SIZINGS AND COUPLING AGENTS — THE “MAGIC” OF COMPOSITE PERFORMANCE

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Why is there magic in sizings and coupling agents?

When something is both secretive and seemingly non-explainable through science or common reasoning, we tend to think of it as “magic”. Much of the technology of sizings is secretive (proprietary), especially since fiber manufacturers guard their sizing technology so carefully. The sizing technology is often the basis on which a manufacturer’s fibers are differentiated from the competition.   Furthermore, the sizing has a tremendous influence on the productivity of the fiber-making process. Thus the first element of magic (secretive) seems to be met.

The second element of magic (seemingly non-scientific) is also met, at least in part. Although we can understand some of the technology of coupling agents and sizings, much is still based on experience and trial and error (often referred to as empirical knowledge) and does not have a good scientific rationale. Furthermore, small changes in sizing formulations can result in major unexplainable changes in the sizing, thus further confusing the scientist and promoting the mystery of the entire technology.

The purpose of this article is to remove a bit of the mystery and then to explore some new innovations in sizings. We will not, of course, disclose company secrets (even if we knew them), but there are certain basic elements to sizings that are common to most systems and which will give us a view into the technology and may help us understand some of the reasons why some small differences between systems can cause major changes. More importantly, we may be able to understand enough of sizings and coupling agent technologies that we will be able to utilize the technology in making better composite products. We will begin by considering sizing and then look at coupling agents, which are one of the components of the sizing.

Sizing – What is it?

The sizing or, as it is sometimes called, the finish, is a mixture of materials that is applied to the surface of the reinforcement fibers. Although sizings are applied to all major types of reinforcement fibers, they are most important for fiberglass and so most of our discussion will involve sizings for fiberglass specifically. Later in the paper, sizings and other considerations for carbon fibers and other advanced fibers will be examined.

Table 1 lists the major components in a typical sizing and, in brief terms, the major purpose for each component. In actual practice, some components may serve more than one function. A somewhat more detailed explanation of each component follows:

- **Water –** Most fiberglass manufacturers now use water as the carrier for the sizing. (We refer to the material as a carrier rather than a solvent because some of the components are not dissolved in the water but are, rather, simply mixed into the water and carried by it, usually as some kind of suspension. The advantages of water as the carrier rather than using an organic solvent (such as styrene) are, of course, less chance of pollution and fewer problems with the potential hazardous materials which may affect the people who work with the sizing. Another critical characteristic of water is its low viscosity (ideally about 2 centipoise when fully mixed as a size) which is very important in quickly coating the fibers as they are processed (at speeds of about 5 kilometers per minute).

- **Coupling Agent –** This component promotes the bonding between the fiber and the resin matrix. Because of the importance of coupling agents, they will be discussed in detail in the next section of this paper.
- **Lubricant –** When fibers are run through equipment to be coated, wound-up, or some other process, they are subject to mechanical damage because of the inherently brittle nature of fiberglass. This damage, often surface cracks and abrasions, will usually result in lower tensile strength of the fiberglass and can also lead to enhanced corrosion as the cracks can serve as inlets for water or other corroding liquids. The lubricant's job is to facilitate the passage of the fibers through the processing equipment, such as through applicator rolls, pulleys, or over angles, by creating a slick surface for the fiber to slide on. The most common lubricants used in sizings are modified fatty acids, polymers (such as low molecular weight polyethylene and polyethylene glycol), mineral oils, and cationic amines.
- **Film Former –** These components are critically important in covering the fibers (for protection) and binding the bundles of fibers together (to minimize fuzz). Originally made of starch materials and now usually polymeric, the film formers provide protection from mechanical damage (along with the lubricant) and from

corrosion. Fiberglass, unless well coated, is susceptible to corrosive attack from water which will pit or crack the surface of the fiberglass and result in a loss in strength. Therefore, the film former covers the surface to prevent water from reaching the fiber surface. Most film formers are low molecular weight polymers, typically polyvinyl acetate, polyesters, epoxies, acrylics, polystyrene, and urethanes. A difficulty with film formers is that the polymers used are usually not soluble in water and must, therefore, be supplied as latex emulsions. (An emulsion is a suspension of a liquid or solid in a carrier liquid, such as milk fat in water or, in the case of interest to us, a polymer in water. The term latex is applied only to those suspensions in which the carrier is water.) These emulsions can themselves be quite complex, often containing several minor constituents, such as emulsifying agents, plasticizers, molecular weight controllers, and surfactants, which assist in maintaining the integrity of the emulsion.

- **Wetting Agent –** These materials assist the film former to wet the entire surface of the fibers and then, when the matrix is applied to the fibers to make the composite, to assist in the wet-out of the fibers by the matrix. Common wetting agents are soaps, detergents, and surfactants. (Surfactants modify the surface energy of a material and make it more easily coated.) The chemistry of surfactants is very important in paint technology as well as fiberglass sizings but will not be considered in detail here. The wetting agents are also critical in the fiber manufacturing process where they assist in ensuring a uniform coating of the fibers. Occasionally the rapid movement of the fibers through the sizing coating liquid will result in excessive foaming of the sizing. To prevent this from occurring, an anti-foaming agent is often added.

- **Crosslinking Agent –** For maximum effectively, the fiber coating should enter into the crosslinking reaction of the matrix when the matrix is cured. This agent could also participate in the crosslinking of the film former if it is also crosslinked. The nature of the crosslinking agent depends upon the chemical nature of the film former and/or the matrix to be used in coating the fibers. For instance, if a polyester is the matrix, the crosslinking agent could be a peroxide or an accelerator.
- **Antistatic Agent –** Fiberglass can build up a significant static charge as it moves through equipment, especially when the fiberglass moves at high speed. The anti-stat is added to dissipate that charge. If not dissipated, the static charge could shock operators and would cause the fibers to repel each other, thus complicating processing during fiber manufacture and during composite manufacture. Common antistats are inorganic salts (such as $LiCl$ or $MgCl_2$, quaternary ammonium salts, and several complex organic molecules.

Some of the key components in the sizing are emulsions (such as the film former and, perhaps, the lubricant and others). These emulsions, and most others, are notorious for their instability. The nature of emulsions is one of balancing the nature of the emulsified material (such as the size of the suspended globules or their hydrophobicity) with the surrounding nature of the other components. Emulsions can break, that is, the suspended material will fall out of suspension, because of many factors such as: changes in the pH (acidity) of the surrounding carrier, presence of nucleating agents (such as salts), changes in temperature, shearing of the liquid as might occur if it were sprayed, and changes in the chemical nature of the surrounding materials. It is no wonder then, that one of the most critically guarded secrets of fiberglass manufacturers is how to maintain the emulsion of some sizing components in the presence of many other surrounding components which would normally break that emulsion.

The nature of applying the sizing to the fibers is also important in its performance. For instance, after the sizing is applied to the fibers, the water is dried off. The speed of drying and the temperature at which it is done can affect the nature of the film former. If dried too quickly, for instance, the globules of film former which were suspended in the water carrier might not have sufficient time to spread out and fully coat the fiber surface even with the help of a wetting agent. The conditions of drying the sizing also affect the interaction between the coupling agent and the film former which must compete for presence on the fiber surface.

Coupling agents

The heart of the sizing, as far as improving the bond between the fiber and the matrix, is the coupling agent. (Coupling agents are sometimes referred to as “keying agents”, although this term is not common in the United States.) The basic concept of coupling agents is simple – they are molecules in which one end is reactive with the surface of the fiberglass and the other end is compatible or reactive with the matrix. They form bridges between the fiberglass and the matrix, thus increasing the overall fiber-matrix bonding strength. In most applications of composites, the stronger the fiber-matrix bond, the better the performance of the matrix. (Some rare exceptions to this rule will be discussed later in this article.) A typical silane coupling agent is illustrated in Figure 1 where the end that bonds to the glass is shown as a tri-functional alkoxy silane and the end that reacts with the matrix is designated simply as X. The three carbon atoms between the two ends serve to isolate the reactive ends from each other, thus giving a greater variety of choices in the types of reactive groups that can be chosen.

The steps of bonding of the coupling agent to the fiberglass surface and the subsequent bonding of the other end of the coupling agent to the matrix are illustrated in Figure 1. A process involving two main steps is carried out by the fiberglass manufacturers to bind the coupling agent to the fiberglass. These are the hydrolysis step and the reaction/drying step as indicated in Figure 1. When these processes are completed, the dry glass fibers have been coated with the dried sizing and the coupling agent molecules are firmly bonded to some atom on the fiberglass surface, often a metal that is part of the glass formulation (represented as M's in the figure).

The next step in the process is accomplished by the fiberglass molder. The fiberglass is coated with resin during the process of making and molding the composite part. As the resin soaks into and around the fiber bundles, the free end of the coupling agent engages with the resin matrix molecules and bonds within the matrix. To facilitate this bonding, a reactive group (indicated in Figure 1 as an X) is chosen so as to be reactive or, at least, compatible with the polymer matrix. This is another area of difference between the fiberglass manufacturers. The choice of the type of reactive group (X) is quite broad since many different types of groups would be reactive or compatible with a single type of resin matrix. Hence, you may find that the fiberglass from one manufacturer will have better performance characteristics in your resin than would another brand of fiberglass.

Typically, fiberglass manufacturers will have one or two reactive ends for each general class of matrix. For instance, they may sell one reactive type for all ortho and iso unsaturated polyester resins and another for chlorine-modified polyesters. They may have yet another for vinyl ester resins and still another for epoxies. The use of acrylic in your formulation could call for yet another type of active group. In all of these cases, the reactive group can usually be bonded into the matrix during crosslinking of the matrix, thus ensuring a good bond between the resin matrix and the coupling agent reactive group, and through the coupling agent to the fiberglass.

Coupling agents and thermoplastics

When a thermoplastic is used as the composite matrix (as, for instance, in reinforced nylon), there is little chance for direct bonding between the coupling agent and the matrix. (There is no period during a molding cycle for thermoplastics when chemical reactions, like crosslinking, take place.) Therefore, the most that can be hoped for is a compatibility between the end of the coupling agent and the thermoplastic matrix. Even more selections exist in choosing this compatibility than existed for choosing reactive groups for thermosets. Also, each type of thermoplastic resin (nylon, acetal, polycarbonate, acrylic, etc.) needs a separate type of reactive end on the coupling agent. Therefore, coupling agents for thermoplastics tend to be very different from manufacturer to manufacturer. The development of thermoplastic coupling agents continues to be a major area of research for the fiberglass manufacturers.

The poor bonding of thermoplastics to most fibers has led to an interesting innovation to increase the fiber-matrix bond strength. Instead of focusing on the nature of the sizing to increase the bond, some composite manufacturers have worked with matrix resin manufacturers to change the nature of the thermoplastic and make it easier to bond with. For instance, polypropylene is a matrix resin that is particularly difficult to bond to. But, by copolymerizing the polypropylene with a more easily bondable monomer, such as one containing a highly polar group or even a carbon-carbon double bond that survives in the polymer, the bonding of polypropylene can be substantially improved.

Interfaces and Interphases

Some discussions have been carried out among researchers on the physical nature of the way the coupling agent interacts with the fiberglass on one end and the resin matrix on the other. In general, this discussion comes down to a question of whether the surface of the fiberglass or of the resin is hard and closed or soft and open. Most authorities believe that the fiberglass can be adequately represented as being hard and closed. Therefore, the coupling agent is thought to react with the outer layer of molecules on the surface of the fiberglass. This type of interaction is called an **interface**.

The interaction of the coupling agent with the matrix is quite different. The matrix is a liquid during the time that the coupling agent is being integrated and, therefore, no hard surface exists. Therefore, the coupling agent molecules are thought to penetrate into the boundary region of the matrix which is forming as the matrix hardens. This interpenetration region is called the **interphase**.

Not all authorities have come to a consensus on interfaces and interphases, but the basic concepts presented here are adequate to allow you to understand the nature of discussions on this subject and, perhaps, to modify your processing to take advantage of some characteristics which might be best understood by consideration of either the interface or the interphase.

To the extent that the surface is considered an interface, some tests for wettability of the surface can be quite meaningful. These tests involve measuring the angle created between a drop of liquid (often water or some organic solvent) and the surface to be wetted (such as the fiber). When viewed through a special type of microscope, the angle of intersection can be measured. If the angle is large (that is, near 90°), the drop is avoiding the surface. If the angle is low (near 0°), the drop is coating the surface. This system allows researchers to choose solvents and additives for the sizing that will promote wettability. The system also allows reseachers to change the surface to increase or decrease its wettability. Changing the surface (using chemical methods or, perhaps with plasma treatment) is a current area of active research within both universities and fiber manufacturing companies.

How do the sizing and the coupling agent affect how composites should be manufactured?

To assist in the process of making composite parts, the sizing should provide the following functions: bind filaments into a strand, protect the fibers from mechanical damage, allow the matrix to coat the strand and to penetrate between the fibers in the strand to coat each individual fiber, promote choppability, dissipate static electricity, promote strength, not detract from translucency, and enhance electrical properties. Not all of these functions are met by any single sizing and most are not even met with any particular resin. Hence, compromises in these functions are often required.

When the sizing does its job well, the bond between the fibers and the matrix is very strong. When the sizing does poorly, the fibers are not bonded well to the matrix and a significant loss of properties occurs. Good and poor bonding can often be seen in photographs of the fibers in the resin matrix as shown in Figure 2. Note how well the resin coats the fibers in one of the photos and how bare the fibers are in the other.

Most fiberglass manufacturers realize that the composite manufacturing method can profoundly affect the way the sizing performs. For instance, if the composite is to be made by chopper gun, the sizing must have a high anti-stat content and, moreover, must allow for very rapid wetting of the fibers. If the fibers are to be used in SMC, the requirements are less dependent on the quick wettability and, perhaps, may focus on hydrolytic stability of the composite.

The type of cure system can also dictate which type of sizing is to be used. In some cases, optimization with a particular cure can be facilitated by incorporating some of the cure components, such as peroxide or accelerator, in the sizing itself. A fascinating area of work is electron beam and UV curing of composites. Sizing systems developed specifically for these cure systems are commercially available.

Composite properties and testing

The sizing can also affect the properties of the composite. Different sizings may be required for products that are to be used in water environment versus those used at very high temperature. Alternately, transparent applications may require a different sizing from electrical applications. Hence, it is a careful manufacturer who tests the composite in conditions which reflect actual the actual use environment.

Some tests on composites are quite specific for a particular use. For instance, soaking the composite in water or subjecting the composite to electrical current. Other tests, however, are more general and focus on a characteristic inherent in the composite structure, such as the strength of the fiber-matrix bond. This bond strength is strongly affected by the presence of the sizing/coupling agent. Table 2 gives some data which show that the presence of a sizing/coupling agent can increase the flexural strength up to100% under dry conditions and up to 500% in a wet environment.

Considerable research effort has gone into developing a test that will measure the fiber-matrix bond directly. Early tests used single fibers which were coated with a drop of resin and then pulled through a die to measure the force to separate the resin from the fiber. Other tests embedded the fiber in a matrix of resin and measured the optical pattern that developed from stresses along the fiber surface as the fiber was pulled in tension. The most recent test involves cutting a composite sample so that the ends of some of the fibers are exposed and then pressing on the ends of the fibers with a small indentor, thus creating a debonding force between the fiber and the matrix. This force can be measured as the sample is viewed through a microscope. This method even allows for the measurement of bond strength differences between the outer and inner fibers in a bundle, thus monitoring the effectiveness of the resin in penetrating throughout the bundle.

An interesting new test which has been developed to measure the fiber-matrix bond strength involves a spectrographic technique called XPS (x-ray photoelectron spectroscopy). In this method, x-rays are used to measure the ratio of the peak areas associated with charge build-up on the surface of the fibers to those in the matrix. When this ratio is small, the bonding strength is high and vice versa.

In a production environment, the strength of the fiber-matrix interface is usually measured by a transverse tensile test or a short beam shear test, although both of these require that the composite be unidirectional. Otherwise, the best test is probably a standard strength or toughness test which don’t measure the fiber-matrix bond directly but, rather, the effect of the bond strength on other properties.

Toughness

Just a few words about toughness. The effect of the fiber-matrix bond strength on toughness is quite complicated compared to its effect on most of the other mechanical properties. Because toughness, especially impact toughness, is a measure of the ability of the composite quickly to absorb energy, any method for absorbing that energy will be effective in increasing the toughness. One energy absorbing method is to distribute the energy of an impact throughout the entire composite and thus dissipate the effects of the energy. If this is done quickly and enough energy is dissipated, the impact will not result in damage. The dissipation of energy is promoted by good bonding between the fibers and the matrix because the matrix can then efficiently interconnect the entire composite structure, thus allowing for the energy to move throughout it.

Another energy absorbing mechanism is friction of the fibers against the matrix. In this case, a strong fiber-matrix bond decreases the amount of energy that is absorbed.

The optimum bond strength for impact toughness is, therefore, a compromise between these two mechanisms, and any others which might also be present. If the fibers are brittle, as in fiberglass, the compromise is usually tilted toward high fiber-matrix bond strength and quick dissipation. If the fibers are very tough, such as aramids (Kevlar®, for instance), they can often withstand the local impact better and will absorb more energy through friction with the matrix. This friction mechanism is so prevalent that aramids are often sold without any sizing so that the friction can be maximized.

The optimization of toughness is especially important in thermoplastics and is quite different from thermosets because the bonding between the matrix and the fiber is so weak. Hence, optimization is even more important, especially because thermoplastic composites are so widely used in applications where impact toughness is a major performance requirement.

Sizings and coupling agents for advanced fibers

The bonding of the matrix to carbon fibers is quite poor compared to the bonding between the matrix and fiberglass and bonding to aramid is even worse than with carbon fibers. Normal treatment of carbon fibers is to clean the surface of the fiber after the last heat processing step in the fiber-making process. This cleaning is often done electrolytically. Then, a sizing is added from a bath. The sizing is usually epoxy-based since most carbon fibers are used with epoxies, but other sizings can be obtained.

The relatively poor strength of the fiber-matrix bond has spawned considerable research into methods to improve the bonding between advanced fibers, especially carbon, and various matrices. Some recent fiber treatments have resulted in increases of adhesion (peel) properties of more than 1000% with a simultaneous increase in impact strength (300%) and in tensile strength (50%).[1] Shaped fibers and other techniques have also been tried, usually to little benefit.

Summary

The correct choice of sizings and coupling agents is extremely important in optimizing properties. The performance of the composite can be profoundly affected by this choice, especially in adverse environmental conditions such as wet or high temperature. Therefore, some

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[1] DuoMod product bulletin, Zeon Chemicals, Louisville, KY, March 16, 1998

consultation with the fiber manufacture to select the proper sizing to match the resin, the conditions of use, and the manufacturing method. This close cooperation between fiber manufacturer and composite manufacturer may not give all of the answers, but at least some of the magic might be changed into solid science and technology.

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Table 1. Components of a typical sizing for fiberglass

Component	Major Function
Water	Carrier for the sizing mixture
Coupling agent	Improve the bond between the matrix and the reinforcement
Lubricant	Prevent mechanical damage to the fibers
Film former	Hold the fiber bundles together and coat the fibers to protect them
Wetting agent	Assist in wetting the fibers by the resin matrix and the film former
Crosslinking agent	Crosslink to the resin matrix or the film former or both
Antistatic agent	Dissipate static change the might be built up on the fibers

Table 2. Flexural strength of composites when made with and without a coupling agent[2]

Resin System	Coupling Agent Present	Flexural Strength (psi)	
		Dry	Wet
Polyester	No	60,000	35,000
	Yes	87,000	79,000
Epoxy	No	78,000	29,000
	Yes	101,000	66,000
Melamine	No	42,000	17,000
	Yes	91,000	86,000

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[2] This table data derived from “Organofunctional Silane Coupling Agents,” James G. Marsden and Samuel Sterman, *Handbook of Adhesives*, 2nd Ed., Ed. by Irving Skeist, New York: Van Nostrand Reinhold, 1977.