

Effects of Silica Surface Treatment on the Impregnation Process of Silica Fiber/Phenolics Composites

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Received 13 December 2006; accepted 6 March 2007

DOI 10.1002/app.27327

Published online 6 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Effects of silica surface treatment on the impregnation process of silica fiber/phenolics composites were studied. Micro-Wilhelmy method was used to evaluate the surface characterization of silanized silica fibers. The interlaminar shear strength (ILSS) measurements and the void contents of the silica fiber/phenolics composites were also performed. The interactions occurring between silica fiber and the components of phenolic resin solution can affect the contact angle between silica fiber and phenolic solution and the dynamic adsorption behavior of phenolic resin onto silica fiber. There are competitive adsorp-

tions to different extent for phenolic resin and solvent onto silica fibers. Silica fibers as reinforcement treated by silane-coupling agent, such as γ -aminopropyl-triethoxysilane, γ -glycidoxypropyl-trimethoxysilane, trimethylchlorosilane, and γ -methacryloxypropyl-trimethoxysilane, influence the mechanical interfacial properties of silica fiber/phenolics composites and the uniformity of resin distribution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2274–2279, 2008

Key words: silica fiber; phenolic resin; composites; surface treatment; silanization; adsorption

INTRODUCTION

To optimize the properties of silica fiber composites, the silica fibers themselves are often subjected to a variety of surface treatments that alter their adhesion characteristics and significantly influence the properties of the resulting composites.¹

The surface treatments may assist a developing composite material interphase. The interphase refers to an additional (third) phase that may be created at the boundary between the reinforcement and the matrix in composites.^{2–5} Accordingly, the interphase properties may deviate significantly with respect to those of the bulk composites. Because the interphase couples the stress transfer between the reinforcement and the matrix, the characteristics of the interphase are directly responsible for determining the static and dynamic properties of composite materials, as well as their environmental stability.^{2–4,6}

After surface treatment, the fibers are generally sized or coated with a thin polymer layer.^{5,7–11} The purpose of sizing is to insert a polymer interlayer between the silica fiber and the polymer matrix and to use the properties of the sizing to control the level of fiber/matrix adhesion. Sizing has also been reported to improve the wetting of the fiber by the matrix resin so as to protect its surface reactivity.^{12–14}

The improvement in wetting and bonding was directly reflected on the increase of tensile strength of the composite. Also, Mascko¹⁵ reported that poor wetting produces voids at the interface, and such void causes stress concentration and degrades the composite performance. Wetting characteristics of a given liquid can be examined by the contact angle.^{16,17}

The function of a coupling agent is primarily to promote fiber-matrix adhesion by interacting chemically with both the fiber surface and polymer matrix. For example, the most effective-coupling agent for silica fiber/thermosetting resin composites is the organosilanes having the general structure, X_3SiR . The X-groups are hydrolysable in the presence of water to form silanols, which simultaneously react with the silica surface and interreact to form a chemically bonded polysiloxane coating on the fiber surface. The R-group is chosen to be chemically reactive with the matrix phase, for example, a vinylsilane for reaction with phenolic resin, so as to form a covalently bonded “interphase” between fiber and matrix. Similar coupling are also used for silica fiber/thermoplastic composites in which the likelihood of covalent bonding is remote, but the modification of interfacial tension promotes a greater degree of compatibility between components.^{18,19}

In our work, four silane-coupling reagents γ -aminopropyl-triethoxysilane (γ -APS), γ -glycidoxypropyl-trimethoxysilane (γ -GPS), γ -methacryloxypropyl-trimethoxysilane (γ -MPS), and trimethylchlorosilane (TMCS), were employed to modify silica fiber to obtain fiber reinforcements differing in physical and chemical properties. Of the four silane-coupling

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50603004.

TABLE I
Characteristics of Wetting Liquids Used in This Study

Wetting liquid	γ_l^d (mJ m ⁻²)	γ_l^p (mJ m ⁻²)	γ_l^T (mJ m ⁻²)	η (mPa s)	ρ (g cm ⁻³)
Deionized water ^a	21.8	51.0	72.8	1	0.998
Ethylene glycol ^a	31.0	16.7	47.7	17.3	1.100
Phenolic solution ^b	–	–	33.1	140	0.940

^a Data given in Ref. 17.

^b Data provided by manufacturer.

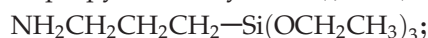
agents, the first three bearing different reactive chemical groups have been extensively used to enhance the interfacial performance of glass and silica fiber-reinforced polymer-based composites. However the fourth, terminated with alkyl groups, is not usually involved in composite field because of its nonreactivity. The motivating factor in this choice was that alkyl-terminated silane could afford silica fiber a nonpolar surface. Thus, resulting silica fibers differing in polarity and reactivity were obtained to evaluate the surface-dependent adsorption of the components of resin matrix. The influences of surface silanization on silica fiber wetting characteristics were experimentally examined. The mechanical performance of silica fiber/phenolics composites was also measured with the intention of developing an understanding of the microscopic phenomena that affect macroscopic behavior response in a resin transfer-molding (RTM) process.

EXPERIMENTAL

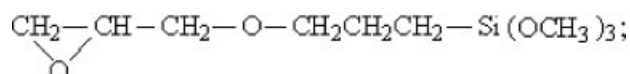
Materials and sample preparation

The woven-silica fabric, with desized surface by extracting with acetone in a Soxhlet apparatus for 48 h, was manufactured by Jingzhou Feilihua Quartz Glass, China (filament specific gravity: 2.2 g cm⁻³, diameter: 8 μm). A resol type of phenolic resin with commercial name Type 616-ammonia was obtained from the Beijing Research Institute of Materials and Technology, China, which is a mixture of phenolic resin and ethanol (weight ratio: 60 : 40), whose physical properties are given in Table I. Four types of silane-coupling agents, γ -APS, γ -GPS, γ -MPS, and TMCS, were purchased from Nanjing Shuguang Chemical Factory, China, and used as received. The structures of silanes-coupling agents are as follows:

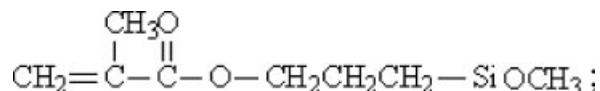
γ -Aminopropyl-triethoxysilane (γ -APS):



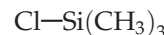
γ -Glycidoxypropyl-trimethoxysilane (γ -GPS):



γ -Methacryloxypropyl-trimethoxysilane (γ -MPS):



Trimethylchlorosilane (TMCS):



All samples were prepared under identical processing conditions. The silane-coupling agents were hydrolyzed for 1 h in aqueous ethanol solution (95%) and then the desized silica fabrics were dipped in the silane solution (0.5%) for 30 min and dried in an oven at 110°C for 30 min. Several fiber bundles were pulled out from the fabric to be used in wettability measurements. The silica fiber/phenolic composites were prepared using a RTM equipment. The phenolic resin solution was injected into the RTM die at a pressure of 20 kPa, in which certain plies of fabric (3.5 cm × 15 cm) had been placed ensuring that fiber volume fraction of bulk specimens was about 55–60%. The system was held at 110°C for 50 min and then cured at 170°C for 3 h. The specimens for mechanical measurements were taken from the inlet and outlet gate region of the RTM equipment.

Wettability measurements

According to micro-Wilhelmy technique,²⁰ wettability measurements of the silane-treated silica fibers were performed using an SB312-II dynamic wetting equipment (KeEn, Beijing, China). Some bundles of fiber were aligned and inserted into a polyethylene pipe and then suspended indirectly to the measuring arm of a precision microbalance (Fig. 1). The adsorption amounts and adsorption time of test liquid were automatically recorded until equilibrium. The wetting liquids used in the experiment were deionized water, ethylene glycol, and the as-received phenolic resin solution, whose surface-free energy and other characteristics are listed in Table I. All measurements were performed at 25°C ± 0.1°C in a small chamber filled with the air saturated with the solvent.

The samples after wettability measurement were dried in vacuum at 80°C until constant weights were

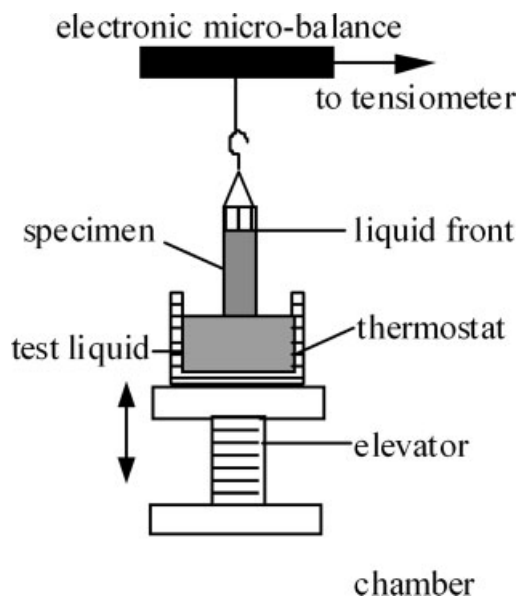


Figure 1 Schematic diagram of dynamic wetting determination equipment.

obtained. Net adsorption percentage of phenolic resin was calculated according to the change in weight of the samples before and after drying operation.

Mechanical measurements

The interlaminar shear strength (ILSS) of silica fiber/phenolic composites was tested on a universal testing machine (WD-1, Changchun, China) using a three-point short-beam bending test method accord to ASTM D-2344-76. The support span-to-depth ratio used was 5 : 1, with a corresponding specimen width-to-thickness ratio of 3 : 1 at the loading speed of 2 mm min⁻¹.

RESULT AND DISCUSSION

Effect of silane treatments on the dynamic adsorption of silica fiber

Effect of surface silane treatments on the dynamic adsorption of silica fiber is shown in Figure 2. It is shown that the adsorption behavior of silica fibers into phenolic resin solution is influenced by fiber surface silane treatments evidently. The total adsorption amount of silica fibers is maximum for desized fibers, to 224.3 mg, and minimum for TMCS-treated fiber, to 136 mg. The time to attain adsorption equilibrium for the two fibers above are short comparatively, and which for silica fibers treated by silane-coupling agents, such as γ -APS, γ -GPS, and γ -MPS are longer than the two fiber samples mentioned earlier.

The reason that the desized silica fibers possess highest amount of adsorption is that lots of hydrox-

yls on desized silica fiber surface can interact strongly with the components of phenolic resin solution. When silica fiber is silane treated, organic functional groups are grafted on silica fiber surface, cover part of hydroxyls and reduce the polarity and interaction between silica fibers and the components of phenolic/ethanol solution. So, the silica fibers treated have lower amount of adsorption. Especially, the silica fibers treated by TMCS interact with phenolic resin solution most weakly among the silica fiber with silicazation and have the least amount of adsorption and the short time to attain adsorption equilibrium. Because —OH as a strong polar functional group is replaced by —CH₃ as a nonpolar functional group on TMCS-treated fiber surface.

Effect of surface treatment on contact angle and surface-free energy

The wettability analysis between the fiber and resin solution can be characterized by the contact angle measurement. According to the method proposed by Chwastiak,²¹ the advancing contact angle, θ , was calculated as a function of time from an energy balance:

$$\gamma_l \cos \theta = \frac{64(1 - \varepsilon)^2 H_f^2 \rho_f \eta_l m^2}{K^2 \varepsilon^3 V_T W_f d_f \rho_f^2 t} \quad (1)$$

where ε is the porosity of the fiber bundle (ε is in the range of 48–52%); W_f , d_f , H_f , and ρ_f are, respectively, the weight, diameter, height, and density of the fiber; ρ_l and η_l are the density and viscosity of wetting liquid, respectively; K is the hydraulic constant, whose value is between 3.3 and 4.0 for the fiber; V_T is the total volume of the system; m is the weight of adsorbed liquid at the equilibrium time, t ; and γ_l is the surface tension of the testing liquid.

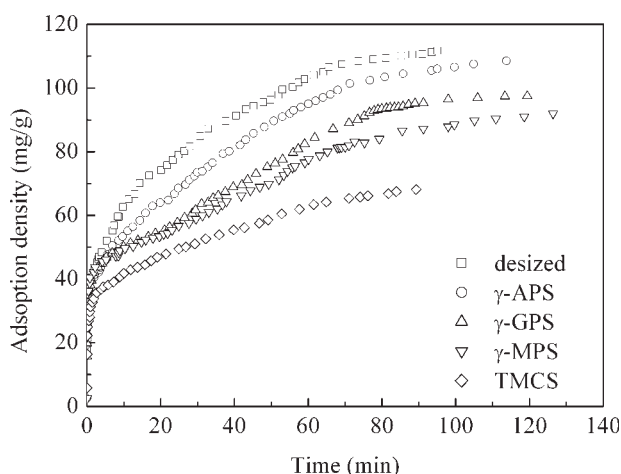


Figure 2 Effect of silane treatments on the dynamic adsorption of silica fiber.

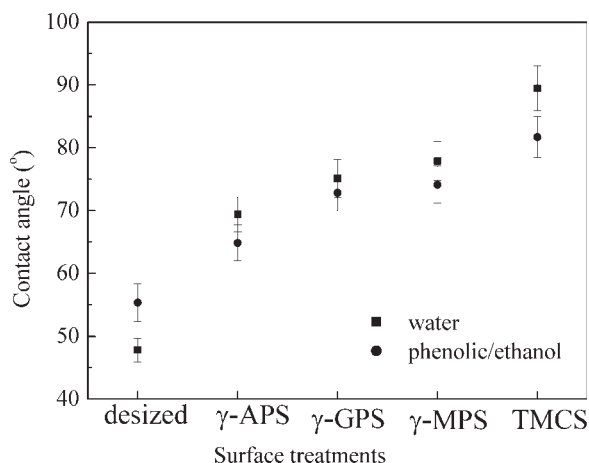


Figure 3 Effect of silanization on contact angle between silica fiber and water and phenolics/ethanol solution.

The silica fiber surface energies (γ_s^T) and their dispersive (γ_s^d) and polar (γ_s^p) components can be calculated by the advancing contact angles between two test liquids of known polar and dispersive surface-free energies and the fiber according to following equations²²:

$$\gamma_l(1 + \cos \theta) = 2(\gamma_l^d \gamma_s^d)^{1/2} + 2(\gamma_l^p \gamma_s^p)^{1/2} \quad (2)$$

$$\gamma_s^T = \gamma_s^d + \gamma_s^p \quad (3)$$

The polarity is defined as the fraction of the polar contribution in relation to the total surface-free energy, γ_s^p/γ_s^T . The advancing contact angles between silica fiber and phenolic resin solution were also measured.

Effect of silanization treatment for the silica fiber on contact angle between silica fiber and phenolics/ethanol solution is shown in Figure 3. It is found that the hydrophobicity of silica fibers surface is heightened, and the contact angle of silica fibers is increased in phenolics/ethanol solution after silanization treatment.

Effect of different silane-coupling agents on surface-free energy of silica fiber is shown in Table II. As can be seen, the surface-free energy of treated

TABLE II
Experimental Data of Surface Free Energy of Silica Fiber, Polarity Between Silica Fiber, and Phenolic Resin Solution

Silica fiber	γ_l^d (mN/m)	γ_l^p (mN/m)	γ_l^T (mN/m)	γ_l^p/γ_l^T
Desized	18.6	32.3	50.9	0.635
γ-APS	18.8	28.5	47.3	0.602
γ-GPS	17.8	25.9	43.7	0.593
γ-MPS	17.3	22.3	39.6	0.562
TMCS	15.1	14.1	29.2	0.486

silica fibers are decreased from 50.9 mN/m for desized fiber to 29.2 mN/m for TMCS-treated fiber, and the surface silanization mainly influence the polar component of surface-free energy for silica fibers.

The surface property of silica fibers is changed after surface silane treatment. There are hydroxyls mostly on the surface of desized silica fibers, which develop high-surface-free energy for silica fibers. The active groups of silane-coupling agents react with the hydroxyls on surface of silica fiber, and silane-coupling agents are grafted onto surface of silica fiber, so as to content of the hydroxyls on fiber surface decreasing. Owing to different organic groups with dispersed polarity contained by silane-coupling agents, which have diverse hydrolysis capacity in this experiment, such as NH_2- , $(\text{CH}_2\text{OCH})-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-$, and CH_3- , the polarity of silica fiber surface decreases to a different extent. TMCS molecule-containing Cl atom with high hydrolysis capacity can react with hydroxyls on silica fiber surface via hydrogen bonding in large degree caused fiber surface covered by hydrophobic methyl molecule to some extent. As a result, the surface of TMCS-treated silica fibers shows high hydrophobicity.

We can use the ratio of the polar component of surface-free energy to the total surface-free energy, γ_l^p/γ_l^T , to scale surface polarity of silica fiber. The surface polarity of treated silica fibers in this experiment are calculated and shown in Table II. As described earlier, the surface polarity plays an important role in the adsorption properties of fibers. Figure 4 gives relationship between adsorption properties of silica fiber, total adsorption amount and net adsorption percentage of solute for silica fiber into phenolic/ethanol solution, and its silanization treatment carrying with corresponding polarity.

It is indicated that, from Figure 4, the total adsorption amount for silica fiber into resin solution

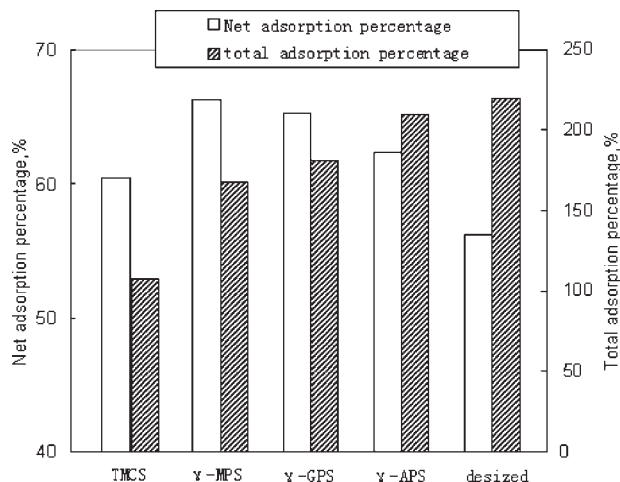


Figure 4 Relationship between adsorption properties of silica fiber and its silanization treatment.

increases linearly, as the polarity of fiber surface increases from TMCS treated to desized. However, the net-adsorption percentage of phenolic resin decreases with the polarity increasing from γ -MPS treated to desized. In this experiment, the resin system is a mixture of phenolic resin and ethanol, which have different physical and chemical properties as a result of the selective adsorption for silica fiber to the mixture. γ -MPS-treated silica fiber provided with the maximum net adsorption percentage of phenolic resin is propitious to the competitive adsorption of the components in the phenolics solution. It also concludes that the polar component of the surface-free energy of silica fiber is the key factor of the adsorption process.

Effect of surface silanization on void content of composites

Void content is an important parameter in token of the effect and quality of wettability for composites. The existence of voids plays a crucial part in the mechanical properties of the materials. The void content of composites is calculated by using the equation:

$$\phi = \frac{100(\rho_t - \rho_m)}{\rho_t} \quad (4)$$

where ρ_t is the theoretical density and ρ_m is the actual density.

Effect of surface silanization for silica fiber on void content of silica/phenolic composites is shown in Figure 5. The composite samples are produced by RTM. Fiber surface treatments not only decrease the void content in inner composites, but also cause the void to uniform distribution. It is important to point that the void content at outlet region of composites specimen produced by RTM process is higher than the void content at inlet region when the silica fibers

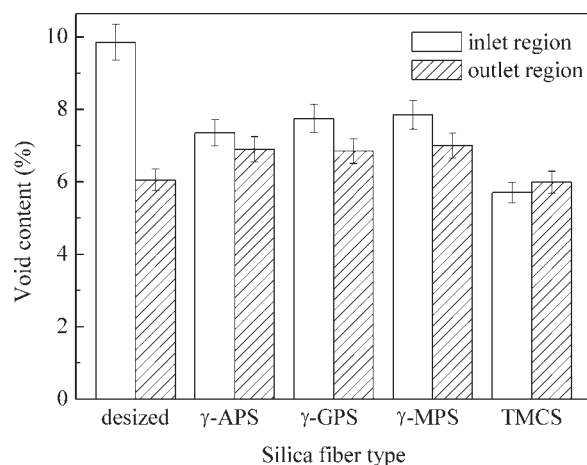


Figure 5 Effect of silanization on void content.

TABLE III
Experimental Data of the ILSS of Silica Fiber/Phenolics Composites

Silica fiber	ILSS ^a (MPa)	ILSS ^b (MPa)	ILSS ^a /ILSS ^b
Desized	28.5	32.1	0.888
γ -APS	42.9	43.3	0.991
γ -GPS	39.2	40.1	0.978
γ -MPS	38.9	39.3	0.990
TMCS	26.4	25.8	1.023

^a The data of ILSS is measured from inlet region.

^b The data of ILSS is measured from outlet region.

as reinforcement were treated by TMCS, compared with the other silane-coupling agents.

Effect of surface silanization on ILSS of composites

Effect of surface silanization on ILSS of composites is shown in Table III. Owing to the silica fibers treated by γ -APS, γ -GPS, and γ -MPS, respectively, the performances of composites improve, and the ILSS values increase from about 30 MPa for desized fiber to about 40 MPa. This is because silica fibers treated with the silane-coupling agents above developing strong interface bonding to phenolic resin due to the reaction of functional group with phenolic resin. However, ILSS of the sample using TMCS decreases. As the effect of silane-coupling agent on the ILSS of silica fiber/phenolics composites produced by RTM process, it is found that the distribution of ILSS in inner composites tend to uniformity after fiber surface silane treatments on one hand, silanization-treated silica fibers with active functional groups develop strong interface bonding to phenolic resin by coupling function of the silane molecule on the other. The phenolic resin cannot develop effective interfacial bonding on the alkyl-terminated fiber surface for TMCS treated, as a result of lower ILSS value.

CONCLUSIONS

The wetting and adsorption behavior of phenolic resin onto silica fibers is a complicated function of contributions from phenolic resin, solvent, and the surface of silica fiber. The silica fibers are treated by four silane-coupling agents. After the process, the surface property of silica fibers is changed, leading increased contact angles between silica fiber and phenolics solution, decreased surface-free energy, especially the component of polarity and reduction of the selectivity for surface adsorption of the silica fibers. The total adsorption amount of silica fibers is maximum for desized fibers, to 224.3 mg and is minimum for TMCS-treated fiber, to 136 mg. Appropriate fiber surface treatments not only decrease the

void content in inner composites but also cause the void to uniform distribution, so as to lead to the improvement of mechanical properties of silica fiber/phenolics composites on one hand and decrease inhomogeneities of phenolic resin distribution and mechanical properties on the other.

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