasticisation and controlled advancement of cure but are not sufficient to gel the resin; they are lower than that of the mould.

6.7.4.5 Extrusion

This is the classic process whereby the homogenised or plasticised melt is forced through a die continuously to give a product of constant cross-section. This technique is used mainly for thermoplastics materials.

6.7.4.6 Fibre management by shear controlled orientation

It is important to control fibre orientation in any moulding process. This can be achieved by careful mould design to provide appropriate flow paths. Allan and Bevis^{5,58} have, however, developed a live feed technology that applies shear forces onto the melt within the mould. In this way, short fibres can be orientated within the artefact to optimise the strength of the component. The same technology has also been applied to extruded pipes, where the fibres can be organised to give high axial or high circumferential stiffness.

6.7.5 Mechanical property of glass fibre composites

6.7.5.1 Continuous fibre reinforcements

The stiffness of a composite artefact can be predicted using the theories presented elsewhere.^{3,5,59-61} For fibres aligned unidirectionally, the modulus in the fibre, 0° or longitudinal direction (E_l) is given to within <1% by the law of mixtures:

$$E_l = E_f V_f + E_m V_m \quad [6.1]$$

where E is the modulus, V is volume fraction, and the subscripts m and f refer to matrix and fibres, respectively.

At 90° to the fibres, the predictions of E_t from equivalent laws of mixtures are poor because the matrix properties dominate. The Halpin-Tsai equation includes corrections for non-uniform fibre distribution (ξ):

$$E_t = E_m (1 + \xi_\eta V_f) (1 - \eta V_f) \quad [6.2]$$

where $\eta = (E_f/E_m - 1)/(E_f/E_m + \xi)$

At angles (θ) other than 0° and 90°, E_θ varies non-linearly and has a rapid fall-off with rotation away from 0°.

The strength of a fibre-reinforced composite is also highly anisotropic

with fibres dominating in the 0° direction but the resin or matrix at most other angles. At 90° , the resin or interface is determinant and the strength is often 50% of the resin alone. As a result, it is necessary to arrange the fibres at angles to each other, either in laminates, with woven rovings or random mat in order to meet the complex stresses encountered.

A consequence of these lay-ups is that the failure of a fibre-reinforced plastic or composite involves in order, multiple transverse (or matrix) cracking, interlaminar or intralaminar shear failure (delamination) and multiple fragmentation of the fibres, before final fracture. In this way, large energies can be absorbed in fracture, which provides the explanation for the toughness of a composite made from these brittle components.

6.7.5.2 Short fibre reinforcement

With GRP, short fibres are often employed in industrial applications for economic and design reasons. The mechanics differ from those of long fibres because the fibre length reinforcing efficiency is reduced. This is because the build up of stress from the end of the fibre occurs over a transfer length (l_t). As the fibres become shorter, the average stress carried by the fibre is reduced because the transfer length at each end becomes more and more dominant.

The simple constant shear model of Kelly and Tyson,³ can be used to define the critical length (l_c) of a fibre for it to be loaded to fracture.

To be 95% efficient, the actual length has to be $>10 l_c$. In short-fibre reinforced plastics a distribution of fibre lengths exists within the moulded artefact. Sub-critical fibres will not break and tend to pull out on fracture of the composite, whereas the super-critical ones will break and become progressively sub-critical. As a result, the stress-strain curves will invariably be non-linear.

The law of mixtures, Equation [6.1], can be modified to account for the reduced reinforcing efficiency of the fibres with length (η_l) and orientation (η_θ)

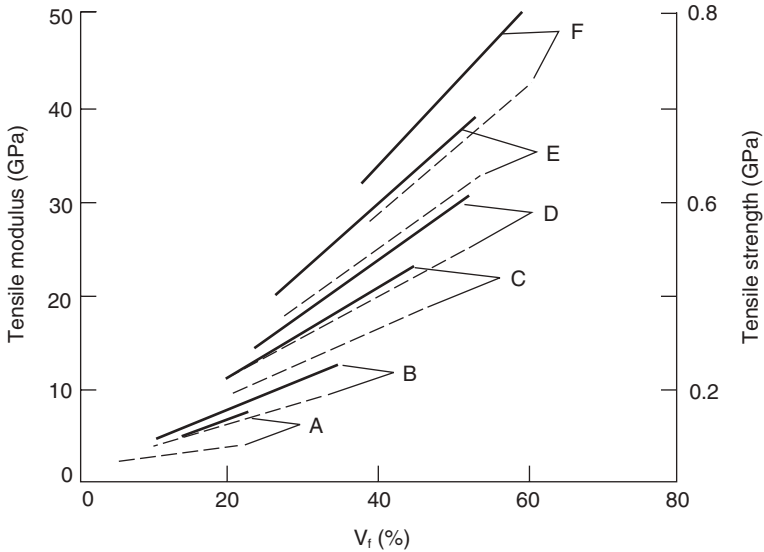
$$E_c = \eta_\theta \eta_l E_f V_f + E_m V_m \quad [6.3]$$

However, this requires knowledge of the fibre length and angle distributions, making predictions of strength and modulus difficult.

For the materials referred to as GRP or 'fibreglass', $l \gg l_c$ as in chopped strand mat and similar reinforced composites, a simple estimate can be obtained from

$$E_c = \frac{3}{8} E_l + \frac{5}{8} E_t \quad [6.4]$$

Typical properties of GRP with differing fibre reinforcements are presented in Fig. 6.13.



6.13 Stiffness (—) and tensile strength (----) of polyester-glass laminates, showing effect of different forms of reinforcement over practical ranges of glass content. A, random short fibre plastic; B, chopped strand mat; C, balanced woven roving; D, crossplied laminate or woven rovings; E, unidirectional woven roving; F, continuous aligned roving (after Jones⁵).

6.8 Design of fibre glass composites

The selection of glass fibres for a particular application depends on the economics and the application process. Two examples will be considered that illustrate some of the aspects.

6.8.1 General aspects

Fig. 6.13 illustrates the fundamental issues because short fibre mouldings (A) clearly have the poorest mechanical performance but can be rapidly moulded into a complex-shaped artefact by injection moulding. An example is a glass fibre-reinforced phenolic water pump housing for an automobile, or a glass reinforced polyamide (nylon) used for inlet manifolds. The best performance is achieved with unidirectional reinforcement (F) but only simple shapes can be manufactured in slow, labour-intensive processes, such as using an autoclave. Pultruded materials need to be cut and assembled into useful components. Thus, the basic competition between performance, processing and economics determines the choice of reinforcement and manufacturing route. The beauty of composite usage is that a variety of low cost/low volume routes (e.g. hand-lay) exist along side high-performance and high-volume solutions. From a direct comparison of material's cost, the

composite solution does not appear to be economic. However, comparison of the overall costs of manufacture shows that significant gains can be made through waste saving, assemblage costs where complex shapes can often be manufactured in one stage, in maintenance costs (helicopter rotor blades), or where improved design and performance not achievable in metals is possible (aerodynamically shaped helicopter rotor blades). Fuel savings through lightweight structures (aircraft or motor vehicles) or corrosion-resistance (yachts, ships, containers and pipes) are other important design requirements.

6.8.2 Electrical circuit boards

Here, shape is not really an issue, but for insulating performance, crucial thermal and mechanical stability is. The choice of matrix resin determines thermal stability and the use of balanced woven rovings will provide the latter. The one issue which is important is the maintenance of insulation. Specialist D-glass formulations are available (Table 6.6). Interfacial stability is required to prevent moisture-induced conduction paths. Thus, the industry utilises starch-sized woven rovings as the reinforcement. These are heat-cleaned prior to deposition of an appropriate coupling agent in the absence of a film former, to provide optimum adhesion without the variability that could be introduced with as-sized fibres.

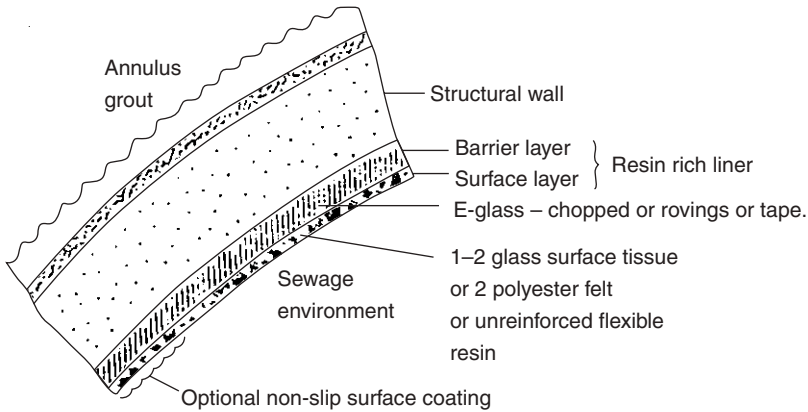
6.8.3 Chemical plant and related products

Environmental stress corrosion of GRP is of major concern. Fig. 6.8 demonstrates how differing composite parameters can be optimised for durability in acidic conditions at differing loading regimes.

For environmental durability, the more durable ECR glass can be used but at a cost penalty over standard E-glass. However, the composite can be designed to utilise the structural properties of E-glass with protection from a more chemically resistant C-glass reinforced gel-coat or barrier layer. The typical structure of a pipe for effluent is shown in Fig. 6.14. Here the important aspect is to prevent stress-corrosion initiated fibre breaks from propagating through the structure. Thus, C-glass veils coupled with chopped fibre-reinforced surface layers can inhibit a brittle crack from forming and protect the structural E-glass of the composite. In combination with higher fracture toughness resins, a durable structure can be manufactured.

6.9 Conclusions

Fibres from a number of glass formulations are available. E-glass fibres can be converted into a number of forms for reinforcement of resins, rubbers



6.14 Typical construction of a durable GRP pipe in corrosive environments.⁶² (Reproduced with permission of Mechanical Engineering Publications, now known as Professional Engineering Publishing Ltd.)

or polymers to give durable structural composites, with a wide range of application. They can also be used to reinforce cementitious products, but for durable structures alkali-resistant zirconia glass should be used. However, there is a growing application of GRP rebars for concrete using pultruded E-glass rod, where there is resin protection.

A-glass fibres are used as insulants in thermal or acoustic applications. E-glass fibres are also used in fire resistant textiles, which can be coloured using dyeable sizing.

The other major and growing application is SiO₂-based glass for optical fibre communications.

In conclusion, fibres from glass represent a major technical resource.

6.10 Acknowledgements

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