

1.08

Glass Fiber Reinforcements

DAVID W. DWIGHT
Materials/Interface Consultants, Granville, OH, USA

1.08.1 INTRODUCTION	1
1.08.2 COMPOSITION AND PROPERTIES OF PRISTINE GLASS FIBERS	2
1.08.2.1 Specifications and Chemical Compositions for Reinforcement Fibers	2
1.08.2.2 Bulk Fiber Structures	4
1.08.2.3 Bulk Fiber Properties	5
1.08.2.4 Surface Composition	11
1.08.3 GLASS BATCH AND MELTING	12
1.08.3.1 Raw Materials	12
1.08.3.2 Production and Transport of Molten Glass	12
1.08.4 FIBER FORMATION AND PROCESSING	13
1.08.4.1 Drawing Molten Glass	13
1.08.4.2 Application of Sizings	15
1.08.4.2.1 Analysis of sized glass fibers	15
1.08.4.2.2 Functions of sizing components	20
1.08.4.3 Properties of Glass Fibers Within Polymer Matrix Composites	23
1.08.5 PRODUCT DIFFERENTIATION	28
1.08.5.1 Continuous Fibers for Woven Roving, Thermosets, and Thermoplastic Pultrusion	29
1.08.5.2 Chopped Fiber Bundles for Thermoplastic Injection Molding and Thermoset Molding Compound	29
1.08.5.3 Yarns, Fabric, Mats, and Other Glass Reinforcement Products	29
1.08.6 REFERENCES	30

1.08.1 INTRODUCTION

The history of glass fibers dates back at least to several centuries BC. In Egypt coarse fibers were drawn from heat-softened glass and made into vessels by winding on a mandrel and fusing. It was not until 1893 that Edward Libbey first demonstrated glass fibers fine enough to weave. The Owens-Illinois Glass Company in Newark, Ohio carried out the developments of commercial processes for both insulation-type (spun) and reinforcement-type (drawn) glass fibers in the 1930s. In a merger with Corning Glass Works, a separate company, Owens-Corning Fiberglas, was formed in 1938. Licenses to the Owens-Corning glass fiber technology were granted in the late 1940s and early 1950s to Pittsburgh Plate Glass

(PPG) in the USA, Pilkington in the UK, and St. Gobain in France. This set the stage for the rapid development in glass fiber reinforced plastic materials over the last 50 years.

Today glass fiber reinforced plastic (GFRP) composites are high-volume, commodity materials. In 1997, the worldwide market for reinforcement glass fibers amounted to about 1.5 billion kg—orders of magnitude greater than all other reinforcement fibers combined. New markets for GFRPs in both transportation and infrastructure applications promise to accelerate the demand for glass fibers well into the twenty-first century. Service lifetime prediction is a critical issue for the acceptance of GFRP into those and other high-performance applications. The thin coating layer, called a “sizing” or “size” that is applied to glass fibers during

manufacture, plays an important role in determining many of the properties of GFRP, especially environmental durability. Previous reviews of glass fibers have not considered those subjects in any detail. Those gaps are filled by (i) introducing modern surface analytical data characterizing sizing layers, (ii) discussing sizing components and their roles in the different GFRP applications, and (iii) elaborating upon the influences of water and temperature on glass fiber structure and properties.

Much of the essential information on the composition, processing, and properties of commercial glass fibers has been collected in one book and a few review articles. The classic text *The Manufacturing Technology of Continuous Glass Fibers* (Lowenstein, 1973, 1983, 1993) provides a detailed picture of each component of the manufacturing process. One could go into glass fiber production with little additional guidance. There is a wealth of practical mechanical and chemical engineering detail on the selection and handling of raw materials, and melting and delivering viscous glass to the “bushings” (a term derived from early technology when glass fibers were drawn from the bottom of a ceramic melter with holes that were lined with platinum or “bushed”). Also discussed thoroughly are the methods of application and types of “sizings,” which are functional coatings that are always applied to the fibers immediately after drawing. Many methods for conversion of continuous fibers into a variety of commercial glass-fiber and reinforced-polymer-composite products are described in detail. It is a sign of the maturity of the glass fiber industry that the original 1973 edition of this book contains essentially all of the same technology as the third edition published in 1993. An earlier, thorough overview of commercial glass fiber (Lowrie, 1967) production includes “pristine” (untouched and uncoated) fiber structure and property data, a discussion of the nature of flaws that limit glass fiber strength, information on coating of fibers with sizings, and the fabrication of GFRP parts. Two handbook chapters focus on modern, commercial glass fiber products. One (Miller, 1987) concentrates on the physical, electrical, thermal, optical, and radiation properties of C-, E-, and S-glass fiber compositions. Basic fiber manufacturing and fabrication processes for the different product forms, such as rovings, chopped strands, milled fibers, mats, papers, and textile yarns are the subjects of the other review (Watson and Raghupathi, 1987).

Drawing heavily on those references, Section 1.08.2 contains basic information on the generic glass compositions, and the corresponding engineering property data and test methods for

“bulk” properties. Following Gupta (1988), the influence on fiber microstructure and properties of the thermomechanical history that fibers experience during forming is reviewed. The possibility of residual stresses or surface micro-porosity in glass fibers is ruled out, and there is little evidence for structural anisotropy. However, it is clear that a metastable structural configuration is frozen into thin fibers because of the high cooling rate. Also there is some structural and/or chemical difference between the fiber surface and its core. The fracture mechanics stress corrosion theory of slow crack growth is summarized to provide a quantitative explanation for the effects of strain rate, temperature, and humidity on glass fiber tensile strength.

The three stages in glass fiber manufacturing are treated sequentially in Sections 1.08.3–1.08.5. Raw materials handling, melting of the specific mixture, and delivery of the molten glass to bushings are outlined in Section 1.08.3. Section 1.08.4 discusses the formation of fibers, with particular emphasis on the multiplicity of factors—other than composition—that influence the actual properties of any specific glass fiber sample. The application of an aqueous suspension or “sizing” to the fibers is elaborated. New insights from surface analytical methods and a discussion of the roles of sizing ingredients is included. Manufacturers use dozens of sizings, each of which is designed for a specific set of GFRP applications. It is at this stage of the process where commercial products are differentiated one from another. Section 1.08.5 summarizes the relevant processing and property issues for the major categories of glass fiber uses.

1.08.2 COMPOSITION AND PROPERTIES OF PRISTINE GLASS FIBERS

1.08.2.1 Specifications and Chemical Compositions for Reinforcement Fibers

Historically, commercial glass compositions were developed to optimize specific bulk properties of the fibers for a particular market. For example, printed circuit boards require low electrical conductivity fibers, and a calcium aluminoborosilicate with a maximum alkali content of 2% evolved, and was given the designation “E-glass” signifying Electrical grade. (Note that commercial E-glasses actually contain less than 0.2% alkali.) The tradition developed of associating a specific letter designation with a glass chemical composition and a

Table 1 Composition ranges for the oxides used in specific commercial glass fibers.

Oxide	A-Glass (%)	C-Glass (%)	D-Glass (%)	E-Glass (%)	ECR-Glass (%)	AR-Glass (%)	R-Glass (%)	S-2-Glass (%)	No boron E-Glass (%)
SiO ₂	63–72	64–68	72–75	52–56	54–62	55–75	55–65	64–66	52–62
Al ₂ O ₃	0–6	3–5	0–1	12–16	9–15	0–5	15–30	24–25	12–16
B ₂ O ₃	0–6	4–6	21–24	5–10		0–8			
CaO	6–10	11–15	0–1	16–25	17–25	1–10	9–25	0–0.1	16–25
MgO	0–4	2–4		0–5	0–4		3–8	9.5–10	0–5
ZnO					2–5				
BaO		0–1							
Li ₂ O						0–1.5			
Na ₂ O + K ₂ O	14–16	7–10	0–4	0–2	0–2	11–21	0–1	0–0.2	0–2
TiO ₂	0–0.6			0–1.5	0–4	0–12			0–1.5
ZrO ₂						1–18			
Fe ₂ O ₃	0–0.5	0–0.8	0–0.3	0–0.8	0–0.8	0–5		0–0.1	0–0.8
F ₂	0–0.4			0–1		0–5	0–0.3		0–1.0

Source: Hartman *et al.*, 1996.**Table 2** Letter designations and average fiber diameters for commercially available glass fibers.

Yarns			Reinforcements					
Letter	m ⁻⁶	in ⁻⁵	Letter	m ⁻⁶	in ⁻⁵	Letter	m ⁻⁶	in ⁻⁵
B	3.2	12.5	GH	10.0	36.9	P	18.4	72.5
C	4.4	17.5	H	10.8	40.0	Q	19.7	77.5
D	5.7	22.5	J	12.1	47.5	R	21.0	82.5
DE	6.5	25	K	13.3	52.5	S	22.2	87.5
E	7.0	27.5	L	14.6	57.5	T	32.5	92.5
F	8.2	32.5	M	15.9	62.5	U	24.8	97.5
G	9.3	37.5	N	17.2	67.5			

corresponding set of unique engineering properties. Engineering and purchasing specifications for glass fibers followed suit, and became standardized in, for example, MilSpec R-60 346 and ASTM C162.

A-glass is a soda lime silicate glass that is less expensive to make (e.g., because of the lower processing temperatures and zero boron content) than E-glass, but has much poorer electrical properties. D-glass is a borosilicate composition developed for low dielectric constant in certain high-performance electrical applications. ECR-glass is a calcium aluminosilicate with a maximum alkali content of 2%, and with properties similar to E-glass, except it is more corrosion resistant in acidic environments. AR-glass is an alkali zirconium silicate composition, which provides a greater alkali resistance necessary in cement and concrete reinforcement. S-glass is a magnesium aluminosilicate glass that delivers the highest combination of mechanical, thermal, and chemical properties of all commercially available glass

fibers. It is used primarily in aerospace and military applications. The percentage range of each oxide used in the various letter designations for glass fibers is listed in Table 1. There are overlaps within the concentration ranges of the various glasses, giving rise to ambiguities in the actual composition used for a given glass type. The composition ranges for a given type of glass are broad enough that different properties are obtained from batches made from one end of the composition range to the other. Therefore, to be precise, one must specify the composition of the glass and not just its letter designation.

A further complication to the letter designations used to specify a glass composition range is the fact that letters, as shown in Table 2, are also used to designate commercial fiber diameters. Note that in commercial manufacturing, diameter distributions are not measured routinely. Instead the average diameter (letter designation) is estimated from measurement of yardage (yd lb⁻¹), which is the inverse of the

weight per unit length of a bundle of fibers (in g km^{-1} ["Tex"] or g/9000 m ["Denier"]). In fact there is a statistically normal distribution of diameters in commercial products, typically ranging $\pm 10\%$ of the average value used to select the commercial letter designation.

Strands which are produced in a "twisted" configuration and contain fiber diameters B through G or H (mostly D and G, commercially) are called yarns. These fibers are thin enough to enable high-speed twisting and weaving into textile fabrics. Yarns are generally coated with a starch-oil-based sizing that is specifically designed to enable the weaving operations *and especially* to burn off the fabric easily and completely. The weaver then coats the fabric with a "finish" whose chemistry is tailored to optimize the properties of a specific end-use product (e.g., circuit boards, filter bags, reinforced paper).

Fiber diameters greater than G are called "reinforcements." They are used in chopped or continuous form in all the conventional thermoplastic and thermosetting plastic processes. In this segment of the business, sizing compositions are extensively tailored by the glass fiber manufacturer, and remain on the fibers throughout subsequent GFRP processing. Thus these sizings must enhance *both* handling properties (strand integrity, lubricity, antistatic, etc.) *and* composite properties (dispersion, compatibility, adhesion, etc.).

Today over 95% of commercial reinforcement glass fibers are made from E-type composites. However, environmental regulations in Europe and North America have made it necessary for glass fiber manufacturers to reduce emissions, primarily due to the volatile borate and fluorine components. In 1997, Owens-Corning introduced a new fluorine- and boron-free glass composition into the reinforcement fiber market (Rossi and Williams, 1997). The new E-type fibers have the corrosion resistance of ECR-glass, while the other properties, including cost, are said to be equivalent to or better than boron-containing E-glass. Neither titania nor zirconia—the costly components in ECR-glass and AR-glass, respectively—is present in the new fiber composition (Eastes *et al.*, 1998). A revised standard recently published, ASTM D578-98, redefines the composition ranges of E-glass to include zero boron (except for fine weaver's yarns and aerospace applications). Furthermore, ASTM and other standards groups are planning to shift emphasis in the future to *property-based* specifications, replacing or supplementing current *composition-based* specifications. This is technically a better way to define the glass types and is more relevant to the GFRP fabricator's needs.

1.08.2.2 Bulk Fiber Structures

Glassy materials have no crystallinity or long-range order, i.e., they are amorphous. All glass fibers used in GFRP are silicates. In these glasses, silica forms a three-dimensional network of Si–O bonds from the fundamental building-block of $[\text{SiO}_4]^{4-}$ tetrahedra. The oxides in Table 1 are classified into three groups according to their function in the network structure. Other than silica, boric oxide is the only other network *former*, with a polyhedral structure that connects with the silica network. Aluminum, titanium, and zirconium oxides provide cations that can substitute for silicon in a network tetrahedron, contributing to the network stability; they are called "intermediates." All the remaining oxides in the table are termed network "modifiers" because they can form only one or two chemical bonds, and thus they disrupt the network structure. The two-dimensional representation of a simplified glass structure in Figure 1 shows the amorphous silica component as an interconnected network of silicon and oxygen atoms. Each monovalent sodium ion forms an ionic bond with a nearby oxygen atom, thus disrupting the covalent network. Network modifiers are essential for lowering the melting temperature of the glass, manipulating the viscosity–temperature relationship, and thus mitigating some of the manufacturing challenges associated with processing refractory materials.

During the drawing process, fibers experience extremely rapid cooling ($> 10\,000\text{ }^\circ\text{C s}^{-1}$) and high axial tension. As a result they are frozen in a metastable, supercooled liquid structure. A parameter called the *fictive temperature*—conceptually equivalent to the temperature at which the structural configuration of the liquid state is frozen—is used to characterize the metastable solid state. Two estimates of the fictive temperature of E-glass fibers have been made (Gupta, 1988). Based upon measurements of the densities and expansion coefficients of bulk glass, its melt and fibers, the fiber fictive temperature was determined to be at least $333\text{ }^\circ\text{C}$ above the liquidus temperature of bulk glass. However, using a theoretical expression involving estimates of the cooling rate and the activation energy for viscosity, a fictive temperature $160\text{ }^\circ\text{C}$ above the liquidus was found. The difference in those two estimates may be reconciled by including the influence of forming tension, which interacts with quench rate to influence glass fiber structure and effectively lowers the fictive temperature (Pahler and Bruckner, 1985). There is general agreement that the atomic structure

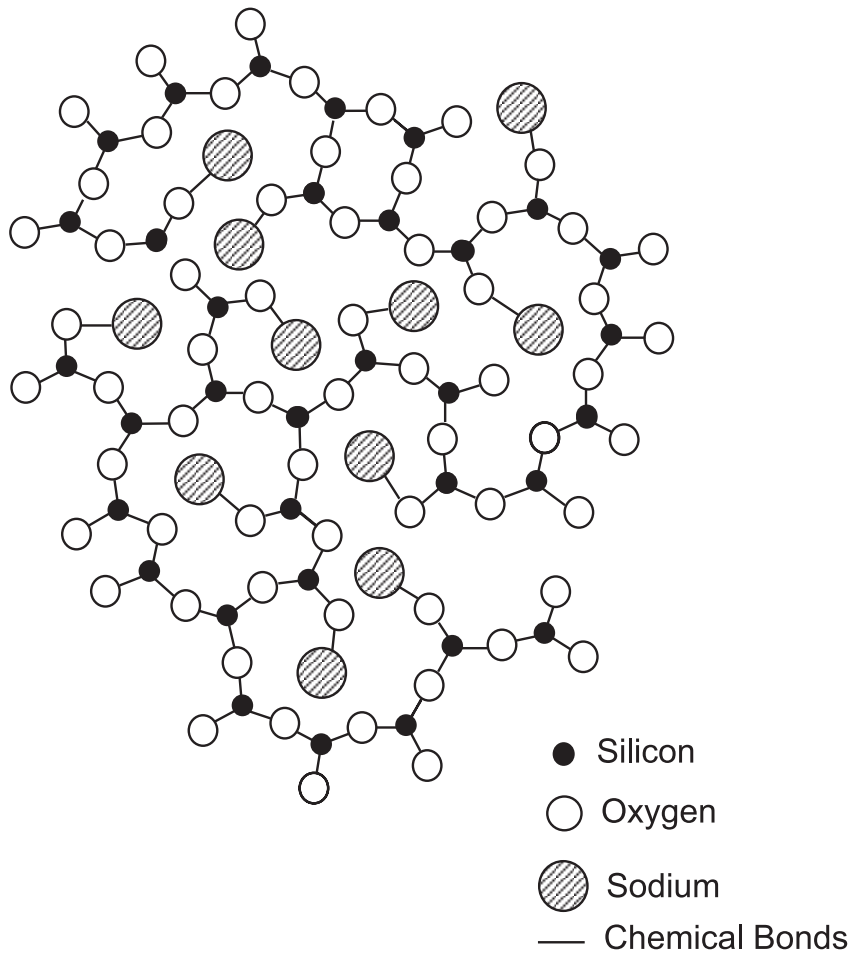


Figure 1 Idealized model of the amorphous atomic structure of a typical glass. There is no long-range order or orientation, and properties are isotropic.

within solid glass fibers is similar to the structure that exists in the glass melt a few hundred degrees Centigrade above the liquidus temperature. As a result, glass fiber properties differ from those of bulk, annealed glass of the same composition. Fiber tensile strength and acid solubility are higher than annealed values, and other properties such as Young's modulus, density, refractive index, thermal conductivity, and heat capacity are lower (Otto, 1955, 1961). Nuclear magnetic resonance (NMR) measurements indicate that the fraction of four-coordinated boron increases from 10% to 16% in a rapidly cooled aluminum borosilicate glass fiber after annealing (Gupta *et al.*, 1985). The general conclusion is that upon heat treatment, the metastable fiber structure of the fiber relaxes gradually, and fiber structure and properties become identical with those of bulk glass. The implication of this phenomenon for GFRP lifetimes at elevated temperatures is discussed later.

1.08.2.3 Bulk Fiber Properties

Tables 3–6 list the engineering properties and the corresponding glass fiber type and composition. The new, zero-boron E-type glass is included. Electrical and thermal properties were measured on bulk glass specimens, whereas the density, refractive index, mechanical, and chemical properties are reported for pristine fibers drawn from a single-tip laboratory bushing. These data represent measurements made under ideal laboratory conditions on model specimens. Some general structure–property relationships can be determined by comparing Table 1 with Tables 3–6, keeping in mind the function of the different oxide ingredients in the silicate glass network. As expected, densities are directly related to the atomic weights of the glass components in a specific composition. Compared with the corresponding bulk glass, fiber densities are 1–3% lower, and refractive indices are 0.3–1% lower.

Table 3 Physical properties of commercial glass fibers.

	<i>Physical properties</i>								
	<i>A-Glass</i>	<i>C-Glass</i>	<i>D-Glass</i>	<i>E-Glass</i>	<i>ECR-Glass</i>	<i>AR-Glass</i>	<i>R-Glass</i>	<i>S-2-Glass</i>	<i>No boron E-Glass</i>
Density (g cm ⁻³)	2.44	2.52	2.11	2.58	2.72	2.70	2.54	2.46	2.62
Refractive index	1.538	1.533	1.465	1.558	1.579	1.562	1.546	1.521	1.561
Softening point °C (°F)	705(1300)	750(1382)	771(1420)	846(1555)	882(1619)	773(1424)	952(1745)	1056(1932)	9161
Annealing point °C (°F)		588(1090)	521(970)	657(1215)				816(1500)	7361
Strain point °C (°F)		522(1025)	477(890)	615(1140)				766(1410)	691

Source: Hartman *et al.*, 1996.

Table 4 Electrical and thermal properties of bulk glasses used to produce glass fibers.

	<i>A-Glass</i>	<i>C-Glass</i>	<i>D-Glass</i>	<i>E-Glass</i>	<i>ECR-Glass</i>	<i>AR-Glass</i>	<i>R-Glass</i>	<i>S-2-Glass</i>	<i>No boron E-Glass</i>
<i>Electric properties</i>									
Dielectric constant 1 MHz	6.2	6.9	3.8	6.6	6.9	8.1	6.4	5.3	7.0
10 GHz			4.0	6.1	7.0			5.2	
Dissipation factor 1 MHz		0.0085	0.0005	0.0025	0.0028		0.0034	0.0020	0.001
10 GHz			0.0026	0.0038	0.0031		0.0051	0.0068	
Volume resistivity (ohm-cm)	1.0E + 10			402E + 14	3.84 + 14		2.03E + 14	9.05E + 12	
Surface resistivity (ohms)				4.20E + 15	1.16E + 16		6.74E + 13	8.86E + 12	
Dielectric strength (V ml ⁻¹)				262	250		274	330	
<i>Thermal properties</i>									
Specific heat									
J/g °C (BTU/lb °F)									
23 °C	0.796(0.190)	0.787(0.188)	0.733(0.176)	0.810(0.193)				0.737(0.176)	
200 °C		0.900(0.215)		1.03(0.247)	0.97(0.232)				
Thermal expansion									
Coefficient (× 10 ⁻⁷)	°C (°F)	°C (°F)	°C (°F)	°C (°F)	°C (°F)	°C (°F)	°C (°F)	°C (°F)	
− 30 °C to 250 °C	73 (41)	63 (35)	25 (14)	54 (30)	59 (33)	65 (36)	33 (18)	16 (8.9)	60 ()

Source: Hartman *et al.*, 1996.

Table 5 Chemical durability of commercial glass fibers.

Durability (% weight loss)	Chemical properties							
	A-Glass	C-Glass	D-Glass	E-Glass	ECR-Glass	AR-Glass	R-Glass	S-2-Glass
H ₂ O: 24 h	1.8	1.1	0.7	0.7	0.6	0.7	0.4	0.5
168 h	4.7	2.9	5.7	0.9	0.7	1.4	0.6	0.7
10% HCl 24 h	1.4	4.1	21.6	42	5.4	2.5	9.5	3.8
168 h		7.5	21.8	43	7.7	3.0	10.2	5.1
10% H ₂ SO ₄ 24 h	0.4	2.2	18.6	39	6.2	1.3	9.9	4.1
168 h	2.3	4.9	19.5	42	10.4	5.4	10.9	5.7
10% Na ₂ CO ₃ 24 h		24	13.6	2.1		1.3	3.0	2.0
168 h		31	36.3	2.1	1.8	1.5		2.1

Source: Hartman *et al.*, 1996.**Table 6** Mechanical properties of pristine glass fibers with commercial compositions.

	Physical properties							
	A-Glass	C-Glass	D-Glass	E-Glass	ECR-Glass	AR-Glass	R-Glass	S-2-Glass
Tensile strength, MPa								
– 196 °C		5380		5310	5310			8275
23 °C	3310	3310	2415	3445	3445	3241	4135	4890
371 °C				2620	2165		2930	4445
538 °C				1725	1725		2140	2415
Young's modulus, GPa								
23 °C	68.9	68.9	51.7	72.3	72.3	73.1	85.5	86.9
538 °C				81.3	81.3			88.9
Elongation at break, %	4.8	4.8	4.6	4.8	4.8	4.4	4.8	5.7

Source: Hartman *et al.*, 1996.

The softening point in Table 3 is the temperature at which the glass will readily flow under its own weight, and the strain point is identical to the glass transition temperature. The values are related to the extent of three-dimensional network structure that results from the specific glass composition. Monovalent cations (sodium and potassium) lower the glass transition temperatures by disrupting the network. On the other hand, more tetravalent silicon leads to higher glass transition temperature glasses (quartz glass represents the upper limit). Higher temperature glasses require more energy to process, and are generally more difficult to manufacture, resulting in higher costs. This is why S-glass fibers are five times more expensive than E-glass fibers.

The electrical properties in Table 4 were measured on bulk glass specimens, but the values for fibers should not differ significantly. In general, these properties are typical for inorganic, nonconducting materials. As

mentioned earlier, E- and D-glass were developed specifically for cost-effective and high-performance electrical insulation and dielectric properties, respectively. Note that E-glass is over three orders of magnitude more electrically resistive than A-glass. D-glass has by far the lowest dielectric constants and dissipation factors (again approaching silica glass).

For comparison purposes, specific heat and thermal expansion data for bulk glass are also listed in Table 4. However, the thermal properties of glass fibers differ significantly from those of bulk glass, due to relaxation of the metastable, supercooled liquid state frozen into fibers during formation. The thermal expansion values apply to fibers only during cooling and during heating up to about 100 °C. Relaxation *shrinkage* in fiber length begins at about 100 °C, and becomes dominant above 400 °C (Otto, 1961).

A detailed study of enthalpy relaxations in glass fibers (Huang and Gupta, 1992)

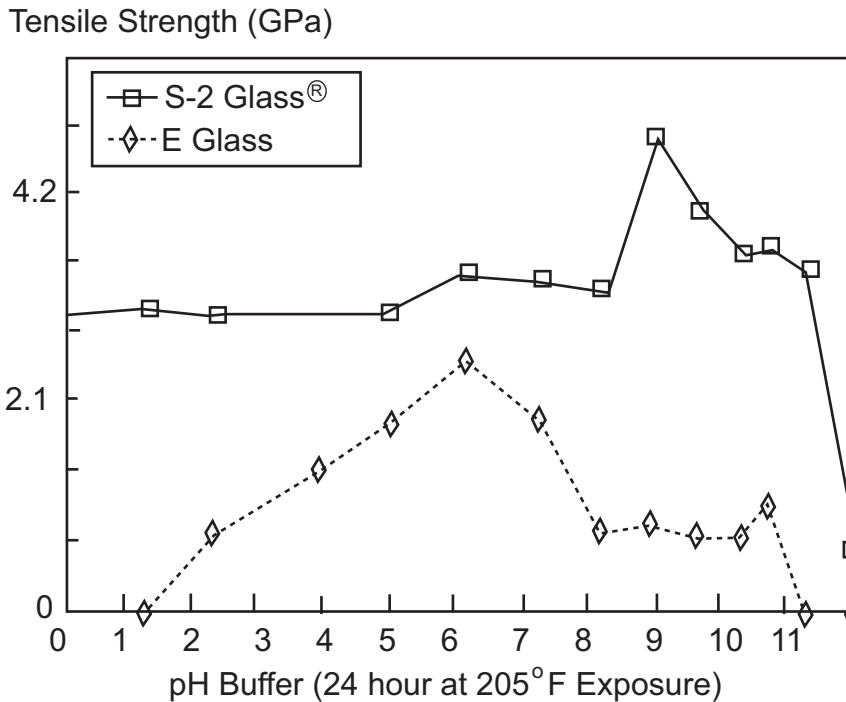


Figure 2 The influence of acid and base exposure on the single filament tensile strength of E- and S-glass fibers (after Hartman *et al.*, 1996).

elaborated upon the pronounced differences in differential scanning calorimetry (DSC) between fibers and bulk glass of the same compositions. Fibers show strong exotherms from about 100 to 500 °C and no glass transition, whereas bulk glasses have sharp, endothermic glass transition peaks around 600 °C and no exotherms. Huang (1992) was able to account quantitatively for the DSC results via an extension of the phenomenological, nonlinear relaxation model of Tool–Narayanaswamy (TN), which includes new terms for non-Newtonian viscous flow to characterize the relaxation times of fiber structures that are far from equilibrium.

Listed in Table 5, the percentage weight loss experienced by 10 µm diameter pristine, unsized fibers, after a fixed time of exposure at 96 °C to aqueous solutions, is offered as a measure of the “chemical durability” of glass fibers, which generally are inert in organic solvents. Note that such tests are static extractions, and weight losses may be significantly greater under conditions of fresh solution replenishment (Baillif *et al.*, 1995). Results of standard exposure testing to water and solutions of hydrochloric and sulfuric acids and sodium carbonate are listed for the different glass fiber compositions. In water, the weight loss is proportional to the amount of highly soluble cations (B, Na, K) in the glass.

The leaching mechanisms are very different in acidic vs. basic media. In acid, removal of cations other than silicon begins rapidly, but slows down as a barrier of leached glass (high in silica) is formed. When E-, AR-, and ECR-glass fibers were loaded in static tension under 5 N sulfuric acid solutions, E-glass fibers failed at much shorter times than the other two. Only the E-glass fibers showed a leached “skin” with spiral cracking after exposure to acid (Lewis *et al.*, 1984). It can be concluded that AR- and ECR-glass compositions are more resistant to acid leaching and fiber strength reduction under static loading conditions. The reduction in fiber strength seems to be associated with cracking in a brittle surface layer, which has been depleted in cations and is relatively porous as a result.

Basic solutions, on the other hand, effectively attack the silica network, but some of the metal oxides can be reprecipitated on the fibers in static solution tests, leading to ambiguity in interpretation of the weight loss data. That problem can be circumvented by determining the tensile strength after exposure to either acidic or basic solutions, although the experimental work involved is difficult and time-consuming. Typical results for E- and S-glass are shown in Figure 2. The high silica S-glass fibers show no decrease in strength from pH1 to

pH 11, whereas E-glass fibers degrade in strength significantly either above or below a pH of 6. (Note that the weight loss of the E-glass fibers was negligible between pH 6 and pH 9.)

While those data are useful for relative comparisons of pristine fiber durability, there are questions to bear in mind when considering the durability of GFRP composites. First, matrix resin may be influenced differently by the exposure. Second, the sizing layer that coats commercial glass fibers has a significant influence on the kinetics and mechanism of weight loss in solution. Third, in a GFRP composite, the solution has to diffuse through the matrix to reach the fibers, which is likely to change the solution composition significantly. Finally, the way fibers are loaded and fractured inside a moisture-saturated GFRP composite is much different than in a single filament tensile test.

In Table 6, the Young's modulus values reflect the cohesive energy density of the specific glass network, in a similar manner to the thermal glass transition temperatures. In E-glass, thermal compaction of the fiber structure leads to an increase in modulus at 538 °C. Poisson's ratio for E-glass fibers is 0.22, and S-glass is 0.23, similar to other materials known to be isotropic. The Young's modulus of thermally compacted glass fibers decreases slowly with increasing temperature (Lowrie, 1967). Poisson's ratio is independent of temperature. The greater elongation at break of S-glass implies greater toughness, which is corroborated by the values of fracture toughness (critical stress intensity factor) determined by Vickers indentation on bulk glass specimens. As a result, composites made from S-glass fibers have exceptional properties for demanding applications such as ballistic armor.

It is important to understand the role of flaws and the brittle fracture behavior of glass fibers. A fracture mechanics model was used by Charles (1958) to derive a relationship between the crack velocity, V , and the applied stress intensity factor, K_I . Subsequently, flaw size and shape were shown to be the basis of the statistical nature of glass fiber tensile strength, as well as its dependence on fiber diameter, gage length, strain rate, temperature, and humidity. Tensile strength data measured on pristine, un-sized single filaments at various temperatures have been interpreted in terms of the slow crack growth model of stress corrosion (Gupta, 1988). This model also explained the measured decrease in room temperature glass fiber strength with increasing relative humidity in terms of the influence of moisture adsorption on crack growth. The stress corrosion susceptibility coefficient, N , depends on flaw size. The

following expression (Pahler and Bruckner, 1985) describes completely the dependence of tensile strength, S , on temperature (T), strain rate ($\dot{\epsilon}$), and humidity (X):

$$S(T, \epsilon, X) = \frac{S_{LN}}{[1 + \Phi S^3(T, \dot{\epsilon}, X)]^{1/(N-2)}} \quad (1)$$

and

$$\Phi = \left[\frac{(N-2)V_c X^a \exp(-Q/RT) Y^2}{2(N+1)\dot{\epsilon} E(T) K_{IC}^2(T)} \right]$$

where S_{LN} is the fiber strength measured in liquid nitrogen, V_c is the critical crack velocity leading to rapid, brittle fracture, E is Young's modulus, α is the power law exponent of relative humidity, Q is the activation energy for slow crack growth, R is the gas constant, and Y is the dimensionless constant relating applied stress to the stress intensity factor. For temperatures above about 200 K, this equation reduces to a simple Arrhenius relation for fiber strength vs. temperature:

$$\ln S(T) = \frac{Q}{(N+1)RT} + \text{constant} \quad (2)$$

The data in Figure 3 are plotted accordingly and the fit to the straight line prediction is excellent. The unusually high value of tensile strength measured at liquid nitrogen temperature is consistent with the model, as the slow crack growth mechanism is nonexistent at that temperature. Useful values of the fracture mechanics parameters are $K_{IC} = 0.91 \text{ MPa m}^{1/2}$, $V_c = 2.5 \text{ mm s}^{-1}$, $N = 25\text{--}30$, and $Q = 42 \text{ kJ mol}^{-1}$.

The critical stress intensity factor or fracture toughness, K_{IC} , depends on the square root of the size of the crack that initiates rapid crack growth and tensile failure. Flaws that initiate fracture at high tensile strength values ($> 2 \text{ GPa}$) are difficult to identify experimentally because of their nanometer size. Substitution of typical values of strength, modulus, and surface energy into Griffith's fracture mechanics model leads to a crack depth estimate of 1.4 nm. This size flaw could be accounted for by local composition gradients—within the fiber or from external contamination (e.g., moisture adsorption or deposition of particles), accumulations of vacancies, submicroscopic imperfections of surface topography, etc. Unfortunately, when strong glass fibers fail at their most critical flaw, the release of stored elastic energy shatters the remaining two halves of the filament literally into dust. This makes it impossible to collect a specimen for fractographic analysis.

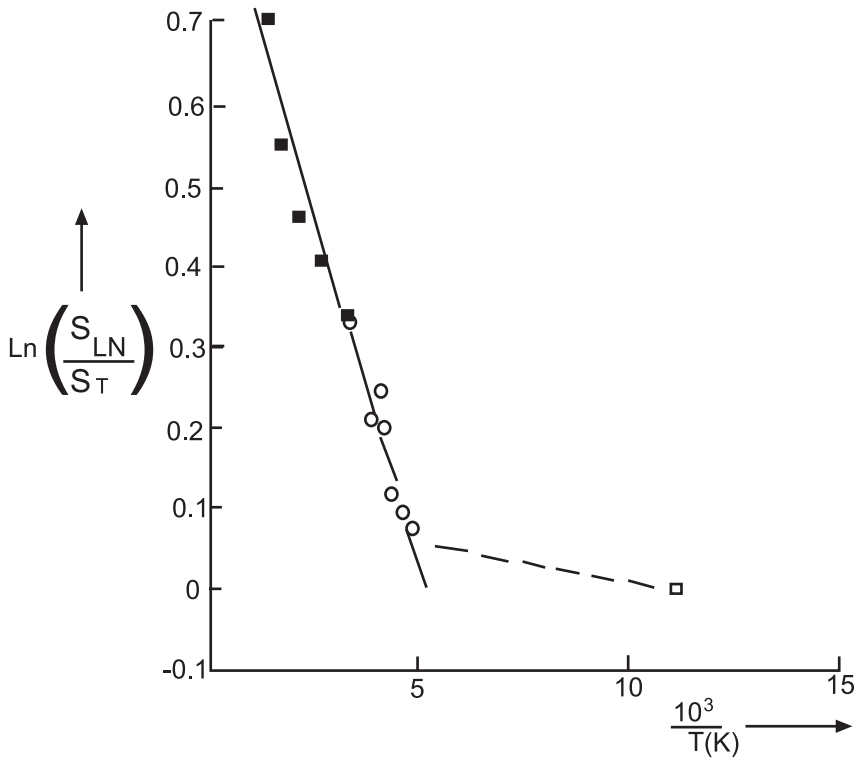


Figure 3 Arrhenius plot of the dependence of glass fiber tensile strength on temperature. There is excellent agreement with the predictions of the fracture mechanics model of slow crack growth (after Gupta, 1988).

1.08.2.4 Surface Composition

The process of drawing molten glass from platinum alloy bushing tips at high cooling rates and linear speeds into a water mist generates a unique composition and structure in the top nanometer of the glass fiber surface. The wetting behavior of molten glass on platinum and its alloys has been explained by the strong affinity of the metals for the nonbridging oxygen atoms in the glass (Copley *et al.*, 1975). Considering that 60–70% of the atoms in glass fibers are oxygen atoms, it is reasonable to expect the fiber surface to be oxygen rich. Molecular dynamics simulations predict that a high concentration of silanol groups (Si–OH) will be generated at strained-ring and bond-defect sites on silica surfaces created in the presence of water (Feuston and Garofalini, 1990). Glass surfaces are known to adsorb water strongly. Temperatures of 773 K are required to remove the chemisorbed water, and 5–10 monolayers of water cover fiber surfaces under normal conditions (Donnet *et al.*, 1975). As a result, contact angle analysis of pristine, unsized glass fibers produces surface energy data equivalent to liquid water (Wesson and Jen, 1984). This is one of the reasons why attempts to quantify the surface thermodynamic properties of glass fibers remains a controversial topic.

Using nitrogen and argon adsorption isotherms, and precise analysis of water desorption vs. temperature on glass fibers of various compositions and diameters, Wesson and Vajo (1998) determined that the amount of chemisorbed water was inversely proportional to the cooling rate during fiber forming, and to the silica content of the fibers. As discussed in Section 1.08.2.2, the cooling rate determines the fictive temperature, which is an index of the glass fiber structure. Thus, glass fibers formed at different fictive temperatures will have unique surface structures and bonding characteristics. This may help to explain both the discrepancies in the scientific literature and the wide variability in commercial glass fibers, because there is rarely any attempt to determine or control the fictive temperature of individual filaments.

Attempts to determine the atomic composition and bonding of glass fibers with modern surface analysis instrumentation have met with limited success. The results of the early studies using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), and Auger electron spectroscopy (AES) were reviewed, and the unique nature of glass surfaces was confirmed (Pantano, 1989). These techniques provide atomic or molecular spectra from the top

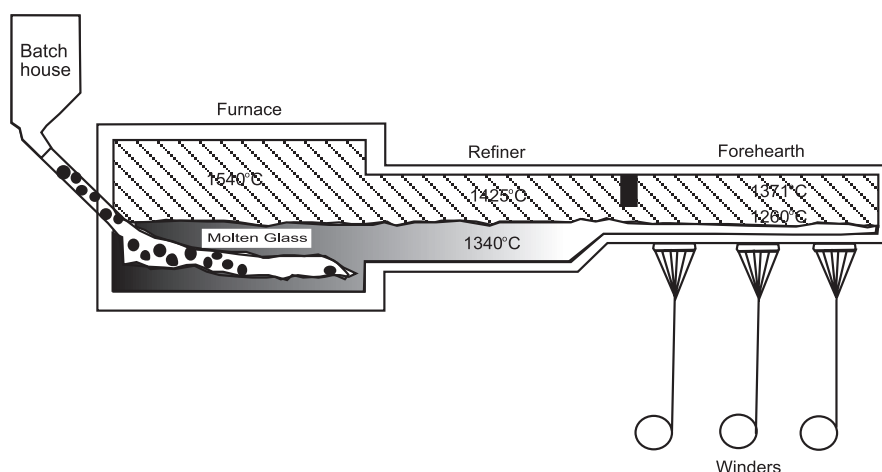


Figure 4 Simplified schematic diagram of a large glass fiber melting and drawing operation.

0.5–10 nm, using energetic beam probes in high-vacuum chambers. Note that, even in a high vacuum of 10^{-8} torr, it took 4 h at 473 K to remove all the adsorbed water from a glass sample that had been fractured in the laboratory atmosphere (D'Sousa *et al.*, 1997). The low values of the isoelectric point (IEP) reported for E-glass fibers (Maeder *et al.*, 1994; Wu *et al.*, 1997) are consistent with the first atom layers being dominated by silanol groups. This top-layer composition certainly will have an influence on the subsequent adsorption and bonding of sizing ingredients on glass fibers, and on the initial properties and wet aging of GFRP composite materials. The evolution of chemistry and texture of glass fibers in moist atmospheres is known to be a function of composition (Trens *et al.*, 1996).

1.08.3 GLASS BATCH AND MELTING

A simplified schematic diagram of the batch house, furnace, and fore-hearth sections of a typical glass fiber manufacturing plant is shown in Figure 4. Glass fibers are formed by drawing the viscous melt through many small holes in a plate or bushing positioned under the forehearth. It is essential for the economic operation of this type of plant to run continuously over the entire life of the furnace and forehearth.

1.08.3.1 Raw Materials

Glass fiber manufacturing plants usually are located within the proximity of a reliable, economic supply of raw materials other than boric oxide which is always imported to the plant.

“Glassmaking sand” is the source of silica. China clay (aluminosilicate) of low alkali content is often the source for alumina. Magnesia is introduced either with dolomite, an equimolar magnesium/calcium carbonate, or with burnt dolomite, the corresponding mixed oxide, which is less of a pollution problem. Calcium oxide comes from limestone. Boric oxide is introduced either with colemanite (calcium borate) or boric acid (hydrous boric oxide).

Great care is taken to ensure that these raw materials are free from impurities. With a typical glass fiber manufacturing plant processing 50–100 tons per day of glass, even ppm levels of certain impurities can disturb the melter behavior (e.g., carbon), corrode the furnace (e.g., chlorides), and cause fiber breaks (e.g., ceramics). Batch handling is enclosed and computer controlled. After the individual raw materials are weighed, the batch is thoroughly blended and fed into the “back end” of the furnace by screw conveyers.

1.08.3.2 Production and Transport of Molten Glass

Furnaces in the glass fiber industry are constructed with bricks made from several types of refractory materials. In order of decreasing temperature service, they are: (i) dense chrome oxide, (ii) dense zircon, (iii) pressed zircon, (iv) mullite, (v) insulation 2300, (vi) flux clay, and (vii) superduty clay. Most regions in a furnace are constructed with multiple brick layers, increasing in thermal resistance toward the melt. Glass fiber furnaces typically are viewed as consisting of three sections: (i) melting, (ii) refining, (iii) cooling (fore-hearths). Traditional furnaces heat the air above the batch with gas

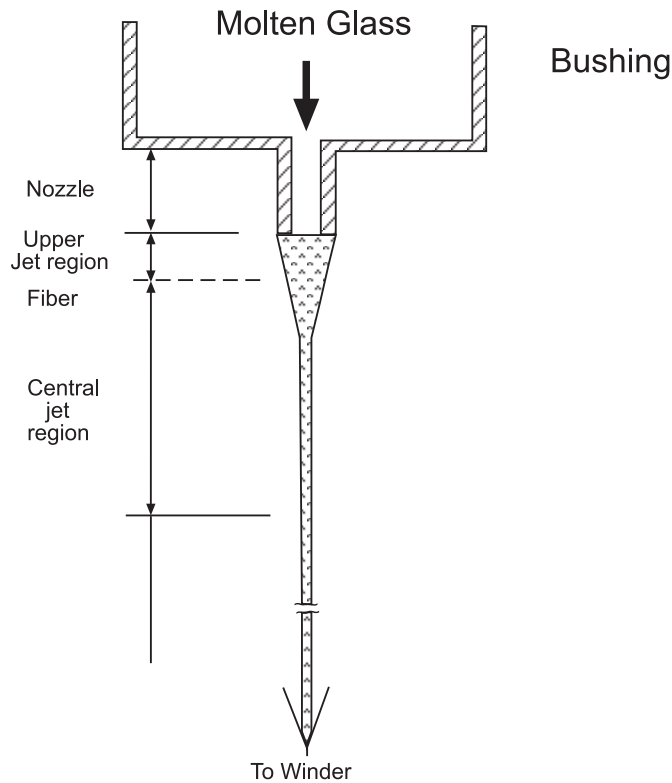


Figure 5 Sketch of the formation of a glass fiber and a bushing tip.

or oil burners; electric heating within the melt is a modern development and is widely used to boost production. Today many furnaces employ a combination of both. The temperatures are highest in the first section where melting, removal of gases, and some homogenization takes place. Rows of air bubblers are placed across the furnace about two-thirds of the distance from the back wall, at the location where the melt is hottest. Bubblers add velocity to the thermal convection currents, helping to homogenize the melt, and they help to keep incompletely fused raw materials from entering the fore-hearth. Initial cooling and homogenization is completed in the refining section. The fore-hearths are designed to further cool and maintain the molten glass close to the fiberizing temperature and distribute it to the individual fiber-forming positions (bushings).

Marble melters are used for a limited amount of commercial glass fiber production, typically on small throughput units. In this case, individual electric heating elements are placed above each bushing, and are fed with marbles (usually 2–5 cm in diameter) that have been made from the appropriate glass composition. However, the cost of melting the glass twice, as well as the expense of the precious metal heating elements, have relegated the use of marbles to small, specialty operations which require fre-

quent glass changes and for irregular periods of production.

1.08.4 FIBER FORMATION AND PROCESSING

1.08.4.1 Drawing Molten Glass

The final drawing temperature of the glass melt is controlled as carefully as possible by electrically heating the platinum–rhodium alloy plate, called a “bushing.” Molten glass flows normally by gravity through 1–2 mm diameter cylindrical “tips” as depicted in Figure 5. One bushing or “forming position” will have up to 10 000 tips. A rotating drum or take-up wheel usually located one floor below the bushing level pulls the fibers at very high rates ($450\text{--}4500\text{ m min}^{-1}$). The individual filaments are rapidly cooled by a factor of $10^4\text{--}10^5\text{ deg s}^{-1}$ and “attenuated” or elongated. The fiber diameter decreases by a factor of 100–300 within about a centimeter of the bushing tip. To a large degree, the fluid dynamics of this extraordinary phenomenon determine which glass compositions can be fiberized, as well as their optimum manufacturing conditions (bushing temperature, winder speed, depth of the melt glass above the bushing). This attenuation process

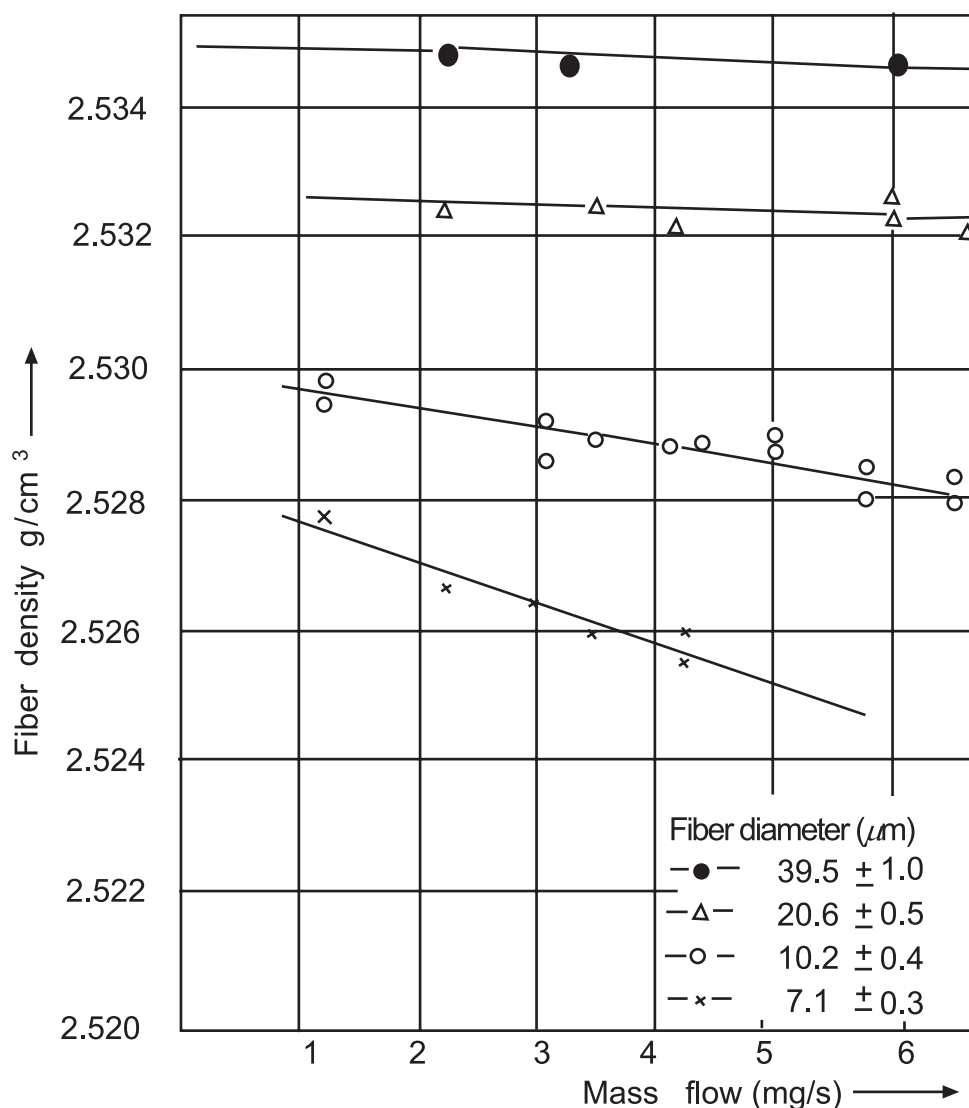


Figure 6 The dependence of fiber density upon glass flow rate during fiber formation illustrates the influence of quench rate on the structure frozen into glass fibers (after Gupta, 1988).

also creates the thermomechanical “forming history” that influences fiber properties such as density, refractive index, Young’s modulus, and chemical durability. Figure 6 illustrates the dependence of fiber density on fiber diameter and glass flow rate. The cooling rate, which is inversely proportional to the square of fiber diameter, is the primary factor, and flow rate is significant only for fine diameters (i.e., 10 μ m and less).

The “fiberizing temperature” is defined by the point where the glass melt viscosity is 5000–10 000 Pa. s, a value that is generally ideal for the fluid dynamics of fiber drawing. In order to avoid devitrification (formation of crystallites within the glass), fiberizing temperatures are maintained at least 40 °C above the

liquidus temperature. The difference between the fiberizing and liquidus temperatures is known as “delta T .” Its value for a specific glass composition is used as a rough indication of the “processing window” for commercial feasibility of forming fibers from that composition. If delta T is too small (< 50 °C), devitrification is likely to plague manufacturing since it is very difficult to avoid “cool” spots in the melter and/or fore-hearth. There are only few glass compositions with commercially attractive combinations of (i) cost of raw materials, (ii) delta T , (iii) processing economics, and (iv) fiber properties. The importance of glass viscosity, surface tension, contact angle with the bushing tip, and emissivity have been summarized in a quantitative treatment (Gupta, 1988).

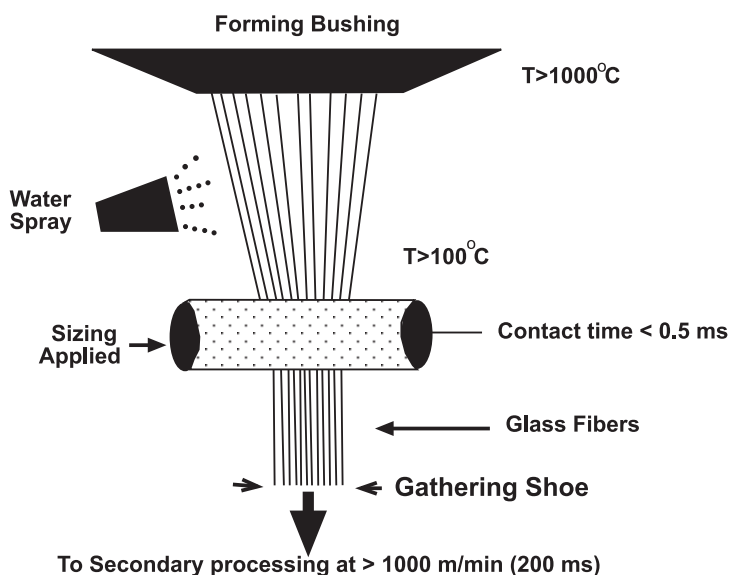


Figure 7 Simplified schematic of a commercial glass fiber forming position, identifying the extraordinary process speed and times.

The strong dependence of glass viscosity on temperature is responsible for stabilizing fiber formation at high attenuation ratios.

1.08.4.2 Application of Sizings

Within milliseconds of solidifying, glass fibers pass across an applicator roll where they are coated with sizing solutions as depicted in Figure 7. Commercial glass fiber products generally have 0.2–2% by weight (termed loss on ignition or LOI) of a sizing layer applied during forming. The applicator consists of a graphite roll partially submerged and rotating slowly in the sizing, which usually circulates continuously through the applicator pan. The fibers pass rapidly (~ 0.5 ms contact time) through a thin sizing layer on the surface of a coating roll. Process alignment from the bushing to the gathering shoe determines the average contact length of the fiber “fan” on the applicator roll. The amount of sizing picked up is proportional to the solids concentration of the sizing dispersion in the applicator reservoir, which normally ranges from 3 to 10 wt.%. Usually the applicator roll speed is the final setting used to adjust the LOI. During the strand consolidation steps, 20–50% of the sizing is removed from the strand at contact points and by the whipping action the strands experience as they travel from the final shoe or contact point to the winder (2–4 m). The thickness and uniformity of the resultant sizing layers on the fibers depends primarily on the nature of the film-

former (the majority component), the mutual compatibility of the sizing components, and the LOI. However, modern surface analytical studies have shown that the coatings are usually heterogeneous, with thicknesses varying from less than 10 nm to more than 1 μ m. Figure 8 schematically illustrates the sizing layer on a bundle of glass fibers, and the cross-section of an individual filament.

1.08.4.2.1 Analysis of sized glass fibers

The traditional approach to analyzing a sized fiber bundle is to extract a quantity of sized glass fibers in a refluxing solvent, e.g., acetone, and use chromatography in combination with infrared or mass spectroscopy, attempting to separate and identify the various sizing components in the extract. However, nothing is learned about the fraction of the sizing (10–50%) that is chemically bound to the fiber. The soluble components of glass fiber sizings are thought to function mainly as handling and processing aids, whereas the chemically bound components are thought to be responsible for stress transfer within a composite. More recent studies have employed modern instrumental surface analyses of the sizing layers, before and after solvent extraction (Thomason, 1995).

Surface thermodynamic and electrokinetic approaches offer the advantages of relatively simple, inexpensive experimental techniques and single-valued parameters. These methods not only characterize the surface but also have

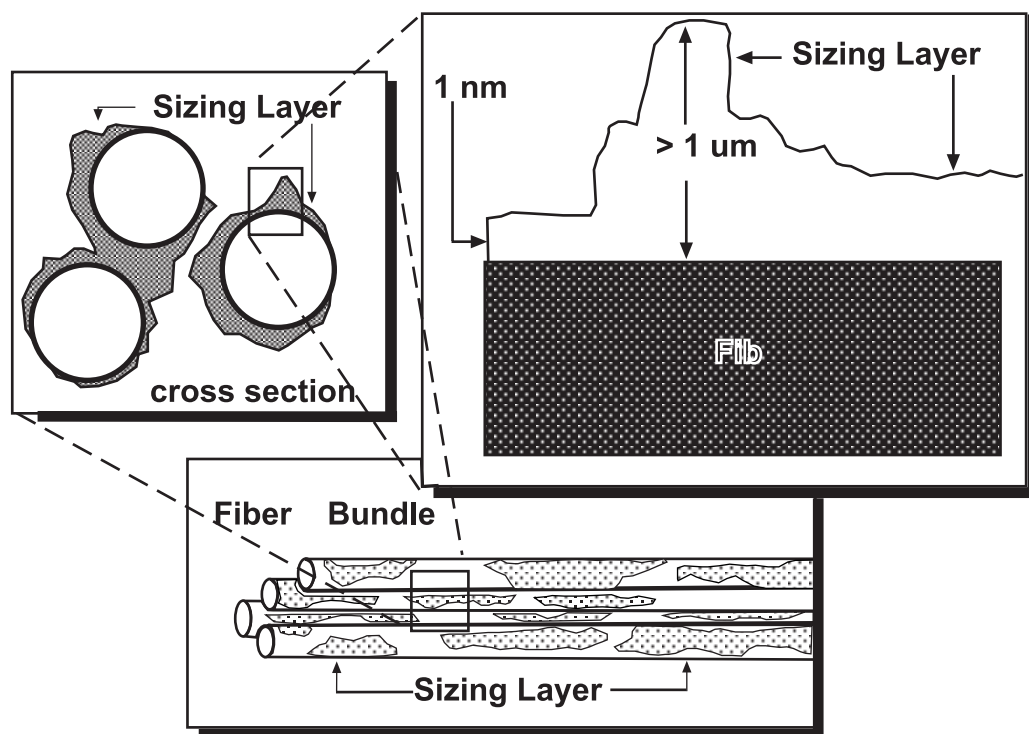


Figure 8 Idealized sketches of the nonuniform distribution of sizing layers that is characteristic of commercial glass fiber products.

the potential to be used in mathematical models of structure–property relationships. Also it is possible to relate the thermodynamic and electrostatic parameters to the surface compositions determined through the use of modern instrumental methods (e.g., XPS). The most reliable conclusions are drawn when data from microscopic, spectroscopic, thermodynamic, and electrokinetic measurements all corroborate one model that explains the technological behavior of a particular materials system.

There are myriad thermodynamic techniques for surface analysis, including inverse gas chromatography (IGC), programmed thermal desorption (PTD), adsorption isotherms, and flow microcalorimetry (Lloyd and Dwight, 1994). However, the analysis of liquid contact angles on single fibers and wicking of liquids into fiber bundles are the most common. Measuring the angle of contact between a probe liquid and the solid sample is used to estimate the thermodynamic properties of surfaces. Strictly speaking, contact angle experiments measure a property of the *liquid–solid interface*, and the data are expressed in terms of the “work of adhesion” between the solid and the liquid. However, using certain approximations and assumptions, a number of ways have been proposed to extract a solid surface free energy from contact angle measurements. Theoretical treatments

have emphasized the separation of forces across interfaces into the ubiquitous dispersion forces and the electron donor–acceptor (or acid–base) interactions. The hydrogen bond is the most common example of acid–base interactions. Such values can be used as a relative index of thermodynamic properties of surfaces, and they have been found useful in predicting wetting, spreading, and adhesion of many dissimilar fluids. For “mimic testing” or quality control purposes, it may be necessary only to select the right test liquid and determine the contact angle.

The “advancing” angle, θ_a , is formed as the liquid advances slowly across the surface: the *low-energy* portion of the surface determines its value. The “receding” angle, θ_r , is formed when the liquid is withdrawn from previously wetted areas: it is characteristic of the *high-energy* portions of the surface. If the surface is perfectly homogeneous, then the advancing and receding contact angles are equal. However, most surfaces are heterogeneous, and display a difference between the advancing and receding contact angles, termed “hysteresis,” which can be used as a relative index of surface heterogeneity. The Wilhelmy method (the “wetting balance”) measures the forces on the sample as it is immersed and withdrawn from the liquid reservoir, and the contact angles are calculated

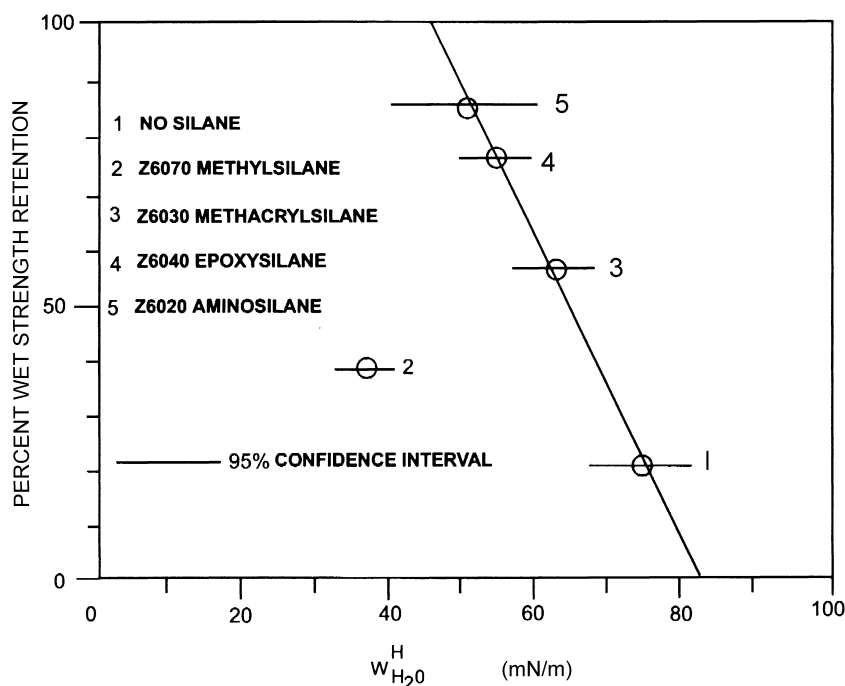


Figure 9 Direct proportionality between the percentage strength retained for a GFRP composite after exposure to boiling water and the work of adhesion for water on a series of silane-treated glass fibers (after Wesson and Jen, 1984).

from the intercepts of the two buoyancy slopes. Another useful wetting balance experiment—called “wicking”—can be performed using samples in the form of a bundle of fibers. In this case, the bundle is held stationary and the weight of liquid taken up by the capillaries between the fibers. Analysis of the wicking rate data on a selected series of liquids can determine a geometrical “capillary constant” and surface energy values independently.

Using water and methylene iodide as probe liquids on pristine glass fibers gave surface energetics equivalent to liquid water (Wesson and Jen, 1984), which is in agreement with earlier studies showing that such fibers are coated with several monolayers of strongly adsorbed water. Treatment with different silanes produced glass fibers with a wide range of hydrogen bonding capacities. An inverse proportionality was shown (Figure 9) between the hydrogen bonding component of the work of adhesion and the ability of the respective epoxy/glass fiber composite to retain its strength after boiling in water. Calculations based on contact angle measurements of the epoxy’s surface energetics showed that the “wet-strength retention” improved in direct proportion to the effective competition of water and epoxy molecules for bonding sites on the silanized glass fiber surfaces. Another study on a similar series of silanized glass fibers used the same wetting

liquids, but a different method of data reduction (Berger and Eckstein, 1984). Again, the mechanical property (single filament interfacial shear strength) after water boiling was directly proportional to the interfacial thermodynamics. However, in a study that included five fully formulated commercial-type sizings in 50% glass fiber/vinyl ester composites, only general trends among surface energetics, interfacial shear strengths, and dry composite strength were noted. Factors such as solubility of the sizing’s polymeric ingredients in the matrix were found to be important (Larson and Drzal, 1994). Contact angle hysteresis of liquid epoxy resin on glass fibers with a series of epoxy-compatible sizings was related to the degree of coverage as indexed by the surface C:Si ratio determined by XPS, and to the interlaminar shear strength of epoxy composites (Thomason, 1989).

Electrokinetic analysis with a “streaming current” apparatus is used to determine the “Zeta potential” (or corresponding electrical charge) of fiber surfaces immersed in a liquid. The pH at which the surface is neutral (Zeta potential equals zero) is called the isoelectric point (IEP), and is the value used to quantify the solid surface in terms of its Brönsted acid–base character. The theoretical basis for the IEP values of metal oxide surfaces has been developed, and the IEPs of mixed oxide glasses were

Table 7 Isoelectric points (IEP) of some E-glass fibers.

Glass fiber coating	IEP (pH)
Water	3.5 ^a
Water	2.5 ^b
Aminosilane (A-1100)	10.0 ^a
Aminosilane (A-1100)	6.0 ^b
Methacryloxysilane (A-174)	2.0 ^b
Epoxy	4.2 ^a
A-1100 + epoxy	9.5 ^a
A-1100 + polyethylene/polyurethane	10.0 ^a
A-1100 + maleated polypropylene	4.0 ^c

^a Maeder *et al.*, 1994. ^b Wu *et al.*, 1997. ^c Maeder *et al.*, 1996.

accurately predicted by a mixture rule based on surface molar components (Carre *et al.*, 1992).

As discussed above, the drawing process for glass fibers produces a nonequilibrium structure that is less dense than bulk glass of the same composition. Another manifestation of the difference in structure is that fibers have IEP values 3–4 pH units lower than calculated from the surface molarity mixture rule: fiber surfaces must be strongly enriched in silica. There are only a few publications with IEP values of glass fibers coated with water, silanes, and polymeric film formers. Representative results are collected in Table 7. The IEP values for water-sized glass are essentially equivalent to that of pure silica. The increase in IEP upon treatment with aminosilane indicates that the original glass-surface silanols have been eliminated, and that there are residual amine groups increasing the basicity. Obviously the degree of basicity can differ according to the specific silane application. Some nitrogen-containing

surfactants also shift the Zeta potential curve to higher pH values; this may explain the result in Table 7 for the epoxy coating. On the other hand, from the very low IEP for methacryloxysilane, it is apparent that the silane layer on the glass surface *contributes additional silanol groups*. Comparing the last two lines in the table, it appears that aminosilane interacts with the maleate groups of the polypropylene emulsion, but does not react with the epoxy emulsion.

The advent of XPS opened up the possibility of obtaining quantitative information on the atomic concentrations in the top ~10 nm of glass surfaces. Interactions between glass surface atoms (e.g. boron) and silane overlayers has been documented (Pantano *et al.*, 1992). Correlation of surface composition and bonding of silanes with other properties, such as surface energies and moisture desorption, became possible (Wesson *et al.*, 1992).

Now it is possible to model the sizing layers on commercial glass fibers and compare the results with XPS data. Figure 10 depicts the physical basis for the model. From that diagram, it can be seen that the carbon:silicon ratio is proportional to sizing thickness and coverage. At complete coverage and infinite thickness (10 nm on the XPS depth scale) the carbon:oxygen ratio is related to the chemical stoichiometry of the sizing layer. To extract information on both the *chemical composition* and *surface coverage* of sizings from the XPS data, a mathematical model was developed, based on a patchy overlayer hypothesis (Thomason and Dwight, 1999). The sizing layer thickness is first calculated from the known LOI, fiber diameter, fiber and sizing densities, and trial values of the fractional coverage of the glass fiber by the sizing layer. Then the number

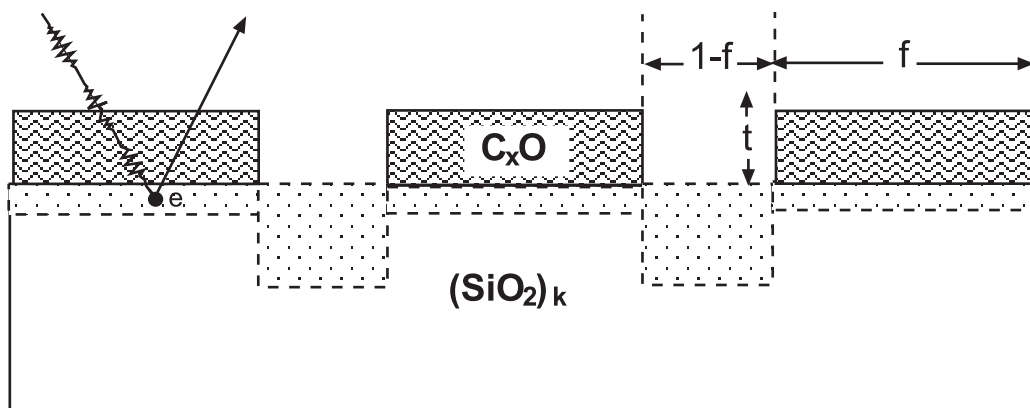


Figure 10 Physical model and parameters used to relate XPS analysis of sized glass fibers to the thickness and stoichiometry of the sizing layers (after Thomason and Dwight, 1999).

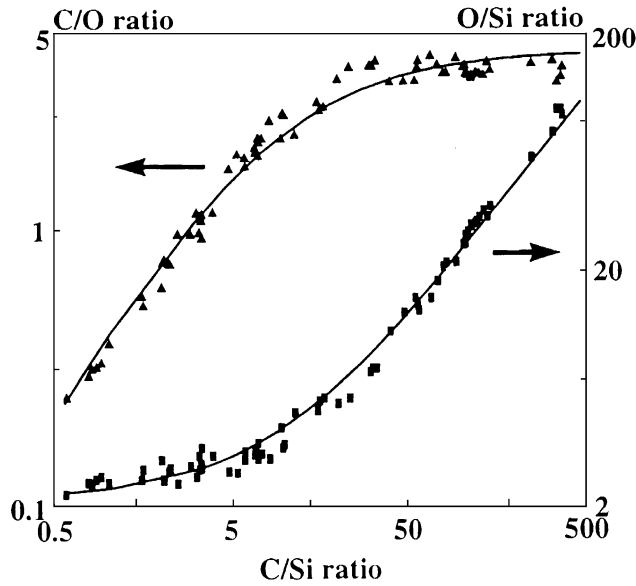


Figure 11 Log-log plot of XPS data on a number of commercial glass fiber products. The lines were generated with the theoretical patchy overlayer model (after Thomason and Dwight, 1999).

of carbon, oxygen, and silicon atoms within the XPS sampling depth is calculated and compared graphically with atomic ratios determined by XPS. Figure 11 shows a log-log plot of the XPS data for C:O and O:Si ratios vs. the C:Si ratio from 12 epoxy-compatible commercial glass fibers (before and after acetone extraction). The excellent fit by the solid lines calculated from the mathematical model verifies the utility of the physical model in Figure 10, in spite of its oversimplifications. Approximately one monolayer of sizing coverage can be inferred from the break in the slope of the O/Si curve at C:Si = 10. Below that value, the O/Si ratio is relatively unchanged, reflecting the silica content of the glass fiber surface.

It can be shown that the slope of a linear plot of the O/Si ratio vs. the C:Si ratio is a direct measure of the O:C ratio—the stoichiometry—of the sizing layer, and the intercept is equal to the silica stoichiometry in the glass surface. Figure 12 shows such plots for many replicate samples of five different sizings (Thomason and Dwight, 1999). In each case, slopes of the lines for each sizing are significantly different, and each gives a C:O ratio equivalent to the values calculated from the known sizing formulation. This plot also shows that the scatter in XPS atom ratios is entirely due to variations in thickness and coverage of sizing along the strand of a given commercial product as well as before and after extraction of the physically bound components.

A comparison of typical thermosetting and thermoplastic sizings in the light of the model

applied to XPS atom concentration data is presented in Figures 13 and 14. Four commercial epoxy-compatible glass fiber products with LOI between 0.5 and 0.6% and four polypropylene-compatible products with LOI values between 0.6 and 0.8% were selected to be as comparable as possible in terms of the amount of sizing applied to each sample. The histograms show that there is much more variation in both chemical composition and coverage on the polypropylene-compatible fibers than on epoxy-compatible fibers. This may reflect the fact that new sizings for polypropylene compatibility are currently under development, whereas epoxy-compatible sizings reached maturity decades ago. As expected, the stoichiometry of the polypropylene-compatible sizings is enriched in hydrocarbon (higher C:O ratio) relative to epoxy-compatible sizings.

In terms of coverage, one important conclusion derived from matching XPS data to the model is that many sizings cover at least 90% of the glass fibers. Thus the XPS ratios are a very sensitive measure of small changes in coverage levels from 90 to 100%. Composite properties appear to be sensitive to the coverage levels as well. Figure 14 presents the coverage results in terms of the percentage of glass fiber surface that is not covered with sizing, which is meant to imply that it is a measure of flaw density. In fact, the trends in composite properties are the same as the trends in coverage. Note that the level of coverage on polypropylene-compatible fibers is actually lower than on the epoxy-compatible fibers, even though the LOI values are

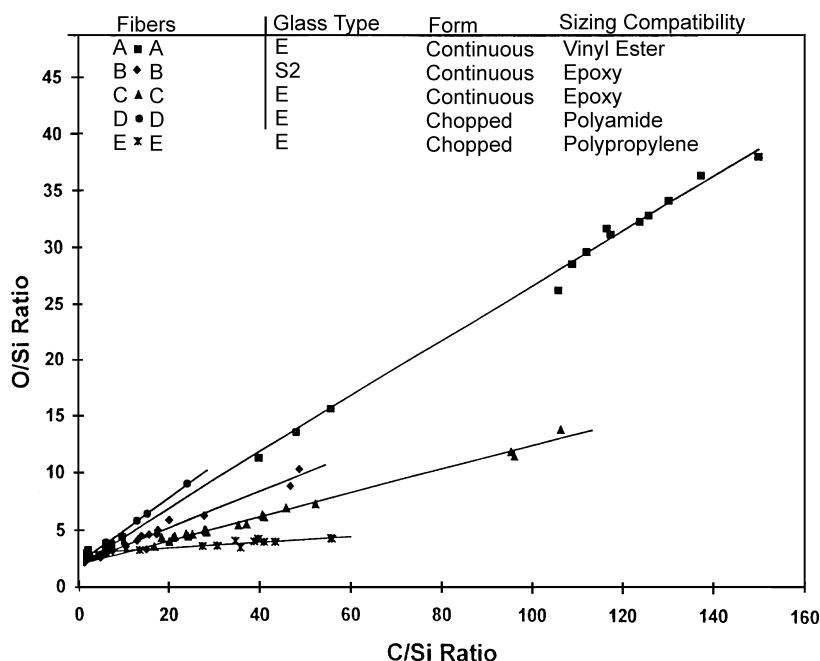


Figure 12 Linear plots of the XPS data from five commercial glass fiber products. The solid lines were generated with the theoretical patchy overlayer model using a unique stoichiometry (C:O ratio) for each line (after Thomason and Dwight, 1999).

20–40% greater in the former case. This probably is due to lower spreading and leveling related to the higher molecular weight and larger particle-size emulsions used in thermoplastic sizings. Furthermore, in-line drying of chopped bundles with thermoplastic sizings reduces the degree of spreading because of the very short time at high temperature. The “lumpy” morphology and/or the higher molecular weight film formers may enhance the bonding between fibers via “spot welding” and greater adhesive strength, respectively. Certainly the relatively extreme conditions of thermoplastic extrusion and injection molding require greater “strand integrity.”

1.08.4.2.2 Functions of sizing components

Sizings on glass fibers are supposed to provide a variety of attributes including lubricity and strand integrity to enable high-speed processing, as well as compatibility with specific matrix resins to promote strength and durability in the final composite. Table 8 lists the general classes of chemical compounds found in glass fiber sizings and the primary roles each is intended to play in fiber handling, composite processing, or properties.

Most reinforcement sizings contain at least two ingredients: an organometallic “coupling

agent” and a polymeric “film-former.” Sizings for filament winding and pultrusion often contain lubricants, molecular aspects of which have been addressed by Guzzetta (1968). Emulsifying agents are necessary to stabilize aqueous dispersions of film-formers, lubricants, and other insoluble organic components. Nonaqueous sizings may have advantages for some sizings, but they are less adaptable to commercial production because of potential flammability and emissions control problems and are thus rarely used.

Many authors have applied a variety of analysis tools to study the bonding of organosilanes to glass. However, many of the publications do not apply to the conditions, and especially the extraordinary dynamics, of the commercial glass fiber sizing application process. For example, calculations based upon XPS results on five different unhydroyzed silane coupling agents adsorbed on glass fibers under laboratory conditions showed that the thickness of the adsorbed layer was proportional to the length of the organic “tail” (Pantano and Wittberg, 1990).

Using glass fibers prepared under commercial application conditions, XPS and SIMS were combined with extraction and epoxidation procedures to generate evidence for chemical bond formation of an aminosilane coupling agent simultaneously with glass fiber and epoxy (Wang and Jones, 1994). Adhesion to

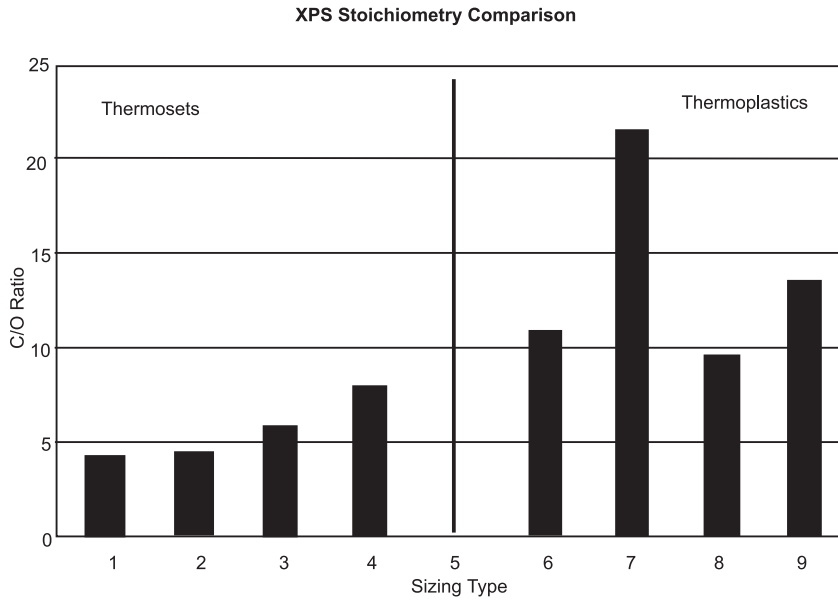


Figure 13 Histogram comparing eight commercial glass fiber products in terms of stoichiometry (after Thomason and Dwight, 1999).

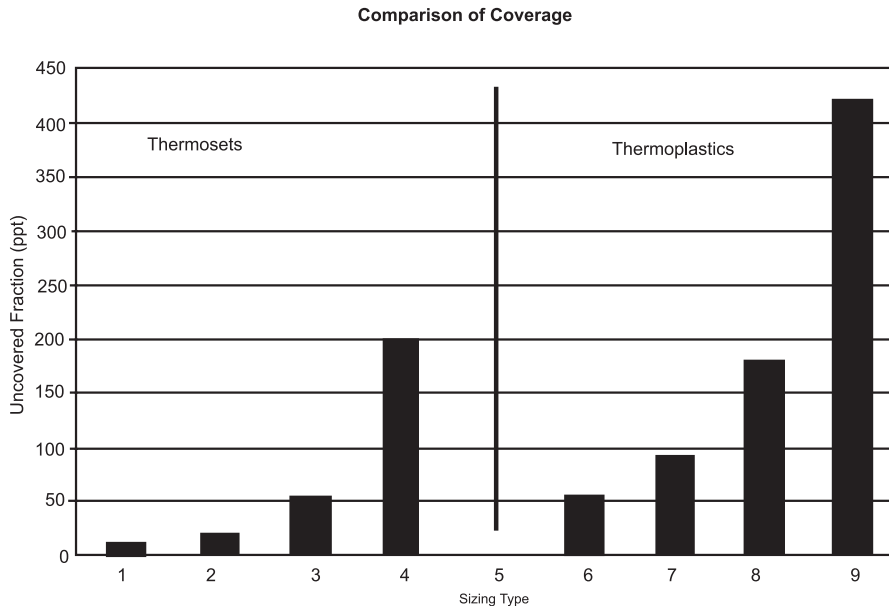


Figure 14 Histogram comparing eight commercial glass fiber products in terms of the relative amount of exposed glass surface, i.e., not covered with sizing (after Thomason and Dwight, 1999).

glass fiber has been related to acid–base interactions between the sites on the glass fiber surface, the silane coupling agent, and the polymer. Surface acidity and basicity determined by flow microcalorimetry combined with XPS analyses provided the basis for models for silane adsorption mechanisms as well as bonding to the matrix. Those results, in addition to microscopic study of micro- and macro-composite specimens, helped to rationalize the

properties of filament-wound, unidirectional epoxy and polyester composites (Fowkes *et al.*, 1990; Dwight *et al.*, 1991). Another study inferred the amount of silane chemically bonded to the glass fibers from the XPS carbon:calcium ratios after acetone extraction of the physically adsorbed silane layers (Wu *et al.*, 1997). Figure 15 shows that the flexural strengths of unidirectional polyester composites increase with increasing silane coverage. The effect is

Table 8 Glass fiber sizing ingredients and functions.

<i>Ingredient</i>	<i>Function</i>	<i>Typical chemistry</i>
Film formers	Compatibilize with matrix, protect fibers, provide strand integrity	PVAc, epoxies, polyesters, polyurethanes, polyolefins, etc.
Lubricants	Protect fibers, improve forming efficiency	Imidazolines, pentamine strearates, hydrocarbon waxes, polyethylene glycols, mineral oil/amide esters, etc.
Coupling agents	Reduce aqueous stress corrosion, bonding between glass and resin	Organosilanes, chromates, titanates, and zirconates
Antistats	Reduce static charging via moisture adsorption	Quaternary ammonium compounds, halide salts
Nucleating agents	Increase number of spherulites in semicrystalline matrices	Maleated polypropylene
Surfactants	Emulsify resins, antifoam, adjust viscosity	Polyoxyethylene nonylphenyl ether, glycol ethers, EO/PO
Acids, bases	pH adjustment	Acetic acid, ammonium hydroxide

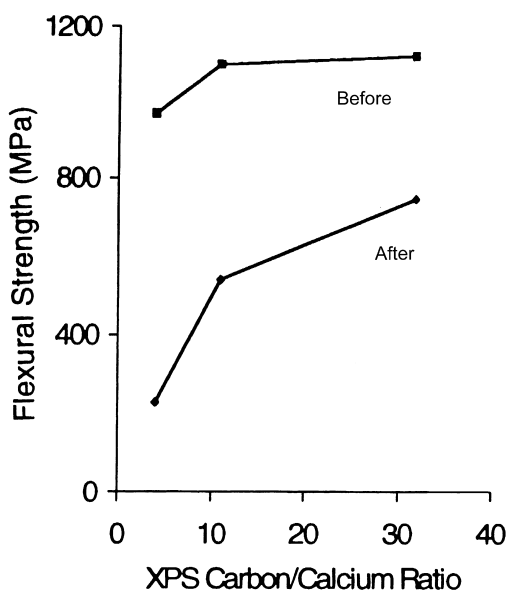


Figure 15 Dependence of polyester GFRP rod flexural strength on degree of coverage of the glass fibers by silane coupling agent layers, before and after exposure to boiling water (after Wu *et al.*, 1997).

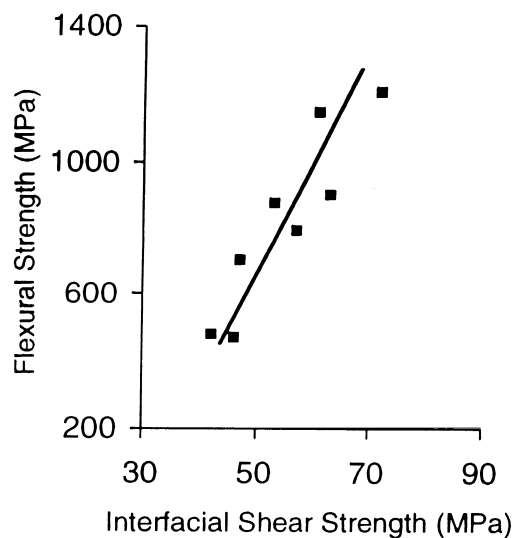


Figure 16 Linear relationship between flexural strength and the corresponding interfacial shear strength before and after boiling water exposure from a series of polyester GFRP rods using different silane coupling agents (after Wu *et al.*, 1997).

even more pronounced after subjecting the composites to a three-day water boil, confirming the importance of silanes for enhanced durability after exposure to moisture. The differences in coverage and exposure resulted in samples with differences in interfacial shear strengths. The latter was found to be directly proportional to composite flexural strength, as seen in Figure 16.

In work on a large selection of commercial glass fibers, the total amount of sizing, the T_g of extracted sizing, and the fraction (acetone insoluble) bound to the glass were found to vary widely (Thomason and Morsink, 1988). Different interphases were formed by making epoxy matrix composites at temperatures both below and above the sizing T_g . Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to show the influence on the mechanical and thermal properties of the composites. SIMS was used to show the effects on interphase chemistry. There was a direct correlation between the short beam shear strength (at fixed void content) and the concentration of material bound to the glass surface. The influence of the type of coupling agent and epoxy curing agent was also shown by Thomason (1995).

In research focused upon the effects of the T_g , solubility, and surface energy of the film formers, lubricants, and antistats in glass fiber sizings (Larson and Drzal, 1994). A series of commercially sized glass fibers were studied in a reacting vinyl ester matrix system. Axial and transverse wicking rates were measured to quantify the change in total surface free energy of the fiber/matrix systems. The sizing surface free energy and its solubility in the matrix were shown to affect interphase formation strongly, and consequently fiber/matrix adhesion and composite shear and flexural strengths.

There are significant differences in the role of sizings in thermoplastic matrices. In polypropylene (PP) composites, silane coupling agents alone did not improve interfacial shear strength (ISS) relative to bare fibers. However, ISS varied by an order of magnitude and the flexural strength of a unidirectional laminate varied by a factor of two, depending upon other sizing components. Also, ISS was correlated with the level of fiber surface coverage as measured by XPS (Thomason and Schoolenberg, 1994). A corroborating paper points out the dominant influence upon matrix and composite properties of PP nucleating agents included in glass fiber sizings (Scholtens and Brackman, 1995). Furthermore, confocal scanning laser microscopy demonstrated that the nonuniform topography of the sizing layers is preserved inside injection molded parts. Note that although

there is evidence that silanes may not be crucial for dry strength, their primary attribute is enhancing wet strength (Wesson and Jen, 1984). In glass fiber reinforced Nylon-6, relationships among surface, interphase, and composite properties have been determined by wicking and Zeta potential, fiber pull-out and fragmentation, and short-beam shear tests (Maeder *et al.*, 1994). As valuable as they are, those studies limit their concern to understanding how multicomponent, commercial sizings influence the initial properties of composite materials. Also it is important to consider the influence of mechanical and environmental stresses on the long-term durability of glass fibers and GFRP materials.

1.08.4.3 Properties of Glass Fibers Within Polymer Matrix Composites

A review of the early measurements on commercial, continuous fiber products concluded that glass fiber strength in composites “is surprisingly high, 70 to 80% of the tensile strength of virgin fibers” (Lowrie, 1967). These high retained-strength values were actually calculated from the tensile strength of resin-impregnated strands in accordance with ASTM D2343. However, when single glass filaments were “teased” from commercial roving packages and tested in tension, values ranging from 30% (Oleesky and Mohr, 1964) to 60% (Edmunds, 1961; Metcalfe and Schmitz, 1964) of the pristine fiber values were obtained for both E- and S-glass.

Part of this apparent discrepancy may be due to the statistical nature of bundle failure. However, fiber strength in a composite is effectively 2–4 times greater than the single filament strength because of the effects of matrix stress transfer in a composite. Certainly the fibers are loaded differently in single-filament vs. unidirectional composite tests. In the first case, the single largest flaw in a 1–2 cm gage length determines strength, whereas it is the average strength over gage lengths as short as 0.1 mm that controls composite strength.

There are two main types of strength-limiting flaws in glass fibers—inclusions and flaws (surface defects or bulk voids). Inclusions generally limit strength to less than 2 GPa, and they can be studied easily with SEM fractography (Gupta, 1994). Relatively large flaws can also reduce average strength values below 2 GPa, and can be detected by SEM fractography (Chang, 1990).

The latter study contains important insights on the difference between pristine fiber tensile

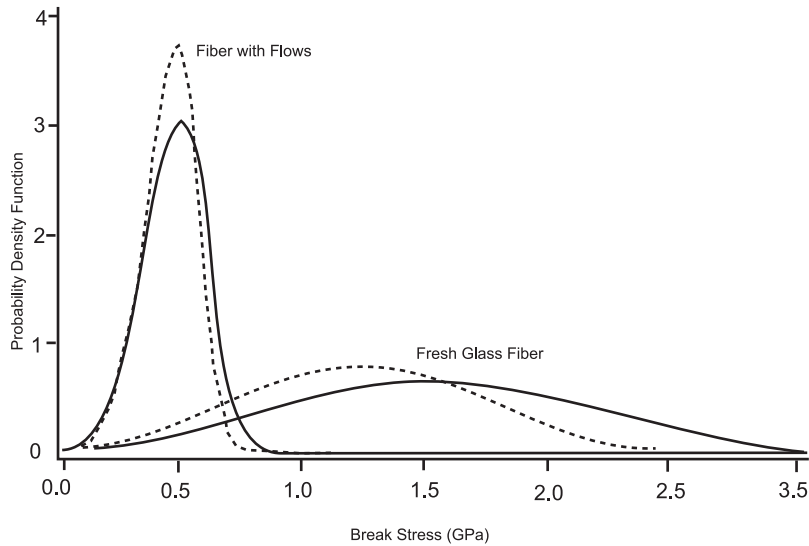


Figure 17 Glass fiber strength distributions before [—] and after [---] heating at 873 K for 4 h. Clearly, much more severe, strength-limiting flaws are introduced by self-abrasion than by thermal compaction (after Chang, 1990).

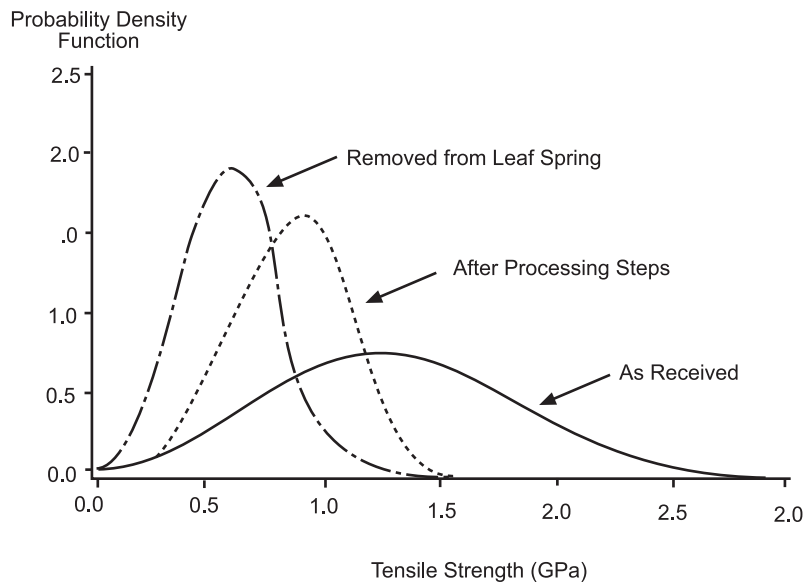


Figure 18 A comparison of glass fiber strength distributions before and after processing steps in the production of GFRP composite leaf springs (after Chang, 1990).

strength values and commercial fiber properties, before and after composite processing steps. The influence on the fiber strength distributions of composite fabricating and molding conditions, fiber-to-fiber contact, and annealing of various specimens was interpreted in terms of changes in the severity of Weibull flaws. Using single filaments that had been separated from commercial strands, the average strength was reported to be 1.5 GPa, which is only 43% of the value quoted in Table 6 for

pristine E-glass fibers. Heating the fibers at 600 °C for 4 h reduced strength by only a few percent to 1.4 GPa, compared with at least a 50% reduction in strength upon similar heating of pristine fibers (Lowrie, 1967). Apparently the flaws induced by compaction of pristine fibers are not as severe as those induced by the handling that the fibers experience during ordinary glass fiber manufacturing and packaging. Artificial surface flaws were introduced by rubbing two as-received strands against each other

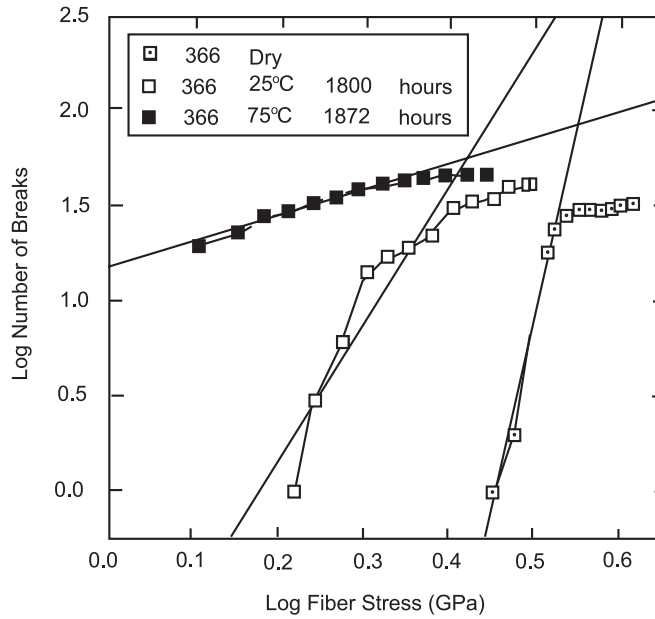


Figure 19 Log-log plots of single-glass-fiber/epoxy-dogbone fragmentation data before and after various times of water exposure at 298 K and 348 K (after Schultheisz *et al.*, 1997).

10 times. The actual distributions of fiber strengths before and after abrasion and annealing are compared in Figure 17.

The influence of abrasion experienced by the fibers during the fabrication of composite leaf springs is illustrated in Figure 18, in which the fiber strength distributions from the beginning to the end of the process are compared. Note the significant overlap of these distributions, which indicates that the differences between the averages may be misleading.

It can be concluded that commercial glass fiber products have average values of tensile strength that are at least 20% lower than the published values measured on pristine laboratory fibers. Furthermore, those values are likely to be reduced by as much as 50–70% or more, due to abrasion experienced during GFRP composite fabrication steps. Finally, it is important to be aware of the broad distribution of fiber strengths—or more accurately—flaw sizes that are inherent in commercial glass fibers, and that mechanical and thermal fabrication steps are likely to reduce strength by introducing more severe flaws.

The useful lifetime of GFRP materials under service conditions is critical to many new applications, especially in the infrastructure and transportation markets. In the latter market, the ability to recycle scrap from manufacturing and postconsumer sources also is a growing concern. (Although, in 1997, the largest commercial recycling plant for automotive sheet molding went out of business because not en-

ough scrap SMC was available to keep the plant running.) Service lifetime prediction is complicated by the variety, cyclic nature, and interactions among the mechanical, thermal, and chemical stresses, as well as the lack of real-time data on failure mechanisms.

At the US National Institute of Standards and Technology (NIST), Schultheisz *et al.* (1996) developed a rapid, small-scale methodology to determine the influence of environmental exposure on fiber strength and interfacial shear strength. Using the traditional single fiber fragmentation specimen and measuring the number of fiber breaks vs. stress while immersed in water, they find characteristic, bi-linear log-log plots. The analysis by NIST begins with the Weibull expression for probability of survival:

$$\text{Pr} = \exp \left[\frac{-l}{l_0} \left(\frac{\sigma}{\sigma_0} \right)^\rho \right] \quad (3)$$

where l is the fiber length, l_0 is the critical length for stress transfer, σ is the applied stress, and σ_0 and ρ are the Weibull scale and shape parameters, respectively.

Equating the Weibull equation with the Poisson expressions for probability of survival:

$$\text{Pr} = \exp[-\lambda(\sigma)l] \quad (4)$$

where $\lambda(\sigma)$ is the cumulative flaw density up to stress σ . Then, by taking logs of both sides of the equation twice, and assuming that

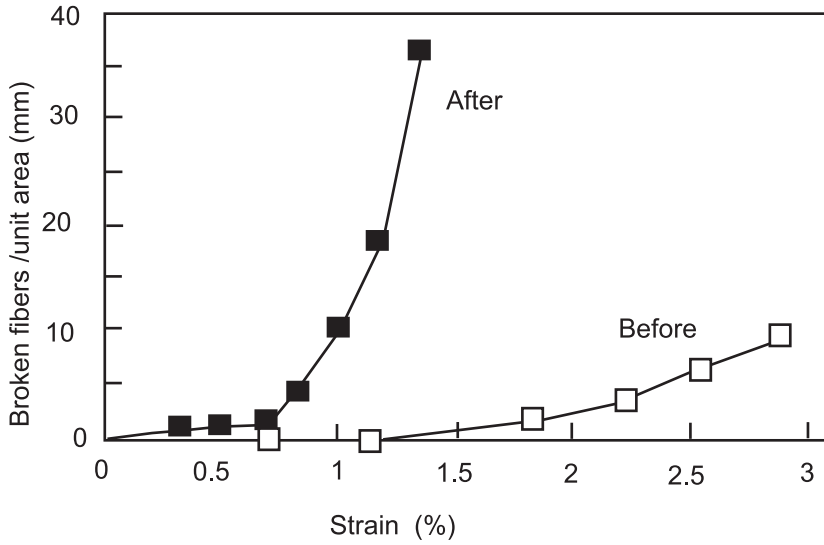


Figure 20 Fiber breakage vs. percentage strain of a GFRP composite tested before and after exposure to water (after Vauthier *et al.*, 1995).

$$\lambda(\sigma) = n(\sigma)/l_0 \quad (5)$$

one obtains

$$\ln[\lambda(\sigma)] = p \ln(\sigma) - p \ln(\sigma_0) \quad (6)$$

Typical results are shown on a log-log plot in Figure 19, comparing fragmentation data for a commercial glass fiber in an epoxy, before and after aqueous immersion at 298 K and 348 K. The Weibull parameters for the fibers within the composite specimen are determined from the straight line fit to the data below the saturation plateau. Those parameters are used to determine the fiber strength at critical length within the composite, using Equation (7):

$$S = \sigma_0 \left[\frac{l_0}{l_c} - 1 \right]^{1/p} \quad (7)$$

Finally, those values of fiber strength at critical length were used to calculate interfacial shear strength, τ , via the following equation (Kelly and Tyson, 1965):

$$\tau = \left[1/2 \frac{d}{l_c} \right] S \quad (8)$$

where d is the fiber diameter and l_c/d is the critical aspect ratio for load transfer.

A comparison of two high-performance sizings on E-glass fibers found that initial differences in interfacial shear strength disappeared during water immersion. Values dropped from about 40 MPa to 20 MPa over 3000 h of immersion (Schultheisz *et al.*, 1996). Fiber strength decreased linearly from about 3.0 GPa to 1.5 GPa, independent of which sizing was

used. Preliminary results comparing high-performance, commercially sized E-, ECR-, and S-2 glass fibers in an epoxy matrix showed that after 12 000 h exposure, l_c/d increased from 30 to 75 for E-glass fibers, but only from 20 to 30 for ECR-glass fibers. In the case of S-glass, l_c/d actually decreased from about 35 to 25.

The influence of aqueous immersion time and temperature on the static and dynamic fatigue behavior of E-glass/epoxy composites (55–60% fibers by volume) cured with dicyanamide (DICY) was studied by Vauthier *et al.* (1995). They noted that the solution pH rose to 9.5 within a few days because of DICY leaching. Following immersion at 60 °C for 340 days, failure strain decreased from 3.6% to 1.7% in monotonic three-point bending. The number of fiber breaks on the tensile face of the flex specimens is plotted vs. strain in Figure 20, from which it is obvious that the fibers in the aged specimen have many more critical flaws. As a result, the fatigue properties followed parallel trends on an S – N diagram, with the aged sample failing at about 1% lower strain level after the same number of fatigue cycles.

Empirical assessment of GFRP durability is usually addressed with accelerated testing protocols such as ASTM D 2992 and ASTM D 3681. Commercial composite parts are mechanically loaded under testing conditions that simulate (or exaggerate) the real service environment, and times-to-failure are measured. Results for pultruded epoxy rods made from both E- and S-glass are shown on a semi-log plot in Figure 21. Extrapolation of the short-term data to an expected service lifetime provides a means of estimating allowable engineering design stresses. Figure 21 indicates that

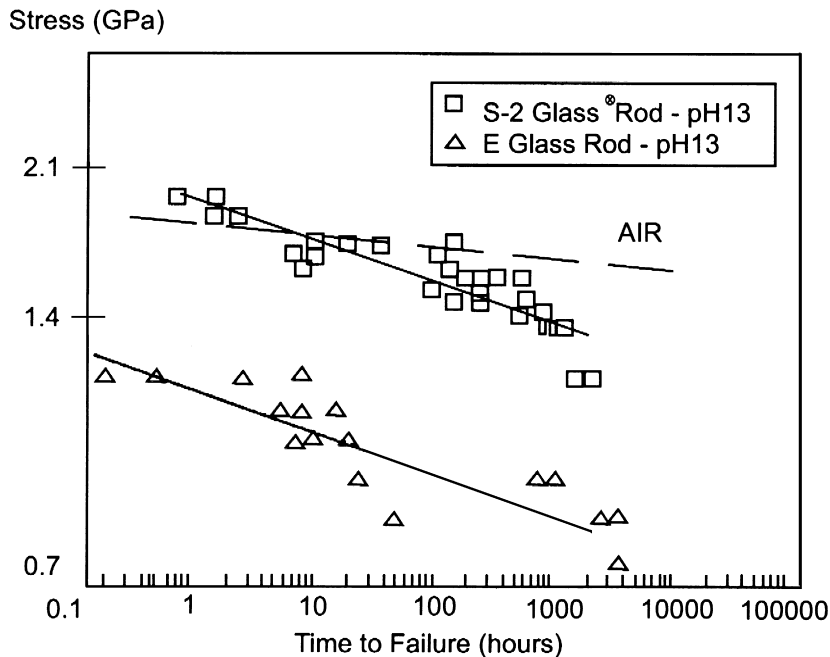


Figure 21 Log-log plot of static fatigue failure stress vs. time for epoxy GFRP composites made from E- and S-glass fibers (after Hartman *et al.*, 1996).

in a strongly basic solution, S- and E-glass fibers in an epoxy matrix produce similar rates of decrease in GFRP properties. Note that the S-glass rods which were tested in air showed relatively little static fatigue.

Schutte (1994) produced a detailed review of myriad mechanisms that can influence the environmental degradation of GFRP. The influence of water on each constituent—matrix, fiber, and especially the interface—was considered, with the goal of arriving at a laboratory testing protocol that would help predict composite lifetimes in environmental service. A simpler experimental approach has been used to make comparisons of GFRP durability in both acidic and basic environments (Santrach and Matzger, 1991). Test coupons were exposed to 1N and 2N sulfuric acid and sodium hydroxide solutions, but without tensile or compressive loading. Laminates were made from both ECR- and E-glass fibers, in both bisphenol A epoxy and isophthalic polyester resins. In general, basic conditions were more aggressive than acidic conditions, and the combination of ECR-glass with epoxy resin gave better GFRP strength. Another study compared high-alkali “N-glass” fibers with E-glass fibers in epoxy, phenolic, and unsaturated polyester composites. (N-glass composition is 68.4% SiO_2 , 7.8% Na_2O , 7.1% CaO , 6.2% B_2O_3 , 3.5% K_2O , 5.2% Al_2O_3 , 0.2% MgO , 1.5% others.) In this case, the composite specimens were boiled for 24 h in 10% hydrochloric acid, 0.5% sodium hydroxide, and 10% sodium

chloride solutions. Although the E-glass fiber composites were stronger initially, N-glass fiber composites were stronger after boiling (Ghosh and Bose, 1995).

When polyester composite laminates were made by impregnating glass fiber cloths that had been heated at 500 °C and 625 °C for times up to 1 h, composite tensile strength was found to be a function of the time and temperature of the heat treatment (Kennerley *et al.*, 1995). The final properties were about 25% of the composites made with virgin fibers. Although a silane treatment made a vast improvement in adhesion between the heat-cleaned fibers and the polyester matrix, as illustrated by SEM fractography, little improvement in composite strength was observed. Apparently, heat treatment introduces severe flaws spaced as closely as the effective fiber length for stress transfer in the composite.

One approach to GFRP recycling—combustion of the matrix resin in a fluidized bed followed by recovery of the fibers in a cyclone collector—has been developed at the University of Nottingham (Kennerley *et al.*, 1997a, 1997b). With residence times approaching 1 h in this process, glass fiber thermal compaction is completed, and simultaneously the potential is high for fiber contact and abrasion. Surprisingly, fluidizing velocity had no effect upon retained fiber strength. The fluidized bed temperature had a strong influence, reducing strength by 50% and 90% at 450 °C and 650 °C,

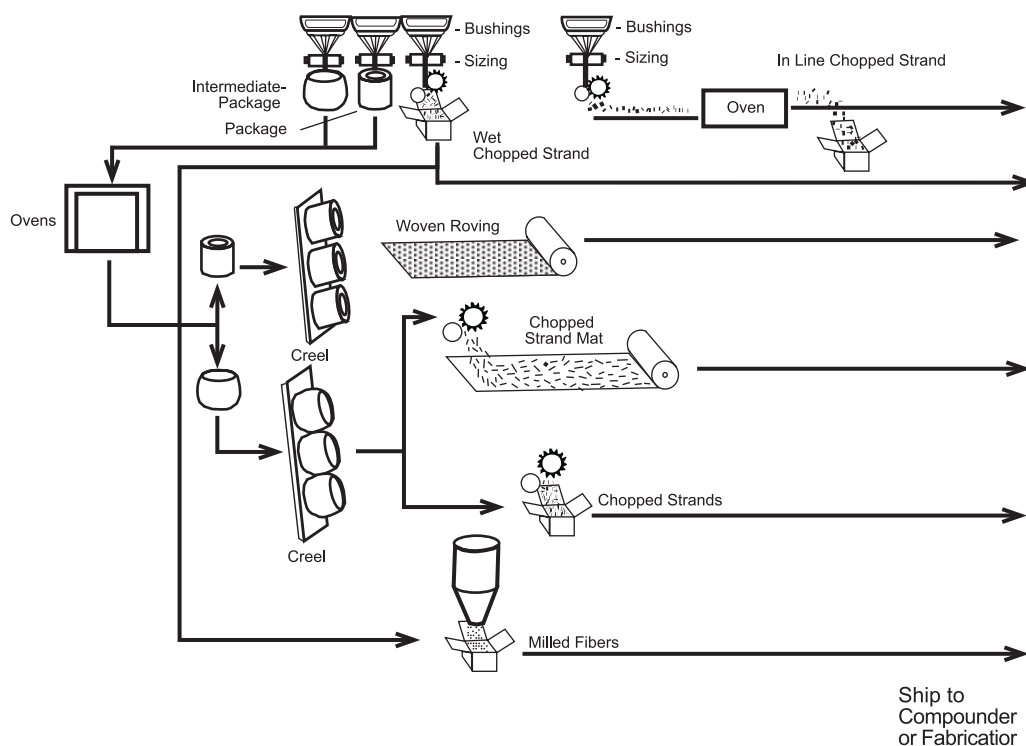


Figure 22 Simplified schematic diagram depicting some of the many different “product consolidation” steps that follow the fiber-formation/sizing-application process in commercial glass fiber production.

respectively. Those values are consistent with those of other investigators, who had simply heated a static pile of fibers in an oven. Apparently, the fluid bed/cyclone action produces Weibull flaws that are not much more severe than those produced by handling during composite manufacture. Fibers reclaimed at 450 °C, obviously removing the original sizing layer, were blended in various proportions with virgin chopped rovings sized for polyester bulk molding compound (BMC). There was no influence on the properties of composites containing up to 50% reclaimed fibers. At 100% reclaimed fiber content, composite tensile strength was 60% of the ordinary commercial product, and composite moduli values were not influenced at all. Another study used polyester/glass fiber fabric laminates and a specially controlled cycle of temperature, time, and atmosphere to remove the polymer matrix (Philipps, 1998). Another laminate was made from the recovered fabric, and showed over 75% of the strength of the original laminate.

1.08.5 PRODUCT DIFFERENTIATION

After the sizing has been applied, the fibers are gathered into bundles (strands) with slotted

fixtures called “shoes.” Subsequently the strands are processed either by winding continuously on a rotating mandrel called a “collet,” or by chopping between a large, polyurethane-covered wheel called a “cot” and a counter-rotating, metal cutter wheel with sharp blades spaced at the specified chop length. One type of chopped product, destined to be converted into a mat by the wet process for papermaking, is packed out wet (10–20% moisture) directly under the cot/cutter; it is stored and shipped in that state. All other glass fiber products are dried directly after consolidation. Continuous filament packages are mounted on a “creel carrier” and are dried for many hours above 100 °C in large circulating air ovens. Strands chopped in line for GFRP molding applications may be dried in line by moving through an oven on a vibrating conveyor belt. Figure 22 outlines this part of glass fiber manufacturing operations. The right-hand side of this figure depicts the variety of glass fiber reinforcement product forms that are shipped to customers who convert them into composite materials and fabricated GFRP parts (see Volume 2 of this work). A complete and concise description of commercial GFRP processing methods and their respective requirements for a particular glass fiber form is available from the Composites Institute (1992).

Traditional glass fiber manufacturing technology utilizes an “intermediate package” with tapered edges. After drying, several intermediate packages are then rewound on a precision winder that creates a stable, shippable package with a square-edge, cylindrical profile called a “multiend roving.” More recently, larger bushings and modern winder technology have led to a new manufacturing process that produces a “single-end roving” directly in forming. This newer process is more economical because it eliminates the rewinding step. Today even multiend rovings, such as those required in the production of sheet molding compound (SMC), are made by the direct winding process. In this case, during forming the gathering shoe has multiple slots which “split” the strand into many bundles, and the sizing is specially formulated to maintain the splits throughout winding and drying.

1.08.5.1 Continuous Fibers for Woven Roving, Thermosets, and Thermoplastic Pultrusion

There are three general kinds of composite processes that utilize rovings and thermosetting polymers. (i) Strands are woven into a fabric that is impregnated with liquid resin in a separate step. (ii) Continuous strands are pulled through liquid resin and wound on a mandrel. (iii) Fibers are chopped in the process just before blending with the resin liquid or paste.

Woven roving is a coarse, heavy fabric that is used in many hand lay-up and cast-panel applications. Filament winding produces high-strength structural composites such as uni- and multidirectional lamina, pipes, tanks, and other axisymmetric shapes. There are two major types of chopped roving applications. One is the traditional open-mold spray-up technology which utilizes a hand-held gun with a small chopper from which a stream of resin and chopped fiber mixture is sprayed several feet onto the mold, which is a preformed screen with negative air pressure behind it. In the other (SMC or panel production), a wide chopper drops glass bundles onto a moving bed of a polyester-based paste.

1.08.5.2 Chopped Fiber Bundles for Thermoplastic Injection Molding and Thermoset Molding Compound

While there may be some similarities between chopped fiber products and choppable roving products, especially for thermosetting bulk

molding compound (BMC), there are many significant differences when it comes to thermoplastic injection molding. In the latter case, bundle length is shorter (generally 6 mm), and there are two process steps—compounding glass fiber filled pellets and molding parts—that involve very high temperatures and shear forces.

Traditionally, chopped glass fibers for thermoplastics were made from moist forming packages. More recently, in-line chopping and drying has provided higher volumes of chopped fibers more economically. Sizings for these products are more varied in composition and function than for continuous fiber applications. This corresponds directly to the greater variety of thermoplastic resin chemistries, additive packages, and processing conditions. For example, changing from a single screw to a twin screw extruder can change the order of performance of a series of sizings.

1.08.5.3 Yarns, Fabric, Mats, and Other Glass Reinforcement Products

Yarn products are distinguished by filament diameters of 10 μm or less, which are “twisted” and/or “plied.” Strands from air-dried forming packages are processed through twist-frame machines that twist them to provide better handling during weaving operations. Sizings for yarns are unique in that they are designed to facilitate weaving the yarns on modern, high-speed air looms and to burn-off completely and easily while passing the fabric through “heat-cleaning” ovens. Starch, oil and polyvinyl alcohol are the film-formers of choice for yarns. After weaving the yarn into a fabric, passing through an oven burns off the sizing. The weaver then applies a proprietary “finish” which often contain ingredients similar to those found in sizings for reinforcements.

Glass fiber mats are nonwoven, two-dimensional product forms that are bonded with polymeric “binders.” Specific end uses such as open- and closed-wet molding, shaped preforms, and roofing shingles have varying requirements that dictate quite different manufacturing input and forming methods for the myriad glass fiber mat products. However, all E-glass mat manufacturing processes have three stages. (i) Forming and transporting a two-dimensional glass fiber mat on a moving wire mesh screen. (ii) Applying binder. (iii) Setting the binder in an oven.

Composite processes such as hand lay-up and pultrusion use a continuous filament mat. Continuous filament mats are made directly in line under a series of bushings that employ a

pull- and finger-wheel technology to simultaneously draw the fibers and throw them back and forth across a wire screen moving perpendicular to the throw. In some of these products the binders are added directly to the sizing. In other cases, the chain carrying the wet continuous strand mat passes under a weir that cascades an aqueous curtain of binder suspension onto the mat. The hydrodynamic forces inherent in the latter method also densify the mat.

To make dry-chopped fiber mats, strands are fed from forming cakes (or rovings) into choppers that spray 6–12.5 mm long bundles into a “forming hood.” There a combination of mechanical, pneumatic, and gravitational forces distribute the bundles uniformly on a moving chain link belt that transports the product through the oven and into rolls.

Wet-chopped and wet-formed mats are variously known as glass fiber “paper,” “tissue,” “veil,” or “shingle mat.” The fibers are chopped in line to 12.5–31.7 mm in length, and are packed out and shipped wet at about 10–15% moisture content. A dilute (1% or less) suspension of wet-chopped fibers is deposited on a fine-mesh wire belt in a papermaking machine. After suction removes most of the water, a binder curtain flows onto the mat. Again the majority of “white water” and binder solution is suctioned off, and the mat passes through an oven where the remaining water is evaporated and the binder cross-links (cures).

The Modigliani process is unique, employing a low-melting glass cullet, a moving bushing, and a large-diameter take-up drum to make continuous glass fiber mats in a batch-continuous mode. The fibers emerge from a bushing that moves slowly back and forth above a rotating metal drum, upon which the fibers are deposited around the circumference (3–6 m) at a slight angle. Binder solutions usually are sprayed onto the fiber mat on the drum. After the mat has built up to the desired thickness, it is slit and removed from the take-up drum. The mat is subsequently stretched in the transverse direction, forming a diamond-shaped pattern of reinforcing strands before the binder curing is complete.

Other glass products such as milled fibers are finely divided and can have aspect ratios below the critical value theoretically required for strength-producing composite action. Nevertheless they are often added to polymers to increase stiffness and reduce cost. Milled fibers are produced from hammer milling glass fibers. The resultant product is a fine powder with millimeter to submillimeter fiber lengths. The small amount of sizing applied during forming is designed to facilitate an efficient milling process and to create a free-flowing product.

1.08.6 REFERENCES

- P. Baillif, B. Chouikhi, L. Barbanson and J. C. Touray, *J. Materials Sci.*, 1995, **30**, 5691–5699.
- E. J. Berger and Y. Eckstein, in ‘Adhesive Joints’, ed. K. L. Mittal, Plenum, New York, 1984, pp. 51–65.
- A. Carre, F. Roger and C. Varinot, *J. Colloid and Interface Sci.*, 1992, **154**, 174–183.
- J. Chang, in ‘Proceedings of the Aerospace Atlantic Conference’, Society of Automotive Engineers, Warrendale, PA, 1990, pp. 250–259.
- Composites Institute, ‘Introduction to Composites’, n., Society of the Plastics Industry, Washington, DC, 1992.
- R. J. Charles, *J. Appl. Phys.*, 1958, **29**, 1549–1553.
- G. J. Copley, A. D. Rivers and R. Smith, *J. Materials Sci.*, 1975, **10**, 1285–1290.
- J. B. Donnett, R. Bathistella and B. Chatenet, *Glass Technol.*, 1975, **16**, 139.
- A. S. D’Souza, C. G. Pantano and K. M. R. Kallury, *J. Vac. Sci. Technol.*, 1997, **A12**, 526–531.
- D. W. Dwight, F. M. Fowkes, D. A. Cole, M. J. Kulp, P. J. Sabat, L. Salvati, Jr. and T. C. Huang, in ‘Acid-Base Interactions’, eds. K. L. Mittal and H. R. Anderson, Jr., VSP, Utrecht, 1991, pp. 243–256.
- W. L. Eastes, D. A. Hofmann and J. W. Wingert, *US Pat.* 5 789 329 (1998).
- W. M. Edmunds, ‘High Temperature Properties of Vitreous Fibers and Coatings’, Owens-Corning Fiberglas Corp., Final Report, Contract No. 60-6028-c, April 1961.
- B. P. Feuston and S. H. Garofalini, *J. Appl. Phys.*, 1990, **68**, 4830–4836.
- F. M. Fowkes, D. W. Dwight and D. A. Cole, *J. Non-Crystalline Solids*, 1990, **120**, 47–60.
- P. Ghosh and N. R. Bose, *J. Appl. Polym. Sci.*, 1995, **58**, 2177–2184.
- P. K. Gupta, in ‘Fibre Reinforcements for Composite Materials’, ed. A. R. Bunsell, Elsevier, Amsterdam, 1988, pp. 19–71.
- P. K. Gupta, in ‘Fractography of Glass’, eds. R. C. Bradt and R. E. Tressler, Plenum, New York, 1994, pp. 185–206.
- P. K. Gupta, M. L. Lui and P. J. Bray, *J. Am. Ceram. Soc.*, 1985, **68**, C-82.
- F. H. Guzzetta, in ‘Fundamental Aspects of Fiber Reinforced Plastic Composites’, eds. R. T. Schwartz and H. S. Schwartz, Interscience, New York, 1968, pp. 217–224.
- D. R. Hartman, M. E. Greenwood and D. M. Miller, Owens-Corning Pub. No. 1-PL-19025-A (1996).
- J. Huang, Ph. D. Dissertation, Ohio State University, 1992.
- J. Huang and P. K. Gupta, *J. Non-Crystalline Solids*, 1992, **151**, 175–181.
- A. Kelly and W. R. Tyson, *J. Mech. Phys. Solids*, 1965, **13**, 329.
- J. R. Kennerley, N. J. Fenwick, S. J. Pickering and C. D. Rudd, *Adv. Composite Lett.*, 1995, **4**, 105–109.
- J. R. Kennerley, N. J. Fenwick, S. J. Pickering and C. D. Rudd, *J. Vinyl Additive Technol.*, 1997a, **3**, 58–63.
- J. R. Kennerley, R. M. Kelly, N. J. Fenwick, S. J. Pickering and C. D. Rudd, in ‘Proceedings of the 5th International Conference on Automated Composites’, Glasgow, 1997b, pp. 23–30.
- B. K. Larson and L. T. Drzal, *Composites*, 1994, **25**, 711–721.
- T. B. Lloyd and D. W. Dwight, in ‘Characterization of Polymers’, eds. H. M. Tong, S. P. Kowalczyk, R. Saraf and N. J. Chou, Butterworth-Heinemann, Boston, MA, 1994, pp. 150–168.
- K. L. Lowenstein, ‘The Manufacturing Technology of Continuous Glass Fibers’, Elsevier, Amsterdam, 1st edn., 1973; 2nd edn., 1983; 3rd edn., 1993.

- G. Lewis, S. W. Bedder and I. Reid, *J. Mat. Sci. Lett.*, 1984, **3**, 728–732.
- R. E. Lowrie, in 'Modern Composite Materials', eds. L. J. Broutman and R. H. Krock, Addison-Wesley, New York, 1967, pp. 270–323.
- E. Maeder, K. Grundke, H.-J. Jacobasch and G. Wachinger, *Composites*, 1994, **25**, 739–744.
- E. Maeder, H.-J. Jacobasch, K. Grundke and T. Gietzelt, *Composites Part A*, 1996, **27A**, 907–912.
- A. G. Metcalfe and G. K. Schmitz, *Proc. ASTM*, 1964, 1075–1093.
- D. M. Miller, 'Engineered Materials Handbook', ASM International, Metals Park, OH, 1987.
- G. M. Nishioka, *J. Non-Crystalline Solids*, 1990, **120**, 102–107.
- W. H. Otto, *J. Am. Ceram. Soc.*, 1955, **38**, 122–124.
- W. H. Otto, *J. Am. Ceram. Soc.*, 1961, **44**, 68–72.
- G. Pahler and R. Bruckner, *Glastech. Ber.*, 1985, **45**.
- C. G. Pantano, *Rev. Solid State Sci.*, 1989, **3**, 379–408.
- C. G. Pantano, L. A. Carman and S. Warner, *J. Adhesion Sci. Technol.*, 1992, **6**, 49–60.
- C. G. Pantano and T. N. Wittberg, *Surface and Interface Anal.*, 1990, **15**, 498–501.
- T. Philipps, 1998, Isorca Inc., Technical Note.
- F. Rossi and G. Williams, in 'Proceedings of the 28th AVK Conference', Baden-Baden, Germany, 1997, pp. 1–10.
- D. Santrach and R. Matzeg, Owens-Corning Pub. No. 1-PL-16 720-A, 1991.
- B. J. R. Scholtens and J. C. Brackman, *J. Adhes.*, 1995, **52**, 115–129.
- C. J. Schultheisz, C. L. Schutte, W. G. McDonough, K. S. Macturk, M. McAuliffe, S. Kondagunta and D. L. Huston, in 'Proceedings of the ASTM Symposium on Fiber, Matrix and Interface Properties, ASTM STP 1290', eds. C. J. Spragg and L. T. Drzal, ASTM, Philadelphia, PA, 1996, pp. 103–131.
- C. L. Schutte, *Mat. Sci. Eng.*, 1994, **R13**(7).
- T. P. Skourlis and R. L. McCullough, *Composites Sci. Technol.*, 1993, **49**, 363–368.
- J. L. Thomason, *Composites*, 1995, **26**, 487–498.
- J. L. Thomason and D. W. Dwight, *Composites: Part A*, 1999, **30A**, 1401–1413.
- J. L. Thomason and J. B. W. Morsink, 'Interfaces in Polymer, Ceramic and Metal Matrix Composites', Elsevier, Amsterdam, 1988.
- J. L. Thomason and G. E. Schoolenberg, *Composites*, 1994, **25**, 197–207.
- P. Trens, R. Denoyel and E. Guilleoteau, *Langmuir*, 1996, **12**, 1245–1250.
- E. Vauthier, A. Chateauminois and T. Bailliez, in 'ICCM-10', Whistler, BC, August, Woodhead Publishing, Cambridge, UK, 1995, vol. 6, pp. 185–192.
- H. D. Wagner and A. Lustiger, *Composites*, 1994, **25**, 613–616.
- D. Wang and F. R. Jones, *Composites Sci. Technol.*, 1994, **50**, 215–228.
- J. C. Watson and N. Raghupathi, in 'Engineered Materials Handbook', ASM International, Metals Park, OH, 1987, vol. 1, pp. 107–111.
- S. P. Wesson and J. S. Jen, in 'Proceedings of the 16th National SAMPE Technical Conference', SAMPE, Covina, CA, 1984, pp. 375–387.
- S. P. Wesson, J. S. Jen and G. M. Nishioka, *J. Adhesion Sci. Technol.*, 1992, **6**, 151–169.
- S. P. Wesson and J. J. Vajo, *Adv. Colloid Interface Sci.*, 1998, **76/77**, 107–135.
- H. F. Wu, D. W. Dwight and N. T. Huff, *Composites Sci. Technol.*, 1997, **57**, 975–983.