

Practical Aspects of Carbon Fiber Surface Treatment and Sizing

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Abstract:

In the next to the last step during the production of carbon fibers from precursor, the carbon fibers are subjected to an electrolytic oxidation that removes weak surface layers, etches the fibers, and generates reactive or polar groups. The new surface is easily wetted by thermosetting resins due to their low viscosities and bonds well to epoxy resins. The bonding to other thermosets such as vinyl and polyesters is variable as is the adhesion of thermoplastics. This can result from additives and modifiers formulated into the resin. The last step is the application of a protective material called sizing to the carbon fiber. In contrast to glass fibers, this material usually does not promote adhesion but is present to prevent fiber damage during fiber handling in filament winding, prepregging and weaving operations. The sizing best suited for a given process must be selected to maximize the speed and minimize accumulation of defects and broken fiber. Since the sizing is typically an uncured epoxy resin, it may actually interfere with bonding between the fiber and the matrix. Analytical techniques are discussed as well as how to detect possible problems.

Introduction:

Carbon fibers have been manufactured commercially for over thirty years. Their high modulus, high strength, low density and resistance to chemical environments have led to their wide spread use in many applications in preference to other fibers such as glass. For recent reviews of carbon fiber technology see Donnet et al (1) and Peebles et al (2). It was recognized that the as made carbon fiber surface did not bond well to matrix resins such as epoxies which resulted in poor shear and compression strength composite properties. Manufacturers of continuous carbon fibers discovered that anodic oxidation in an aqueous bath provided a cheap, rapid, and in line process for rendering the fiber bondable to the matrix. Prior to this step PAN based fibers undergo oxidation and graphitization processes at high temperatures precluding the use of flammable or toxic substances. Other surface treatments such as plasma discharge or ozone are also difficult to implement in the current production processes. The surface generated by this treatment greatly improved adhesion to thermoset and to some thermoplastic resins.

Carbon fibers are brittle, with the higher modulus fibers being worse than the high strength fibers. The fibers are easily broken by passing over and through fiber handling devices which direct, spread, weave and braid the fiber bundles. The simple act of unwinding a high modulus fiber from a spool can result in damage. This damage is evidenced by the accumulation of fiber debris which can result in low process speeds, additional line workers to remove the debris, and the formation of defects. Immediately after surface treatment and drying, the fibers pass through an aqueous bath where they are coated with a sizing material which protects the fiber from damage. The sizing material must be soluble or dispersible in water. After the application of the water based material, the tow bundle is dried. Finally, the tows are wound on spools and packaged.

Neither the surface treatment nor the sizing operations are readily or quickly changed. The surface treatment step on a given fiber line is usually adjusted for changes in fiber types such as standard or intermediate modulus as each fiber type is more or less easily oxidized. Sizing changes are done infrequently and manufactures try to minimize the number of changes to achieve process efficiencies.

Surface Treatment

Untreated carbon fibers show inferior composite performance compared to the same

fibers after treatment. In Table 1 are shown comparative data for treated and untreated Torayca T-300 fibers in the same matrix (3). The treatment level does not reduce the tension capability of the fiber as shown as the fiber tensile strength and the unidirectional composite properties. The properties most enhanced are inter laminar shear strength and the 90° tensile strength. Both of these are sensitive measures of fiber resin interactions. Resin systems respond to specific fibers in subtly different ways. Conversely, fiber performance can be affected by different resin systems. By changing the resin formulation a fiber can deliver somewhat higher tensile performance or composite toughness.

Table 2 Fiber properties of Torayca T-300 treated at different levels of commercial surface preparation and composite properties made with a proprietary epoxy

Property	Level of Surface Preparation			
	0	1/2	1	2
Density	1.77	1.77	1.77	1.77
CO ₂ ^a , cc/g	0.02	0.06	0.07	0.07
O _{1s} /C _{1s} ^b	0.08	0.28	0.29	0.29
Surface area m ² /g	1.0	1.2	1.1	1.1
Tensile strength, GPa	3.86	3.81	3.84	3.84
Tensile modulus, GPa	238	238	237	236
Strain at failure, %	1.62	1.60	1.62	1.62
Unidirectional composite properties, v_f = 60%				
Tensile strength, GPa	1.95	1.90	1.82	1.82
Tensile modulus, GPa	143	143	142	142
Compressive strength	1.20	1.36	1.36	1.36
Compressive modulus	127	126	126	128
90° tension, MPa	28	42	50	50
90° modulus, GPa	9.5	9.1	9.1	9.1
ILSS, MPa	101	125	123	129

^a Evolution of CO₂ measured by heated gas chromatography at unspecified temperature but probably below 300°C. ^b Measured by XPS.
After Norita et al.¹⁶

Table 1

Electrolytic Oxidation

Many surface modifications have been described in the literature. Following Peebles (2), they can be generally broken down into gas phase oxidation, liquid phase oxidation, electrochemical oxidation, plasma treatment and electrodeposition/polymerization among others. Most are academically interesting, but are difficult to put into commercial practice. Electrochemical oxidation is relatively inexpensive, easily controlled, has relatively benign chemical needs and wastes, and most importantly, it allows continuous processing and can be therefore linked to the manufacture of the fiber itself (4, 5). The fiber emerges from the graphitizing furnace and passes around a positively charged roller (anode) and into an aqueous electrolytic cell. Various electrolytes are used to conduct current and to create surface groups (6). The fiber is washed and dried before entering the size application section. A schematic is shown in Figure 1.

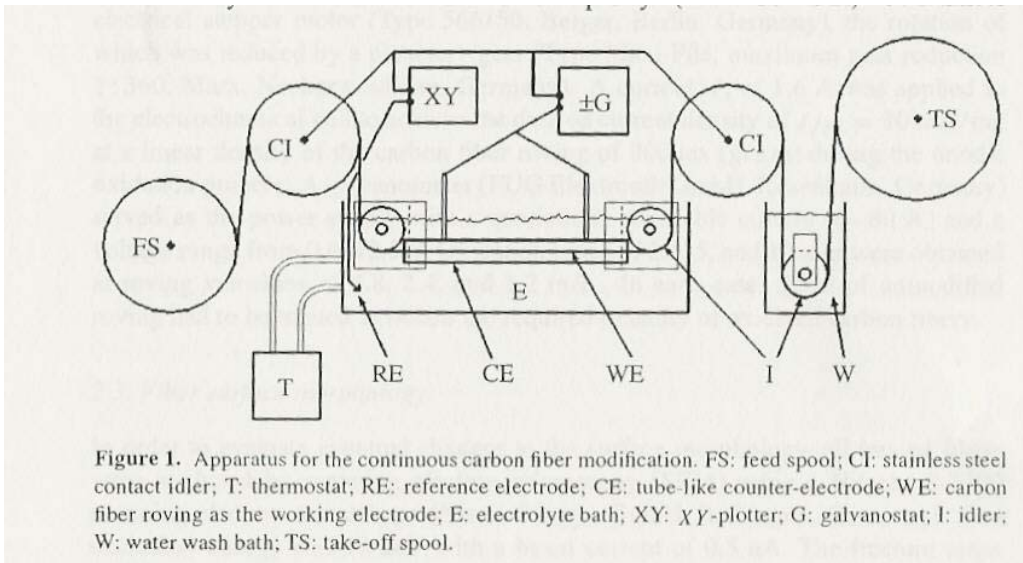


Figure 1

The specific details of the electrolytic oxidation are proprietary to a given supplier, but electrochemical studies conducted on untreated fiber and analysis of the surface chemistry, roughness and polarity of commercially available fibers shed light on why the surface becomes more bondable. It is likely that all of the effects of surface treatment work together to enhance bonding particularly to epoxy resins.

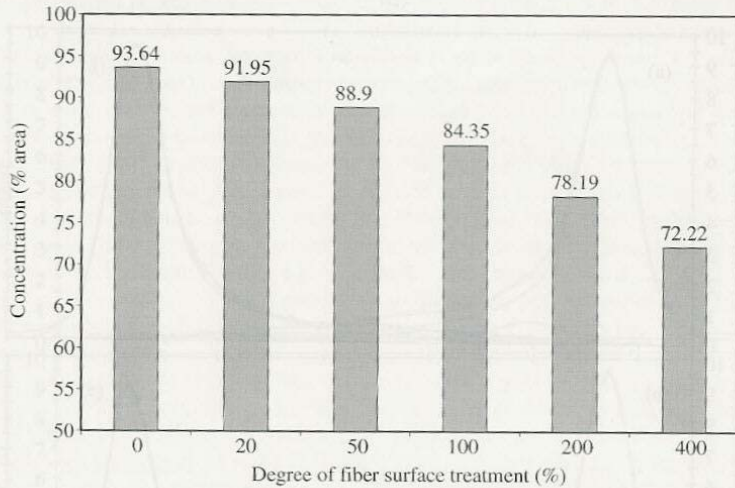


Figure 7. The carbon contents of the IM7 series carbon fiber with varying degree of surface treatment.

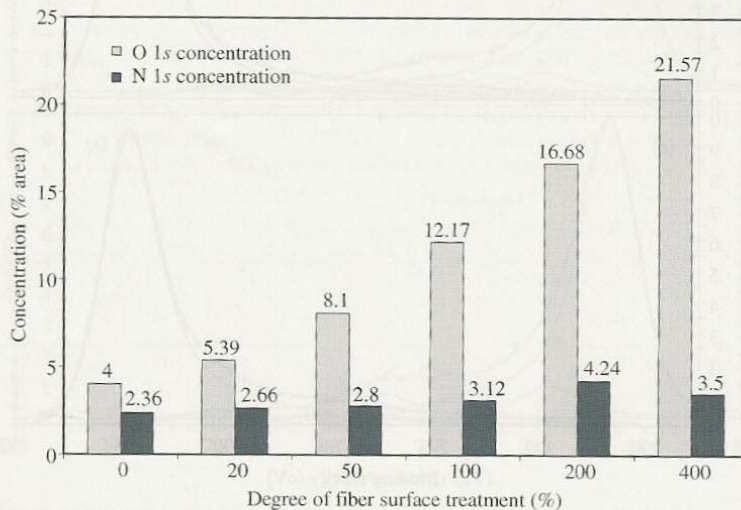


Figure 8. The oxygen and nitrogen contents of the IM7 series fiber with varying degree of surface treatment.

Table 2

defects which can reduce tensile strength while improving shear strength. In conjunction with the physical effects, the outer carbon atoms are oxidized. It is thought that this is due to the electrolytic decomposition of water into oxygen at the electrode surface and that it is this oxygen that reacts with the surface of the carbon fiber. These can be in the form of hydroxyl, carbonyl, and carboxylic acid groups (9). The type and concentration of these groups can be followed with XPS. In Table 2 are shown the results of oxidizing Hexcel IM 7 carbon fiber. The total oxygen content goes up, and the concentration of each of the oxidized carbon functionality can be determined. In contrast, the concentration of surface carbon goes down. These polar and potentially reactive groups are partially responsible for the high level of adhesion to thermoset matrices such as epoxies, bismaleimides and others.

These groups improve the wettability of the carbon fiber and provide polar functionality to increase the work of adhesion. The contact angle of various liquids in contact with the fiber can be measured and the work of adhesion determined. If the surface is clean, however, simple dispersive forces can be sufficient to provide rather good adhesion. It has been shown that

It is clear that the treatment removes contaminated or weak layers which interfere with strong bonds (7). When a basic electrolyte is used the electrolytic bath becomes dark due to the removal of highly oxidized colloidal degradation products (5). During this process, the fiber surface can be etched or roughened by over treatment (8) and in addition it is thought that this can also cause pit and pore formation which increases surface area (9). The roughening and increase in surface area can contribute to bonding. However it has been found that the initial effect of anodic oxidation is smoothing of the fiber surface. A clean surface with no polar groups and minimal roughening has been found to bond to polycarbonate through dispersive forces only (10). Over treatment can result in an increase in fiber surface flaws and

reduction of the surface groups formed during the original treatment, or thermal treatment to remove the same groups, leads to strong adhesion.

Measurement of Surface Properties, Chemistry, and Topography

Of the many techniques for determining the surface composition and characteristics of carbon fibers, very few are available for the typical user. Most do not have access to x-ray photoelectron spectroscopy (ESCA), scanning tunneling microscopy (STM), infrared and Raman spectroscopy as well as other ways to directly evaluate the surface. If the fiber is unsized, a wicking method which uses plastic drinking straws can measure gross changes in fiber surface chemistry (11).

Measurement of Fiber Resin Adhesion

Several common methods for measuring the fiber/resin interface are shown in Figure 2. These focus on evaluating a single fiber and also are dependent on the user having fairly

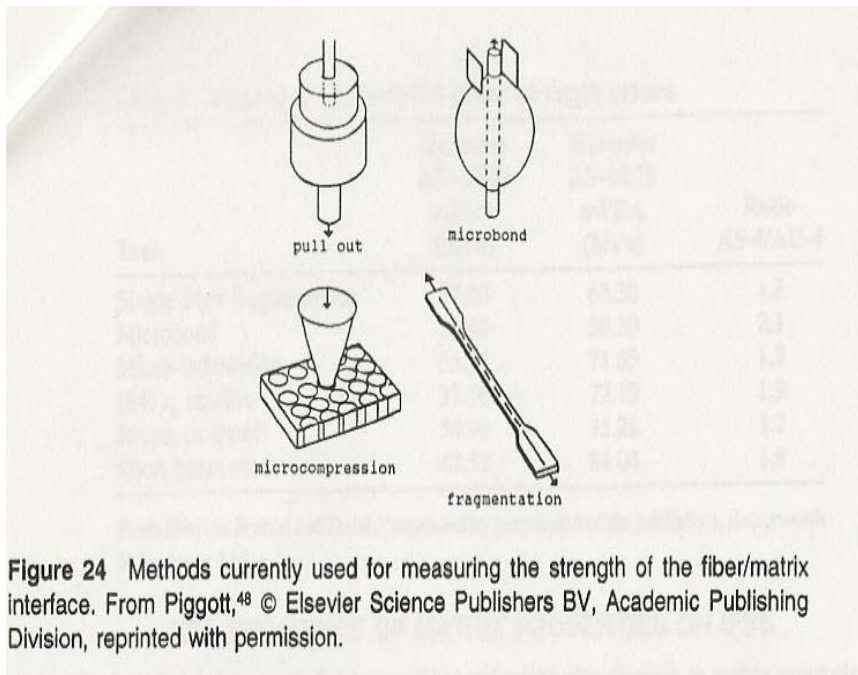


Figure 24 Methods currently used for measuring the strength of the fiber/matrix interface. From Piggott,⁴⁸ © Elsevier Science Publishers BV, Academic Publishing Division, reprinted with permission.

Figure 2

database with these methods and periodically test materials. Some fiber suppliers maintain a database of shear properties and can monitor the performance on an ongoing basis. The delivery of consistent shear performance implies that the surface treatment process is under control at the supplier.

A reduction in shear properties may not be caused by changes in surface treatment or sizing. Just as the performance of adhesives and paints are affected by their formulations, composite properties can be affected by seemingly minor changes to the base resin composition (12). Air release agents, internal mold releases, low profile agents, and wetting agents have the potential of accumulating at the fiber/resin interface and reducing shear strength. These should be added carefully and if several modifications are to be done, making one change at a time is essential to isolate a problem additive.

Control of Surface Treatment

sophisticated lab capabilities.

Composite test procedures such as ASTM D2344 (Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method) and ASTM D3518 (Standard Test Method for In-plane Shear Response of Polymer Matrix Composite Materials by Tensile Test of a +/- 45° Laminate) should be more accessible to the user. Care should be taken to establish a

The carbon fiber supplier should be in control of fiber speed through the bath, the type and concentration of electrolyte, the length of fiber wetted in the bath, bath temperature and applied voltage and current.

Sizing

Carbon fibers are brittle and require some protection or lubrication as they are handled. Size materials are selected to provide the right blend of physical characteristics to provide this protection. The size material must provide consistent handling and not build up residue on the processing equipment. It must not increase friction between the fiber and any point that is touched during handling. It should also not impede the penetration of resin into the fiber bundle. Commercial carbon fibers display a variety of surface characteristics: some are smooth, some are striated, and some are round while others are kidney shaped. It is likely that each form requires a different blend of physical characteristics optimized for the fiber shape and surface texture. These different fiber forms can also affect resin distribution in prepreg and in the cured composite. Non-round fibers will provide a less dense fiber bed than round filaments. They therefore can absorb more resin inside the fiber bed and have less resin at the surface. This can reduce prepreg tack and change the fiber resin distribution. Changing from a fiber that is round to one that is not can have profound effects on handling and processing characteristics resulting in longer fabrication times and higher defect levels.

Size materials must also be compatible with the matrix resin. This includes solubility in and/or reactivity with the formulated resin. This allows the resin to penetrate the fiber bundle and interact with the fiber surface. Typically, sizes that are used with epoxy resins use an epoxy formulation as the sizing material. The size should not change in chemical or physical characteristics during storage of the sized fiber to allow consistent handling after ageing. Some sizes are water soluble and are designed to be washed off after weaving or braiding, but before the application of resin. In some applications the sizing is burned off at high temperatures prior to resin infusion.

Sizes also fall into two categories. The first are sizes that are relatively low in molecular weight and allow the tow bundle to be soft and easily spread. These are typically used for prepregging. The second class is that of film forming materials. These are higher molecular weight polymers that form a tough film after the fiber is dried. The film offers more protection to the tow bundle and also prevents broken filaments from depositing on process equipment. Some fiber bundles are twisted to provide this extra level of protection from broken filaments.

Many size materials, such as epoxy resins, are not soluble in water and must be applied as a dispersion or emulsion in water. This can result in the size being uniformly distributed on the surface of the fibers, or the size can exist as droplets either on the fiber surface or sticking together a number of individual fibers. Care must be taken at the manufacturer to control composition, concentration, and particle size of the emulsion in the sizing bath to provide a dependable product. The manner of drying the wet fiber after size application can also play a role in the handling characteristics of the fiber bundle. Tow bundles that are dried on a drum tend to be flat. Those that are dried in towers tend to be round.

In the case of unidirectional prepreg made via the hot melt process a fiber that spreads easily and has consistent incoming width will eliminate gaps and will allow for thin prepregs to be made from less expensive larger tow bundles. Since the handling of the fiber is relatively benign lower levels of sizing (< 1%) provide adequate protection. It is likely that the sizing does not migrate very far from the fiber surface.

When carbon fiber is used in operations that subject it to much greater levels of abuse such as weaving and braiding a higher level of protection is required. Typically higher levels (>1%) of sizing are needed. The need for protection must be balanced with the need to have

degree of spreading to make a fabric that has a closed weave. Higher size levels are also required for the production of flat tow products. These are fiber bundles that are spread to a highly uniform width on the spool. These are used to make low weight fabrics from the lower cost higher tow bundle products. If the hot melt process is used to make prepreg the size will remain close to the fiber surface. If solvated processes are used to make either unidirectional or fabric prepreg it is likely that the sizing will dissolve in the solvent solution used to impregnate and will therefore be more uniformly distributed throughout the matrix resin.

Carbon fiber that is chopped to be used as a short fiber reinforcement in thermoplastic resins typically has a high (>>1%) size level. This is to allow easier chopping, preventing short fiber fly, and allowing easier handling by the compounder.

Size Level

Manufacturers typically use a solvent to wash sizing off to determine over all size content. ASTM D 4018 describes a burn off method for size determination. Because the sizing is applied at low levels versus the surface area of the fiber bundle, it is very difficult to assess the uniformity of coverage. Some manufacturers can measure secondary characteristics such as friction, fiber damage and spreadability that can be related to size level and uniformity of coverage.

Control of Sizing

The FAA considers the fiber sizing, the process to apply sizing, and sizing content to be critical parts of the fiber specification (13). The type of size material and particle size of the aqueous dispersion must be controlled. The type of emulsifier and its concentration are keys to the particle size. Control of size level in the application bath is needed to control the level of size on the fiber. All steps regarding the application of the size to the fiber and drying must also be consistent.