Fiber Surface Treatments and Matrix Interface Effects . . . *Randy Lee*

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The following comments were originally created in an email memo to address issues voiced by colleagues concerning variable fiber surface conditions, chemical functionality with phenolic matrix resins and the removal of sizings for fiber characterization studies. Upon request, these writings were subsequently tailored into a short report format for documentation purposes. However, the topics are not necessarily organized in the most appropriate manner, as the essay is analogous to a personal response with no references utilized. So please keep in mind, this is an informal discussion and no guarantee is given that everything stated here is correct, precise or complete.

Here's some background on carbon fiber surface treatments that you are probably already aware of. It is well known that most PAN carbon fiber manufacturers use an electrolytic process (such as anodic oxidation) to generate active functional groups on the fiber surfaces. These groups will participate in bonding and coupling reactions with specific functional groups in the matrix network along polymer main chains or in pendant (side group) locations. There are three or four protruding functional groups generated along the surfaces of carbon fibers during post-carbonization oxidation treatments which are of importance to polymer matrices in fiber/fabric-reinforced composites. These include carboxyl –COOH, carbonyl (ketone or aldehyde) C=O, hydroxyl –OH and ether –O– as the most prominent groups. In addition to chemical interactivity and coupling with the matrix, most of these groups generally improve the wettability properties of the carbon fiber and provide polar functionality to compliment the work of adhesion.

Undoubtedly, almost the entire carbon fiber industry tailors their products to be compatible with epoxy matrices, not phenolics. Carbonyls and ethers do not interact as well with epoxies as the carboxyl and hydroxyl groups do. These two groups can readily bind with matrix –OH groups along epoxy branches (as long as they are plentiful and easily accessible) by forming ester and ether linkages, directly coupling the two phases together. Additionally, surface carboxyls and hydroxyls can couple directly with unreacted –O– epoxide groups along the ends of the epoxy chain in a ring-opening reaction that generates more –OH groups along the chain. Thus, carbon fiber vendors usually try to control the oxidation process (current, voltage, type of electrolyte, etc…) so that the ratio of functional groups is dominated by carbonyls and hydroxyl groups . . . but how does this affect the fiber's interaction with phenolic resins?

Probably not a whole lot. All three groups will participate in hydrogen bonding with available phenol hydroxyls, with preference given perhaps to interactions between straight surface hydroxyl groups and possibly carboxyl groups both of which can act as either acceptors or donors as

H-bonds are established. However, carboxyls can associate with surface alkali (contaminants) possibly altering their behavior in terms of localized electrostatic and pH changes which may enhance the binding process in some cases or degrade it catastrophically in others. It is probably most favorable to tailor the surface chemistry so that it is heavily populated with hydroxyl groups. Under the appropriate conditions, all of these functional groups will form ether or ester links with the phenol hydroxyl via condensation. Unfortunately however, the content of phenol hydroxyl groups in typical aromatic phenolic networks is relatively low compared to the bulk of the highly carbonaceous phenolic body. Additionally, the few phenol hydroxyls that are available may be shielded by all the bulky aromatic rings which are joined to other aromatic segments through short methylene links.

In other situations, fiber surface groups may tend to undergo substitution at active positions around accessible phenol rings. While the phenol hydroxyl group is strongly activating (directing substitution to the ortho and para ring positions), the processes of heat staging, crosslinking and curing will begin to create substituted phenol nuclei in the which the newly formed methylene links behave as deactivators directing further substitution to the meta ring positions. However, these B-stage phenolic (condensation) reactions also deplete the level of substitution sites available to fiber surface groups. Before crosslinking reaches the post-gelation C-stage, there will be varying levels of available ortho, meta and para openings within the phenolic adduct for coupling-type reactions with fiber surface active groups, as long as these reactive ring sites are in close proximity and in the appropriate orientation relative to the active fiber surface sites. In general, carbon fiber-to-phenolic matrix chemical interactions are often two-fold . . . hydrogen bonding and direct coupling.

Now, these fiber surface groups can become virtually inaccessible after the sizing is applied (sizings may comprise about 1-2% of the net fiber weight). In contrast to glass fibers, carbon fiber sizings may not always be formulated to promote adhesion but employed primarily for handleability purposes. In general, surface treatments introduce (or enhance) the bonding agents while sizings act as handling agents. In either case, the sizing (coating) must either be very soluble with the matrix resin or be intentionally removed after weaving to achieve good interfacial bonding. It should be noted however, traditional epoxy-compatible sizings may or may not react effectively with phenolic resins. In many cases, typical carbon fiber sizings for epoxy matrices are themselves epoxy resins and are usually coated onto the fibers as an emulsion. For such configurations, most of these coatings are epoxy *thermoplastics*, so they can be easily dissolved and removed with the appropriate solvents.

It is no secret, of all the polymer (thermoset) types, phenolic resole resins offer one of the highest char yields available, providing around 50-55% glassy carbon after > 1000°F pyrolysis. Carbon yields for most other polymer types, such as the epoxies and polyesters, are comparatively small (30% and below). However, it should be pointed out that, for sizing quantification or fiber surface characterization (i.e… BET and ASA techniques), these fiber coating materials cannot simply be burnt off or pyrolyzed away, as many workers propose and practice. Since some level of char remnant is almost always inevitable, they must be removed by dissolution with a suitable solvent. Hopefully, this addresses your question about removing sizings by passive pyrolysis techniques.

Short of the more powerful and nastier solvents, such as DMF and DMSO, milder solvents can probably be used for most of your fiber samples. The first to mind is THF (tetrahydrofuran) which is readily available and has much historical usage throughout the industry (I worked with mass production level quantities of THF for a number of years). Another recommended solvent might consist of a mixture of toluene, acetone, alcohol and ester. This would be analogous to common lacquer thinner which is capable of dissolving an array of organic materials from aromatic to highly aliphatic. However, their effects are limited on crosslinked thermosets which have already been cured.

Additionally, if the polymer sizing has already been carmelized or partially charred, more aggressive techniques you may attempt to apply in efforts to remove these semi-inorganic remnants (such as treatment with hot concentrated mineral acids) could conceivably impart undesirable damage to the peripheral fiber structure. However, these types of treatments would almost certainly alter the surface chemistry of the fibers drastically (i.e... the property you are wanting to characterize). Also, it should be noted, once carbonization of a polymer begins, it becomes very difficult to remove with acid treatments. Remnants of fully carbonized glassy or crystalline carbon are completely inert to acids. Indeed, this is the property that allows us to precisely measure resin content (and fiber volume) of composite samples via nitric acid digestion of the polymer matrix without affecting the inert fiber fraction. It should also be noted however, all carbon forms, including carbonized fibers, charred matrices and sizings alike, are quite susceptible to direct oxidation by O_2. The day we discover an oxidation-resistant carbon form, history will be changed.

Now typical carbonized rayons use starch-based sizings as lubrication/processing aids (even though I have experimented with developmental rayon fabrics and their composites processed with custom sizing formulations containing components other than starch). However, synthetic polymer sizings are often required for brittle PAN fibers in order to minimize fiber breakage during fiber/fabric processing, particularly for tight satin configurations (carbonized PAN fibers are generally 4 to 5 times stiffer (and stronger) than carbonized rayons). As mentioned previously, for most of the aerospace composites industry, treatments are tailored to facilitate chemical association with epoxy matrices, and the finishes are usually based on epoxy thermoplastics. Indeed, epoxy-based sizings are perceived by most of the composites industry to enhance fiber-matrix bonding and are often deemed as a requirement for intermediate and high modulus PAN fibers bound for high tech industries.

For the more flexible (lower modulus) rayon fibers, the sizings applied for handling purposes are not so critical, but for brittle PAN fibers, one of the primary functions of the sizing layer is to minimize fiber breakage by providing lubrication. When lubricating components (such as sterates) are incorporated into the sizing formulation and then applied to yarns and tow, contact damage between the filaments, the eyelets and guides during weaving and prepregging is vastly reduced. This also allows for PAN fiber/fabric processors to carbonize the tow and then weave the fabric, which ultimately produces a more consistent carbon fabric (in my opinion). However, there have been many cases where problems and weaknesses in composite systems were directly attributed to the sizing. Throughout the industry, a debate lingers on concerning the potential detriments of fiber sizings, and so do the efforts to try and produce sizing-free PAN fibers.

Now sizing formulations for glass and silica fibers almost always contains a silane coupling agent. However, the specific method utilized to apply the fiber/fabric coating can play a critical role in its effectiveness. For coupling purposes, the slurry should be applied directly onto the dry fiber/fabric surfaces (rather than mixed into the liquid matrix resin prior to prepregnation, as some practitioners do). Incorporation of most silane agents to neat resins has been shown to form micelles when blended straight into the liquid resin (in spite of manufacturer's suggestions). This renders the agent essentially useless . . . the methoxy end-groups from neighboring silane molecules have a tendency to associate (agglomerate) into hydrophilic nuclei preventing these polar reactive sites from ever interacting with or even reaching the intended fiber (or particle) surfaces.

By design, the methoxy segments comprise the hydrophilic ends of the silane molecule which are suppose to migrate to and associate with hydrophilic hydroxyls on the oxide surfaces while the hydrophobic segments (primary and secondary amine groups) associate with the appropriate matrix functional sites, perhaps available ortho and para-directed positions on the phenolic rings. However, in typical E-glass and S-glass fiber sizing formulations, the coupling agent is only one of several components. These coatings are optimally applied in an alcoholic vehicle or aqueous slurry directly to the (dry) fiber and filler surfaces by spraying or dipping.

Again, sizings must be very soluble in the particular resin systems they are supposed to interface with in the composite phase. For glass reinforcements, these are usually formulated mixtures of several components which can enhance (1) fiber-matrix interactions (coupling agents), (2) processability during spooling and weaving (lubricants), (3) wettability (surfactants), (4) cure activation and acceleration (napthanates, amines), (5) static control, (6) pH control, and several other functions. Glass fiber sizings are typically tailored for free radical crosslinked polyester and vinyl ester matrices. In these particular systems, the sizing layer must dissolve quickly to allow the silane agents to interact with the matrix before heat is applied or generated (all ester-based resins are exothermic and can reach a couple hundred degrees during room-temperature cure).

More importantly however, common glass fiber sizing formulations are not generally optimized for phenolic matrices. This is understandable sine phenolic/glass composite systems are not very common relative to polyester, epoxy and vinyl ester matrix systems). Many vendors presume that ester-optimized treatments and sizings will work just fine with other resin systems, but this is not always the case. There have been incidences reported exemplifying these incompatibilities. One case involved a situation where somebody fabricated two composites with the same constituents except one used something like a 3K tow continuous reinforcement and the other used a 12K tow (of the exact same fiber) . . . but the resin matrix in the 3K laminate would not cure. It was later found that the only difference was the fiber sizing. The sizing used on the 3K tow material was tailored for a different resin system which completely inhibited the curing process for the other resin.

It goes without saying, fiber surface materials and treatment processes are usually proprietary secrets that each fiber vendor does not want anybody else to know about. There are vendors who believe that this is the primary factor that differentiates their product from their competitors. Unfortunately, when they make an error, alter their process for some reason or another, or ignore the potential matrix incompatibilities, we (the end user) may never know about it until a string of major defects have already occurred.

Now, there are no known organic solvents that can actually damage inorganic glass or carbon fibers. Passive removal of sizings from glass fibers would likely require multiple solvents in several steps because all the formulation components may not be soluble in a single solvent. Fortunately, for carbon fibers, moderate solvents such as THF (tetrahydrofuran), acetone, MIBK (methyl isobutyl ketone), MEK (methyl ethyl ketone), toluene and xylene are all compatible solvents for these types of thermoset resins (namely, epoxies, polyesters and phenolics). Also, appropriate mixtures of these solvents would likely dissolve the sizings on carbon fiber surfaces in a single step. While candidates such as DMF (dimethyl formamide) and NMP (methyl pyrrolidone) are very strong organic solvents that used extensively throughout the resins and polymer industries, they can potentially leave amine residues which would probably require a second washing step with another solvent. Not only are THF and acetone powerful solvents but these compounds volatilize easily and leave no remnants.

With any solvent, the possibility of it interacting with the fiber surface functional groups must be considered. If the washing solvent changes the active surface area (ASA) in some way or another or alters the functional group content, then either another solvent must be found or the solvent-surface interaction chemistry must already be understood well enough to devise an effective functional group protection mechanism. Note that for fibers designed to work with epoxy matrices, surface treatments and finishes are usually tailored to accommodate hydroxyl, amine and residual epoxide groups along the liquid polymer chains, and these groups are not nearly as reactive with fiber surface aldehyde groups as they are with carboxyls, hydroxyls and ether groups.

It should also be noted that pre-sizing surface treatments utilizing O_2 and/or H_2 can oxidize existing C=O and –OH groups or reduce –COOH groups (to C=O or –OH) respectively. Analogously, solvents with redox capabilities can also do the same thing. If this scenario is likely, one may completely convert (oxidize) all the surface functional groups to –COOH, and then take the ASA measurement. However, this would obviously destroy the capability to directly identify and partition all the specific functional groups present on the unaltered fiber surfaces since test emissions would consist solely of CO_2 rather than the corresponding mixture of CO_2 and CO.

On amorphous glass fibers, surface groups are produced naturally with atmospheric exposure and are dominated by –OH groups protruding from silicon atoms. These form along the fiber-to-air interface when peripheral oxide groups are forced to cap off with the interface reactants (oxygen and water) due to surface energetics and nearest neighbor effects. These protruding silyl hydroxyl groups are generated under conditions favorable to hydrolytic oxidation. On the other hand, carbon fibers are comprised of graphene lamina which have strong 2-D order with weak 3-D interactions (they are turbostratic). These structures are comprised of ribbon-like layers with no *d*-space indexing, and the surface groups must be generated with more aggressive approaches. While plasma etching treatments are experimentally feasible, the predominant (and most commercial) process utilizes electrolytic oxidation which produces a mixture of the functional groups along the surfaces of the fiber.

Vendors can tweak their process to minimize the level of C=O groups and maximize the content of –COOH and –OH groups. The oxidation/hydration scenario might include the following representative conversions . . . C (raw fiber surface) ––> C≡O (1st stage of oxidation) ––> C=O (2nd stage of oxidation); C ––> C–OH (hydration); C ––> COOH (complete surface oxidation without decarboxylation). Obviously, this is and over-simplification, but it helps to illustrate the point that techniques intended to oxidize the alcohol groups could also oxidize the aldehyde and ether groups, while techniques intended to reduce the acid groups may also reduce the aldehyde and ether groups. So the ability to analytically distinguish between the four constituents could conceivably become obscured from either approach.

The general reactivity associated with the aldehyde group (C=O) is low for most of the major matrix resins, including the phenolics, epoxies and polyesters (in some systems, –C=O groups may be incompatible with the matrix). Thus, the majority of carbonized PAN fibers worldwide, are probably configured with heavy concentrations of active –COOH and –OH groups, and are finished either with thermoplastic epoxy or epoxy-compatible sizing formulations. The ideas covered here should help to heighten awareness concerning the benefits of fiber-to-matrix binding mechanisms which emphasize mechanical interlocking over chemical bonding, especially for high temperature materials where the chemical bonds begin to break down . . . but they also make it clear that a good understanding of the sizing formulations and surface treatments employed by the fiber/fabric vendors is necessary for the designers and fabricators (us) to make sound decisions.