

Studies on Surface Energetics of Glass Fabrics in an Unsaturated Polyester Matrix System: Effect of Sizing Treatment on Glass Fabrics

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ABSTRACT: The surfaces of glass fibers were sized by polyvinyl alcohol (PVA), polyester, and epoxy resin types in order to improve the mechanical interfacial properties of fibers in the unsaturated polyester matrix. The surface energetics of the glass fibers sized were investigated in terms of contact angle measurements using the wicking method based on the Washburn equation, with deionized water and diiodomethane as the wetting liquids. In addition, the mechanical behaviors of the composites were studied in the context of the interlaminar shear strength (ILSS), critical stress intensity factor (K_{IC}), and flexural measurements. Different evolutions of the London dispersive and specific (or polar) components of the surface free energy of glass fibers were observed after different sizing treatments. The experimental result of the total surface free energies calculated from the sum of their two components showed the highest value in the epoxy-sized glass fibers. From the measurements of mechanical properties of composites, it was observed that the sizing treatment on fibers could improve the fiber–matrix interfacial adhesion, resulting in improved final mechanical behaviors, a result of the effect of the enhanced total surface free energy of glass fibers in a composite system. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1439–1445, 2001

Key words: fiber–matrix adhesion; sizing treatment; surface free energy; mechanical interfacial and mechanical properties

INTRODUCTION

Glass fiber–reinforced plastics (GFRP) have been widely used as materials for reinforcement and electric insulation in aerospace, automotive, and printed circuit board applications because of their good performance/price ratio, good processability, and resistance to chemicals and harsh environments.^{1,2} Recently, it has been found that the fiber–matrix interfacial adhesion is a very important parameter in controlling the toughness of a

composite material, resulting in improved final mechanical properties. The interphase can also serve as a nucleation site, as a preferential adsorption site, and as a locus of chemical reactions. For these reasons the interphase is considered a major factor affecting various physical and mechanical properties of GFRP.^{3–5} The interfacial adhesion cannot be achieved, however, without intimate contact, that is, unless the fiber surface contacts the resin in an intermolecular equilibrium distance level. In addition, the suitable wetting of the fibers by the liquid polymeric matrix should occur when the nature of the fiber surface along with the liquid polymeric surface has been well considered from the viewpoint of the hydro-

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philic and hydrophobic properties or of the specific (or polar) or London dispersive components of the surface free energy.^{5,6}

During production of glass fibers the fibers must be protected against fiber fracture and fuzz formation by a polymeric coating, referred to as the "size," which can also serve as an agent for changing the degree of adhesion at interfaces between fibers and matrix, producing the resulting final mechanical properties of GFRP.⁷⁻⁹ In the past the role of one essential component of the sizing—the silane coupling agent—received a lot of attention because of the pioneering work of Plueddemann.¹⁰ The chemistry of silane and its interaction with both the glass surface and the matrix have been extensively studied.¹¹⁻¹⁴ Yet little information has been reported of a predictive nature on the fundamental surface thermodynamics that would attest to the relationship between sizing application and mechanical properties of the composites.

In this work the role of interphase formation between the glass fibers and the matrix was investigated using a series of sized glass fibers having different ranges of surface free energies in an unsaturated polyester matrix. The effects of the different sizings on interphase formation were quantified by measuring the surface free energies of the sized glass fibers, the fiber–matrix adhesion, and the resulting mechanical properties of composites.

EXPERIMENTAL

Materials and Sample Preparation

The woven-glass fabric (HD 324-01; 23 × 23 count/inch, 246 g/m²), with a desized surface by heat cleaning, was supplied by Hyun-Dai Fiber Company of Korea. The polyvinyl alcohol (PVA), polyester, and epoxy type resins were used as the

Table I Components of Glass Fiber Sizing Agents Used in This Work

Component	Weight Percent
Film former	5.0
γ-Methacryloxypropyltrimethoxysilane	0.5
Glycerin	0.1
Formic acid	0.05
Water	up to 100

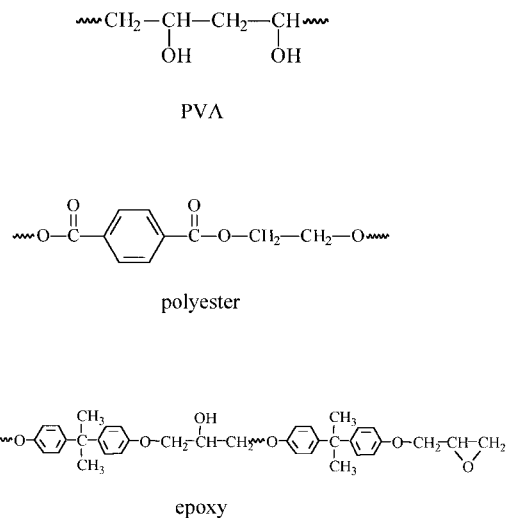


Figure 1 The chemical structures of PVA, polyester, and epoxy sizing agent types.

film formers for the sizing agent. The proportion of components of the sizing agent prepared by mixing are listed in Table I. The PVA, polyester, and epoxy type structures studied are shown in Figure 1.

The glass fabrics were dipped in each sizing agent and then dried at 120°C for 1 h to age the sizing agent. The coated glass fabrics were allowed to stand overnight under room temperature. The amount of sizing composition applied to the glass fabric was about 0.8 wt %.

Unsaturated polyester (R-235; specific gravity: 1.11; viscosity: 2.8 g cm⁻¹ s⁻¹), with a matrix of orthophthalic acid–type resin, was supplied by Seiwon Chemical Company of Korea. Methyl ethyl ketone peroxide (MEKPO) was selected as a hardener for curing. The composites, reinforced with the sized glass fabrics, were prepared in a hot press at 20 atm and 100°C for 1 h using a vacuum bagging method.¹⁵ The fiber volume fraction of bulk specimens was about 52% (±2%) for all composites.

Contact-Angle Measurement

Contact-angle measurements of the sized glass fabrics were performed using the Krüss Processor Tensiometer K12 with fiber apparatus. A scheme of the experimental setup is illustrated in Figure 2. Samples of 5 g each produced by cutting sized woven glass fabrics were packed into an apparatus and then mounted indirectly to the measuring arm of the microbalance. The wetting liquids used for contact-angle measurements during the test

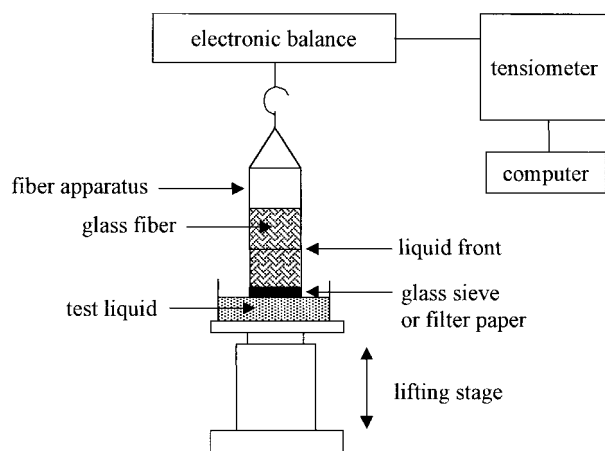


Figure 2 Schematic diagram of capillary rise method.

were *n*-hexane, deionized water, and diiodomethane. The surface free energy (or surface tension) and other characteristics of the wetting liquids are listed in Table II.

Mechanical Interfacial and Mechanical Properties and Fracture Surface Examination

Tests were conducted to measure two types of mechanical interfacial properties of the composites that are sensitive to the degree of adhesion of the fiber–matrix interphase. The interlaminar shear strength (ILSS) was characterized by the short-beam shear test, which was done according to ASTM D2344 and was conducted on 20-ply laminates. The support span-to-depth ratio used was 5:1, with a corresponding specimen length-to-depth ratio of 7:1. The crosshead speed was 2.0 mm/min.

The critical stress-intensity factor (K_{IC}), which is one of the parameters of fracture toughness, can be characterized by the single-edge notched

(SEN) beam fracture toughness test (ASTM E399) in three-point bending flexure. Notches were cut using a diamond wire saw, approximately half the depth of the specimen. A span-to-depth ratio of 4:1 and crosshead speed of 1 mm/min were used.

The flexural properties of composites, which were characterized by three-point bending test (ASTM D790), were performed in 20-ply laminates. Specimens were 25 mm wide and 80 mm long and were tested at a span-to-depth ratio of 16:1. The crosshead speed was 2 mm/min.

The fracture surface of the composites was examined using scanning electron microscopy (SEM) after measurements from the short-beam shear tests and was documented in representative photomicrographs.

RESULTS AND DISCUSSION

Contact-Angle and Surface Free Energy Analyses

In order to investigate the contact angles of the sized glass fibers, wicking-rate measurements¹⁶ were done by enclosing the fiber bundle in a glass tube so that the porosity was fixed for a given strand of fibers. The contact angle, θ , was then determined using Washburn's proposition, which defines the flow of a liquid through a capillary¹⁷:

$$\frac{h^2}{t} = \frac{r \cdot \gamma_L \cdot \cos \theta}{2\eta} \quad (1)$$

where h is the rise height in a capillary of the radius, r ; t is the flow time; γ_L is the surface free energy of a liquid; and η is the viscosity of a liquid, as seen in Table I.

Table III shows contact-angle data of the four glass-fiber types studied. As can be seen, the con-

Table II Characteristics of Wetting Liquids Used in This Work

Wetting Liquids	γ_L^L ^a (mJ m ⁻²)	γ_L^{SP} ^b (mJ m ⁻²)	γ_L^c (mJ m ⁻²)	η^d (mPa s)	ρ^e (g cm ⁻³)
<i>n</i> -hexane	18.4	0	18.4	0.33	0.661
Water	21.8	51	72.8	1	0.998
Diiodomethane	50.42	0.38	50.8	2.76	3.325

^a London dispersive component of surface free energy.

^b Specific or polar component of surface free energy.

^c Surface free energy.

^d Viscosity.

^e Density.

Table III Contact-Angle Determination (in degree) on Glass Fibers Studied

Wetting Liquids	Unsize	PVA-Sized	Polyester-Sized	Epoxy-Sized
Water	85	81	70	73
Diiodomethane	61	60	64	54

tact angle in water is significantly decreased with polyester- and epoxy-sized glass fibers compared to that in the unsize one, while the angle in diiodomethane is nearly constant for all the fibers, except for epoxy-sizing one. As was noted above, that sizing treatment of glass fibers leads to a change in fiber surface nature, such as its hydrophobic–hydrophilic properties. Therefore, it is expected that the sizing treatment will lead to an increase of the hydrophilic properties of the fibers.

In order to obtain more detailed and precise information about the surface energetics of the glass fibers studied, the surface free energy of a solid can be divided by two components, that is, the London dispersive and the specific (or polar) components, an division that is important for evaluating the intermolecular or physical properties.^{5,18–24} In the early 1960s Fowkes²⁵ introduced the concept of the surface free energy of a solid, γ_s , which can be resolved into London dispersive (superscript, L) and specific (or polar, SP) components:

$$\gamma_s = \gamma_s^L + \gamma_s^{SP} \quad (2)$$

where γ_s^L describes the London dispersive attraction of the van der Waals force and γ_s^{SP} ascribes all other nondispersive components of the physical interactions of a solid.

While Owen and Wendt²⁶ and Wu²⁷ extended Fowkes's concept using the geometric mean, as follows:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_L^L \cdot \gamma_s^L)^{1/2} + 2(\gamma_L^{SP} \cdot \gamma_s^{SP})^{1/2} \quad (3)$$

where the subscripts L and S represent the liquid and solid states, respectively.

In a more practical relationship based on two simultaneous liquids of widely different properties on fiber surfaces, γ_s^L and γ_s^{SP} can be solved according to eq. (3).²⁸

The results of surface free energies of the glass fibers studied are shown in Figure 3. As can be seen, the four glass-fiber types provide a range of total surface free energies of about 30–40 mJ m⁻². As can be seen, the sizing treatments effectively lead to an increase of the specific component of the surface free energy of fibers, which is probably due to the active functional groups of the polymeric agents studied. The epoxy sizing of fibers, in particular, shows the highest surface free energy (38.6 mJ m⁻²), which is thought to provide the most favorable wetting conditions.

Interlaminar Shear Strength and Fracture Toughness

It is well known that the mechanical interfacial properties of GFRP depend strongly on the degree of adhesion between the glass fiber and the matrix. The interlaminar shear strength (ILSS) of composites was measured to determine the effect of sizing on adhesion with the matrix. For a rectangular cross section of the composites, the ILSS determined from three-point bending test was calculated as follow²:

$$ILSS = \frac{3F}{4bd} \quad (4)$$

where F is the rupture force, b is the width of the specimen, and d is the thickness of the specimen.

It is known that fracture toughness is a critical property to resist crack propagation loaded from matrix to fiber, and this ought to be considered in

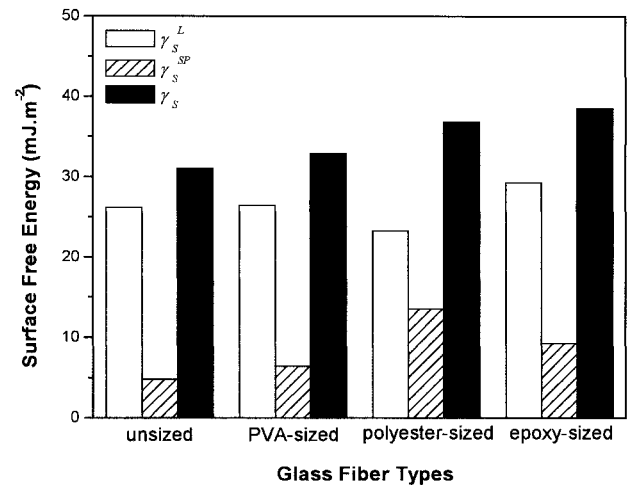


Figure 3 Evolution of surface free energies and their components for the glass fibers studied.

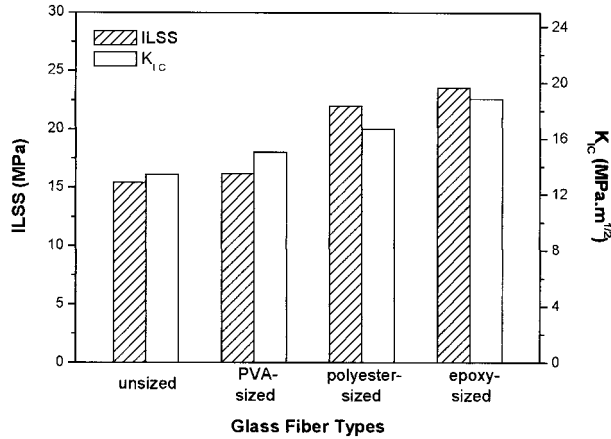


Figure 4 ILSS and K_{IC} of the glass fiber-reinforced composites studied.

evaluating the degree of adhesion at the interface between fibers and matrix. According to previous studies fracture toughness of composites material is greatly affected by the interfacial condition.^{29–32} For a rectangular cross section of composites, the fracture toughness of the composites can be measured by a three-point bending test for the critical stress intensity factor (K_{IC}). For the single-edge notched (SEN) beam fracture toughness test, the value of K_{IC} is calculated as follows³³:

$$K_{IC} = \frac{PL}{bd^{3/2}} \cdot Y \quad (5)$$

where P is the rupture force, L is the span between the supports, Y is the geometry factor described in ASTM E399, and b and d are the specimen width and thickness, respectively.

Figure 4 shows the results of ILSS and K_{IC} of the composites made with and without sizing treatments on the fibers. The experimental result of strong linearity between the surface free energy and both the resulting ILSS and K_{IC} is shown in Figure 5. As mentioned above, the improvement in mechanical interfacial properties, which tends to be higher for fibers with higher surface free energy, is clearly a result of the improvement of the interfaces between the functionalized sizing agents and the matrix in a composite system. The polyester and epoxy sizing agents dissolve into the matrix, allowing the silane-covered glass-fiber surface to interact with the matrix. Interaction between the γ -methacryloxypropyltrimethoxysilane (Table I) of the fiber surface

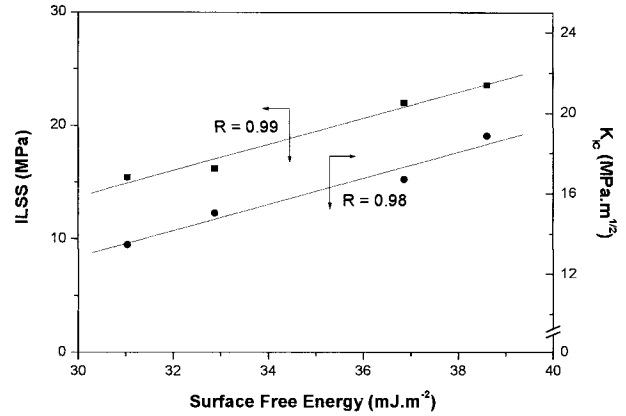


Figure 5 Dependence of the ILSS and K_{IC} on surface free energy of the composites studied.

and matrix is due to its organic functional group which can interact with the double bond of the unsaturated polyester.³⁴ In the case of the unsized glass fiber-reinforced composites, the lowest ILSS is the result of inadequate fiber-matrix interaction. In addition, PVA sizing leads to a weak interlaminar adhesion, producing no significant stress transfer from the matrix to the fibers.

Figure 5 also shows the evolution of K_{IC} in the flexure of the composites with each of the fiber types. As mentioned above, the epoxy-sized fiber composites have high resistance for crack propagation because of a high level of fiber-matrix adhesion.

Flexural Properties

The flexural strength (σ_f) and the elastic modulus in flexure (E_b) of the composites measured using three-point bending tests are calculated as^{9,35}:

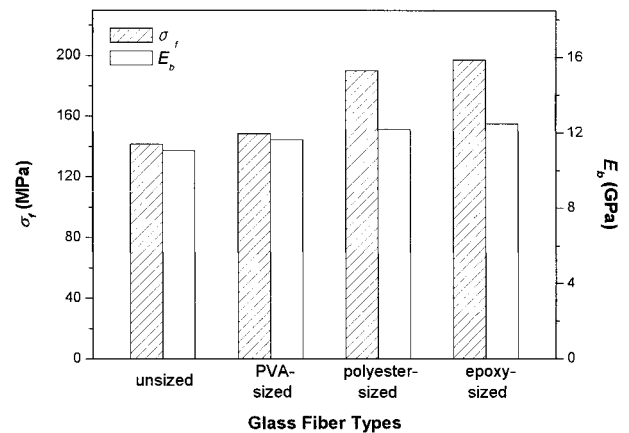


Figure 6 Flexural strength (σ_f) and elastic modulus in flexure (E_b) of the glass fiber-reinforced composites.

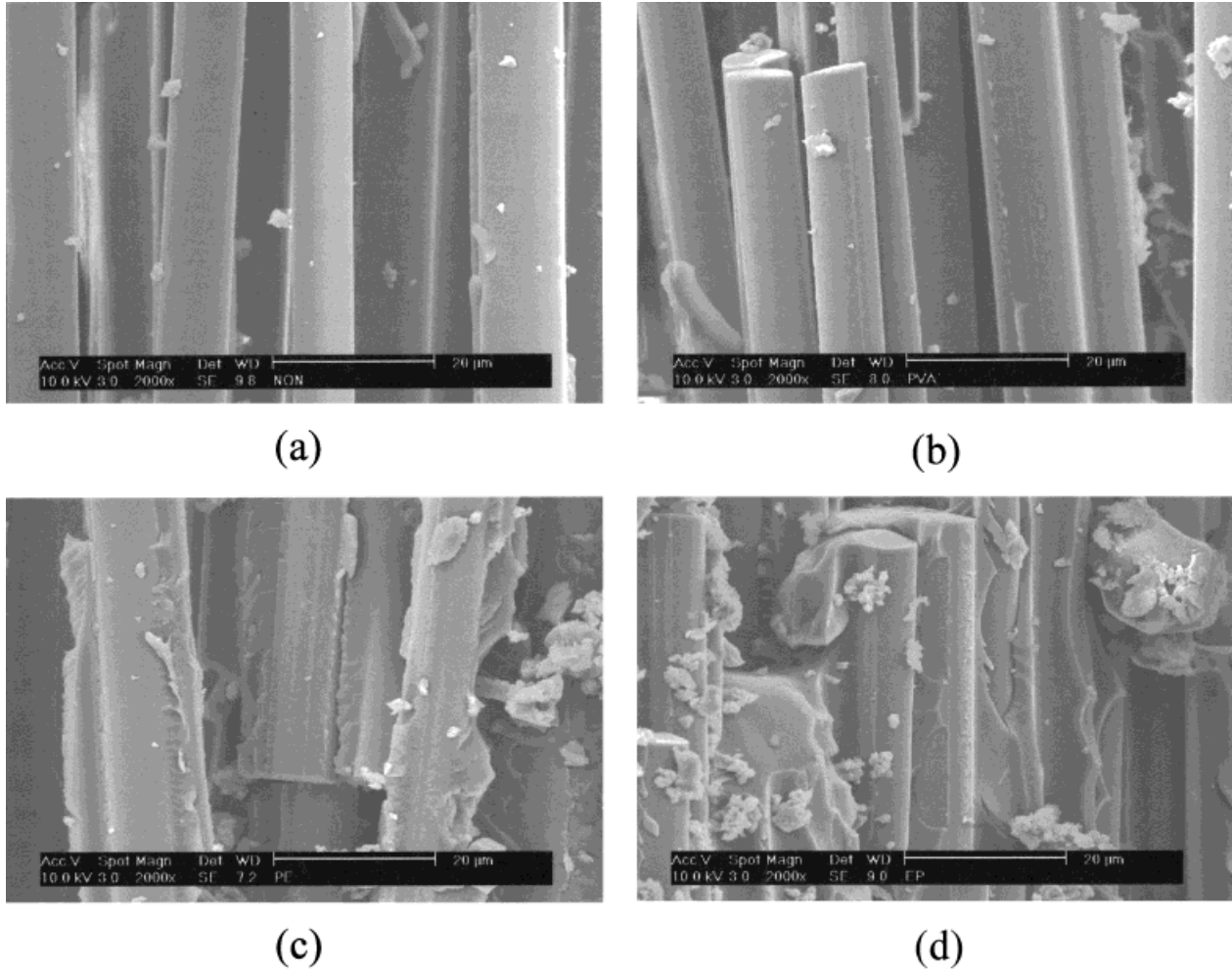


Figure 7 Fracture surfaces of the glass fiber-reinforced composites: (a) unsized, (b) PVA-sized fibers, (c) polyester-sized fibers, and (d) epoxy-sized fibers.

$$\sigma_f = \frac{3PL}{2bd^2} \quad (6)$$

$$E_b = \frac{L^3}{4bd^3} \cdot \frac{\Delta P}{\Delta m} \quad (7)$$

where P is the applied fracture force, L is the distance between the supports, b is the width of the specimen, d is the thickness of the specimen, ΔP is the change in fracture force in the linear portion of the load-deflection curve, and Δm is the change in deflection corresponding to ΔP .

Figure 6 shows the results of flexure behaviors of the composites studied. As experimental results, the flexural strengths of the polyester- and epoxy-sized fibers have similar and higher values than those of the untreated fibers and even of the PVA-

sized fibers, probably because of improvements in the nature of the weak interface, while the elastic moduli in flexure are not significantly sensitive to the series of sizings. This is due to the elastic modulus in flexure being greatly dominated by the fibers.³⁶ Therefore, it was concluded that strong fiber-matrix interactions result in high levels of adhesion at the interfaces between fibers and matrix, which in turn yield high flexural behaviors, especially the flexural strengths of composites.

Fracture Surface

The fracture surfaces of representative specimens from the four groups of composites were examined by SEM. The micrographs of these fracture surfaces are shown in Figure 7. The fracture surfaces show remarkable differences resulting from the

change in fiber–matrix adhesion. The unsized and PVA-sized glass fiber–reinforced composites with low mechanical interfacial properties, such as ILSS and K_{IC} , show almost interfacial failure, while the polyester- and epoxy-sized glass fibers are completely stripped of matrix material. These fracture surfaces reconfirm the evidence of a high degree of fiber–matrix adhesion, causing a more tortuous failure path in a resin matrix.

CONCLUSION

In this work the effect of sizing treatment on glass fibers has been studied in terms of the surface free energy of the fibers and the mechanical interfacial properties of the composites. The results showed that polyester- and epoxy-sized glass fibers could increase the surface free energy calculated by the sum of its London dispersive and specific components, developing an interphase that led to the resulting high mechanical properties of the composites. Thus our sizing treatment on glass fibers shows that the study of surface free energy of a solid surface seems important and is also a simple tool for understanding and predicting the degree of fiber–matrix adhesion and the final mechanical behavior of composites.

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