Universidad Carlos III de Madrid

e-Archivo

Institutional Repository

This is a postprint version of the following published document:

Iglesias, J. G., González-Benito, J., Aznar, A., Bravo, J. & Baselga, J. (2002). Effect of Glass Fiber Surface Treatments on Mechanical Strength of Epoxy Based Composite Materials. *Journal of Colloid and Interface Science*, 250 (1), pp. 251–260.

DOI: 10.1006/jcis.2002.8332

Effect of Glass Fiber Surface Treatments on Mechanical Strength of Epoxy Based Composite Materials

J. G. Iglesias, J. González-Benito, A. J. Aznar, J. Bravo, and J. Baselga[1]

Departamento de Ciencia de Materiales, Universidad Carlos III de Madrid, Madrid, Spain

Sizing glass fibers with silane coupling agents enhances the ad-hesion and the durability of the fiber/polymer matrix interface in composite materials. There are several tests to determine the inter-facial strength between a fiber and resin, but all of them present difficulties in interpreting the results and/or sample preparation. In this study, we observed the influence of different aminosilanes fiber coatings on the resistance of epoxy-based composite materials using a very easy fractographic test. In addition, we tried a new flu-orescence method to get information on a molecular level precisely at the interface. Strength was taken into account from two stand-points: (i) mechanical strength and (ii) the resistance to hydrolysis of the interface in oriented glass-reinforced epoxy-based composi-tes. Three silanes: γ-aminopropyltriethoxysilane, γ-Aminopropyl-methyldiethoxysilane, and γ-Aminopropyldimethylethoxysilane were used to obtain different molecular structures at the interface. It was concluded that: (i) the more accessible amine groups are, the higher the interface rigidity is; (ii) an interpenetrating network mechanism seems to be the most important for adhesion and there-fore to the interfacial strength; and (iii) the higher the degree of crosslinking in the silane coupling layer is, the higher the hydrolytic damage rate is.

Key Words: silane treatment; interface damage; fluorescent labels.

INTRODUCTION

A commonly accepted definitio for composite materials cor-responds to those formed by two or more constituents which are physically delimited from one another. When they are combined there is a synergetic effect between their properties. An exam-ple is glass-fibe -reinforced epoxy composites where embedding high-modulus fibe into the epoxy polymer matrix increases me-chanical properties for high performance materials.

It is well known that properties of composite materials are strongly influence by the type of adhesion between the rein-forcement and the matrix (1–3). If adhesion takes place, the interface must necessarily be controlled. First, because in many cases failure occurs in the interface region due to chemical re-action or plastificatio when impurities (commonly water) pen-etrate the interface (4–7) and, second, because the properties of composites depend on the ability of the interface to transfer stress from the matrix to the reinforcement (8).

Surface treatment of reinforcements was a common method to improve general adhesion properties by increasing electrostatic interactions and/or facilitating chemical bonding between the constituents. Among others, coupling agents have a great effect on the interface structure and properties (1, 9).

They have two different functionalities that can chemically bond with both the reinforcement and the matrix. The most commonly used cou-pling agents are difunctional organosilicon compounds named silanes. They have the general formula Y-Si$(X)_3$, where X rep-resents alkoxy groups or chlorine which, after hydrolyzing to silanol, react with silanol groups present on the surface of glass fiber to form siloxane linkages, and Y represents nonhydrolyz-able organofunctional groups such as amino and methacrylate that react with the matrix functional groups. In the case of epoxy-based composites, amino silanes are typical because of the ad-dition of amine hydrogen to the epoxy ring.

It is quite well known that, because of the chemical and struc-tural differences of this coupling agent interface layer, the me-chanical properties of composite materials change greatly (4, 8, 10, 11). To investigate the effect of different treatments on interfacial reinforcement in glass fiber/epox composites, such single filamen tests as the fibe fragmentation test (4, 12, 13) and the fibe pull-out test (13, 14), are commonly used, among others. However, although they yield conclusive results, these tests tend to hamper the interpretation of results and/or sample preparation. For example, the single fibe tests do not give infor-mation about the influenc of the neighboring glass fiber that can be found in a real composite. To investigate the interfibe effects in a micromechanical test, dual or multi-fibe compos-ites were studied recently, which can be *in situ* real composites (15, 16). Furthermore, to obtain good response in fibe pull-out tests, the values of elongation at failure should be noticeably dif-ferent between the matrix polymer and the fibe and, finall , in single-fibe fragmentation tests, because of the difficultie cited in interpreting results, numerous attempts must be made in or-der to produce quantitative parameters to explain the adhesive properties of glass fiber coatings.

Ikuta *et al.* (17) proposed a parameter which they called "in-terfacial transmissibility" to reveal the transmissibility of tensile force through the silane interface from matrix to glass fibers

Using this parameter Hamada *et al.* (8) found that the crosslink of the silane reduces the interfacial strength, and they proposed that it depresses the permeability of the resin and leads to a lowering of the reactivity between the silane and resin.

From our point of view, most of the research in this field has been focused on macroscopically characterizing composites by mechanical testing, giving to this research a primarily technological slant. Because of this, great efforts need to be made from a basic standpoint to understand better what is actually going on at the interface. Although many techniques such as Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and nuclear magnetic resonance (3) have been used to study composite interfaces on a molecular level, it is very difficult to find a very sensitive nondestructive technique that can give us this kind of information.

Fluorescence probes and labels are widely used in chemistry to study the characteristics of the medium in which they are immersed. Recent studies have focused on the characterization of glass fiber coatings (18, 21). Some fluorescent molecules, such as dansyl derivatives, show appreciable shifting in their fluorescence emission band depending on the polarity and/or rigidity of their surroundings (22, 23). Therefore, if dansyl moiety is attached to the coupling region of glass-reinforced epoxy composites, its fluorescence response could be used as a method to analyze the interface on a molecular level. For fluorophores such as DNS derivatives, which show high dipole moment in the excited state, the interaction forces between the excited molecule and the environment are mainly due to dipole–dipole or dipole–induced-dipole interactions. In low viscosity media, these forces contribute to the stabilization of the excited state via an effective dielectric coupling between the excited molecule and its solvation shell. Hence, the emission energy will be affected by changes in the dielectric constant and the refractive index of the environment. Therefore, the more effective coupling leads to a greater stabilization and this effect is normally observed as a red shift in the emission spectra as polarity of the medium is increased. However, the stabilization of the excited state of the fluorophore depends on the ability of the excited fluorophore/surrounding dipoles system to reorient themselves and relax. The stabilization of the excited state is only possible when the characteristic relaxation time of the reorientation process is shorter than the lifetime of the fluorophore excited state. Thus, the greater the relaxation times the less effectiveness there is in the dielectric coupling and therefore a smaller red shift should be observed. Therefore, a blue shift of the fluorescence emission band is expected, as rigidity of the system increases, since the latter implies less molecular motions and higher relaxation times.

In this paper we study the effect of different silane surface treatments of glass fibers on the mechanical performance of epoxy-based composite materials under both dry and wet conditions. This study was carried out by correlating data from SEM fractographic analysis with mechanical parameters obtained by tensile strength tests. To obtain different molecular structure at the interface, γ-Aminopropyltriethoxysilane (APTES), γ-Aminopropylmethyldiethoxysilane (APDES), and γ-Aminopropyldimethylethoxysilane (APMES) were grafted to E-glass fibers. Finally, a new fluorescence method was tried in order to obtain information exactly at the interface.

MATERIALS AND METHODS

1. Sample Preparation

a. Glass fibe surface pretreatment. (i) Commercial E-glass fibers were obtained from VETROTEX and heat cleaned at 450°C for 1 h to remove any organic substances, such as sizing or impurities, from the surface.

(ii) The fibers were then chemically coated with an aminosilane coupling agent. It was done by immersing 1 g of glass fibers in 50 ml of silane 1% (V/V) aqueous solution for 10 min at room temperature. In order to observe how the rigidity and molecular structure of the interface affect the mechanical properties of composites, surface coatings were made by using different silane coupling agents supplied by Aldrich:

- 3-aminopropyldimethylethoxysilane
- 3-aminopropylmethyldiethoxysilane
- 3-aminopropyltriethoxysilane

(iii) After squeezing the fibers, the adsorbed silane was cured at 110°C for 1 h to accelerate condensation reaction and to remove water.

(iv) It is well known that with these kinds of procedures some unreacted silane monomers or oligomers remain physisorbed on the glass fiber surface (10). Due to this, silanized glass fibers were subjected to a Soxhlet extraction with dry toluene for at least 4 h to remove all physisorbed residues. They were vacuumed for at least 8 h.

In Fig. 1, a possible structure of the three different silane coatings is schematically represented. In the figure, the APMES sample shows monomers directly attached to the glass fiber surface; in the APDES sample we can see mainly linear oligomers; and in the APTES sample, a siloxane crosslinked structure. The chemical reactions of silane coupling agents have been previously
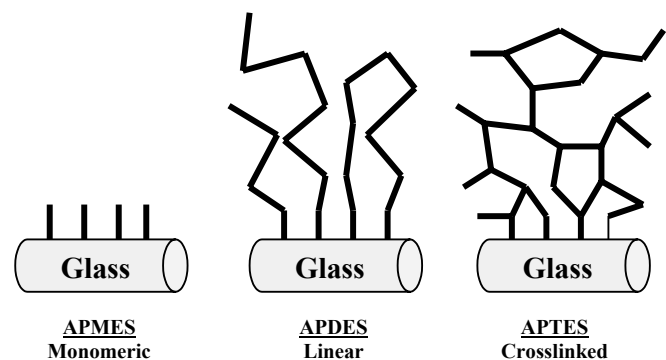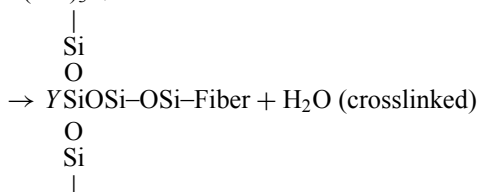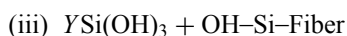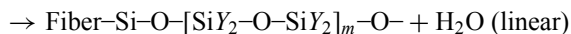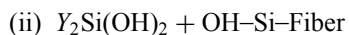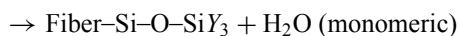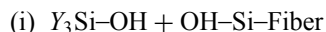

FIG. 1. Scheme of a possible structure for three different silane coatings.

described in literature (1, 3). Considering the previous hydrolysis of the silane, the schematic chemical equations can be written as (see Introduction):

(i) $Y_3Si-OH + OH-Si-Fiber$

   $\rightarrow Fiber-Si-O-SiY_3 + H_2O$ (monomeric)

(ii) $Y_2Si(OH)_2 + OH-Si-Fiber$

   $\rightarrow Fiber-Si-O-[SiY_2-O-SiY_2]_m-O- + H_2O$ (linear)

(iii) $YSi(OH)_3 + OH-Si-Fiber$
$$| $$
$$Si$$
$$O$$
   $\rightarrow YSiOSi-OSi-Fiber + H_2O$ (crosslinked)
$$O$$
$$Si$$
$$|$$

where $Y = -CH_2-CH_2-CH_2-NH_2$. Assuming these structures for the coupling layer one can expect that after adding the polymer matrix to the silanized fibers, three samples with different molecular structure and rigidity will be obtained at the interface.

b. Dansyl labeling. For fluorescence measurements, glass fibers were labeled with 5-dimethylamino-1-naphthalenesulfonylchloride (INC Co.), dansyl moiety, which reacts easily with amines, coming from aminosilanes to yield sulfonamide fluorescent derivative (DNA). The stoichiometry of the reaction was 1 : 1000 (dansyl : NH_2).
The three resulting DNA-labeled silanes were used to silanize glass fibers as it was described above for unlabeled silanes.

c. Epoxy mixture preparation. Two epoxy mixtures were prepared. The first mixture was a commercial system, type code TRIEPOX, supplied by GAIRESA Co. and the second mixture was taken as a model system. The TRIEPOX system was prepared by mixing the first component (high functionality epoxy resin, degassed before use) and second component (cycloaliphatic amines) in a stoichiometric proportion (2.34/1, w/w). The model system was prepared by mixing first component (Diglycidyl ether of Bisphenol A obtained from Aldrich Co., degassed before use) and second component (ethylendiamine) in a stoichiometric proportion.

d. Specimens for mechanical testing. To prepare specimens for mechanical testing, a mould was made using single-sided adhesive Teflon sheet. A bundle of fibers was glued between two adhesive Teflon sheets to ensure that they would be geometrically centered in the composite. The mold was then sealed by pressing with two glass plates. One of the glass plates had three holes, one to inject the epoxy resin mixture and the others to maintain constant pressure.

For curing, the TRIEPOX systems remained at room temperature for 24 h and subsequently they were postcured at 60°C for 24 h. The model epoxy system was cured at 90°C for 24 h and postcured at 115°C for 4 h. These curing procedures were selected to ensure an epoxy group conversion of at least 98%. When the epoxy system was cured, an accurate cutting machine was used to prepare specimens with controlled size (50 × 15 × 0.5 mm). The fiber volume fraction was 0.3%.

2. Analysis Methods

At least five specimens for each sample type were subjected to a simple tensile strength test at a test speed of 2 mm/min with the aid of a universal testing machine (Microtest, Spain).
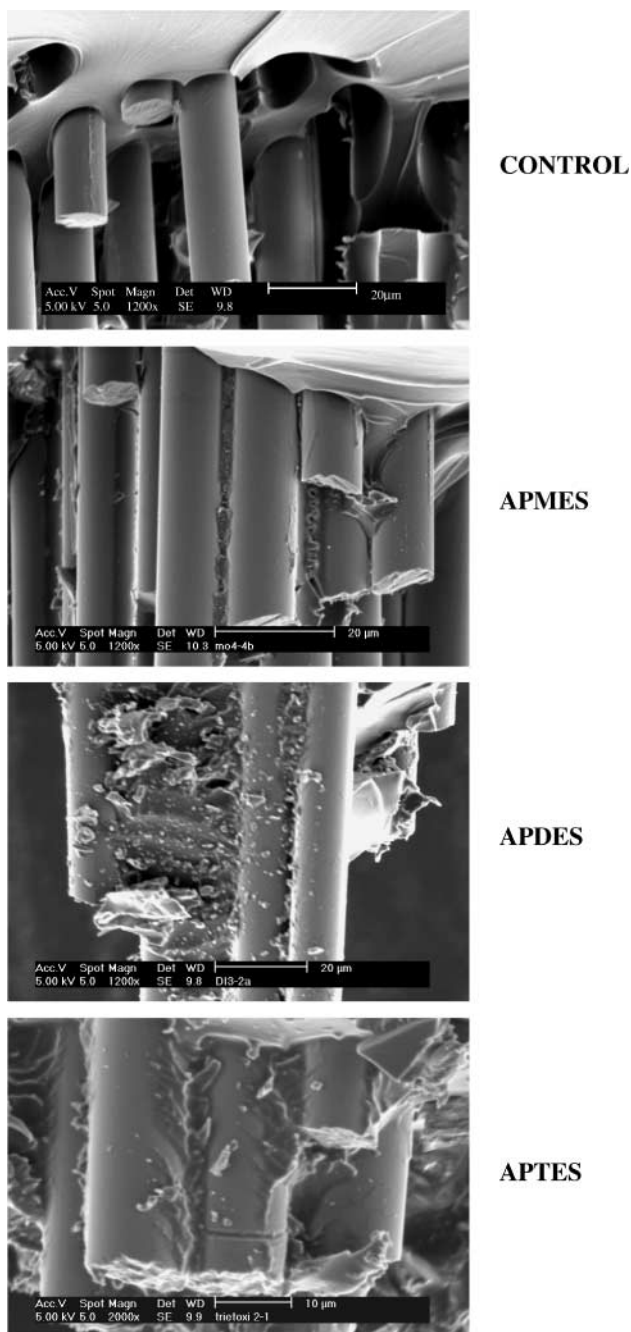

FIG. 2. Representative SEM images of the breakage region for different specimens that were tensile tested before water absorption.
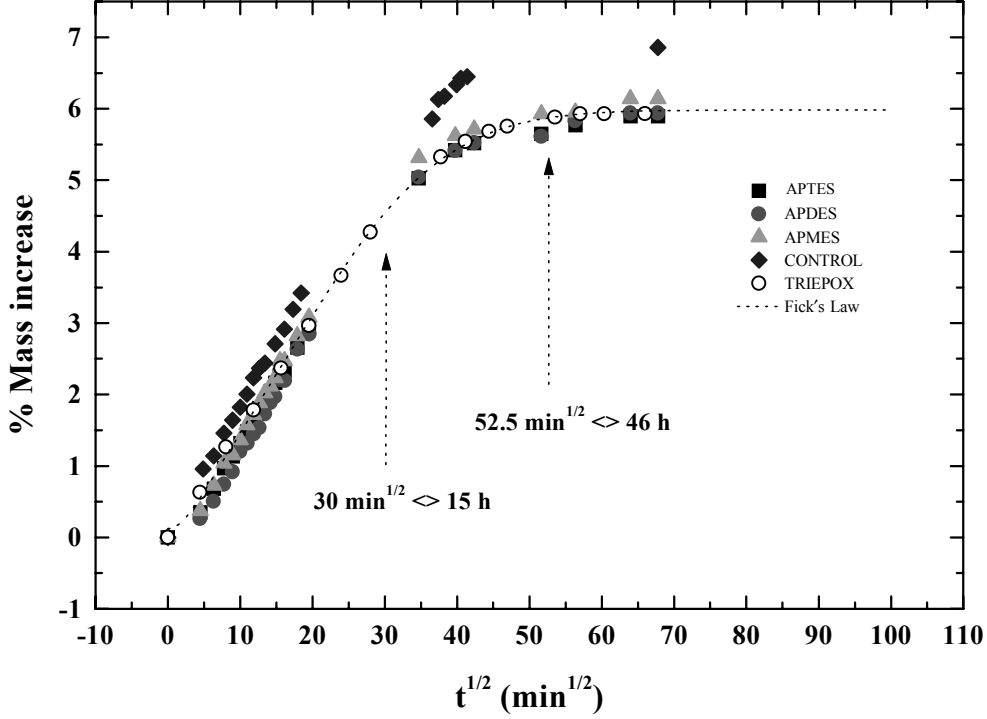
3

FIG. 3. Water absorption for four composite materials and TRIEPOX epoxy polymer as a function of the square root of time.

To perform the fractographic analysis, a Philips XL30 scanning electron microscope (SEM) was used. Qualitative analysis was performed by simple observation of images, and quantitative analysis was done by measuring glass fiber lengths in the fracture region after tensile strength testing. It is reasonable to think that this length must be related to the interfacial strength, in other words, with the facility of a glass fiber surface and a polymer matrix to slide against each other. More than 100 lengths per specimen were measured, and, therefore, more than 500 lengths for each sample. The number average debonded fiber length, $\langle L_N \rangle$, was calculated according to

$$\langle L_N \rangle = \frac{\sum N_i L_i}{\sum N_i},$$

where N_i is the number of filaments with length L_i.

One specimen of each sample that had been specifically prepared for water absorption was immersed in double-distilled water at a temperature of $50°C$ controlled by means of a thermostatic bath, and moisture content determination was monitored gravimetrically. The percentage mass increase was calculated as follows:

$$M = \frac{m - m_0}{m_0} \times 100, \tag{1}$$

where m and m_0 are the mass of the specimen after immersion time, t, and $t = 0$ respectively.

Fluorescence was recorded on an Edinburgh Instruments fluorimeter using an optical fiber cable both to excite and collect fluorescence of samples "*in situ.*" The excitation wavelength was set at 360 nm and the spectra were recorded from 375 to 700 nm using excitation and emission slits of 2.7 nm.

RESULTS AND DISCUSSION

1. Mechanical Properties: Tensile Strength Test

Table 1 shows Young's modulus, E, and maximum tensile strength for dry glass fiber/TRIEPOX composites. The CONTROL sample was prepared using simply calcinated fibers, without coating, and TRIEPOX is the epoxide system without reinforcement.

a. Young's modulus. It can be observed that CONTROL and APTES composites have the same E values, while APDES and

TABLE 1
Young's Modulus, E, and Maximum Tensile Strength, σ, for Dry Glass Fiber/TRIEPOX Composites

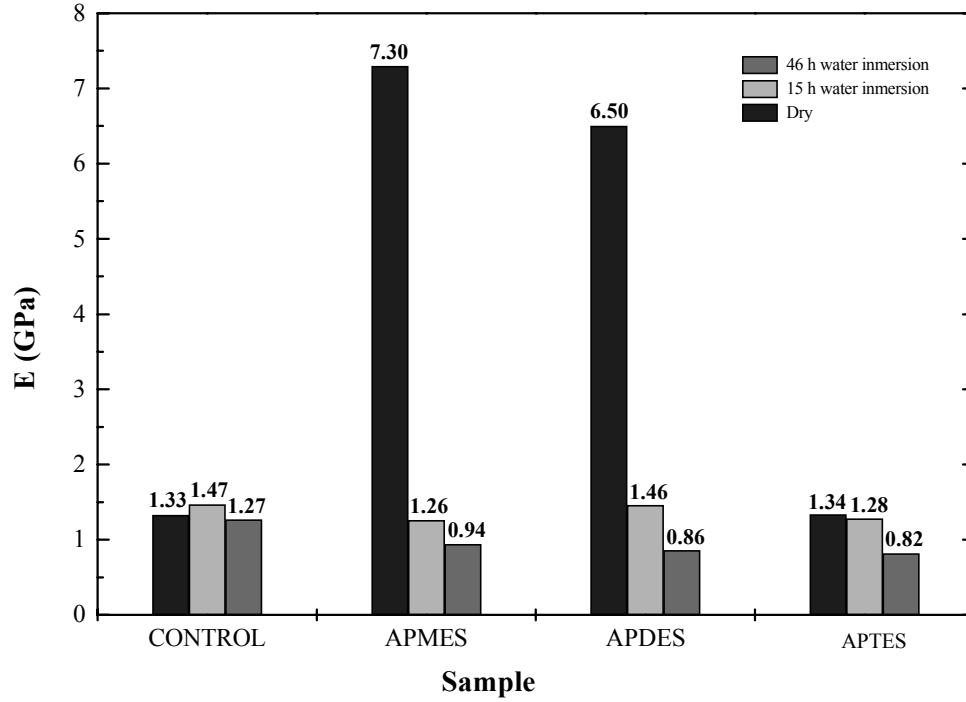| Sample	E (GPa)	σ (MPa)
CONTROL	1.33 ± 0.08	57.4 ± 5.20
APMES	7.30 ± 2.50	53.8 ± 1.60
APDES	6.50 ± 0.80	60.2 ± 2.60
APTES	1.34 ± 0.07	54.6 ± 3.00
TRIEPOX	1.25 ± 0.10	50.5 ± 5.00

4

FIG. 4. Bar graph of the Young's modulus values as a function of samples and water immersion time.

APMES composites have a Young's modulus about 5 or 6 times higher. Since the volume fraction of the reinforcement and the polymer matrix were the same in all of the composites, the rigidity of the materials must ref ect the rigidity at the interface.

Therefore, the rigidity at the interface could be sequenced as follows: APMES ≥ APDES > APTES ≈ CONTROL. These results can be explained assuming different accessibility of epoxy groups of the polymer to the amine functionalities of the glass
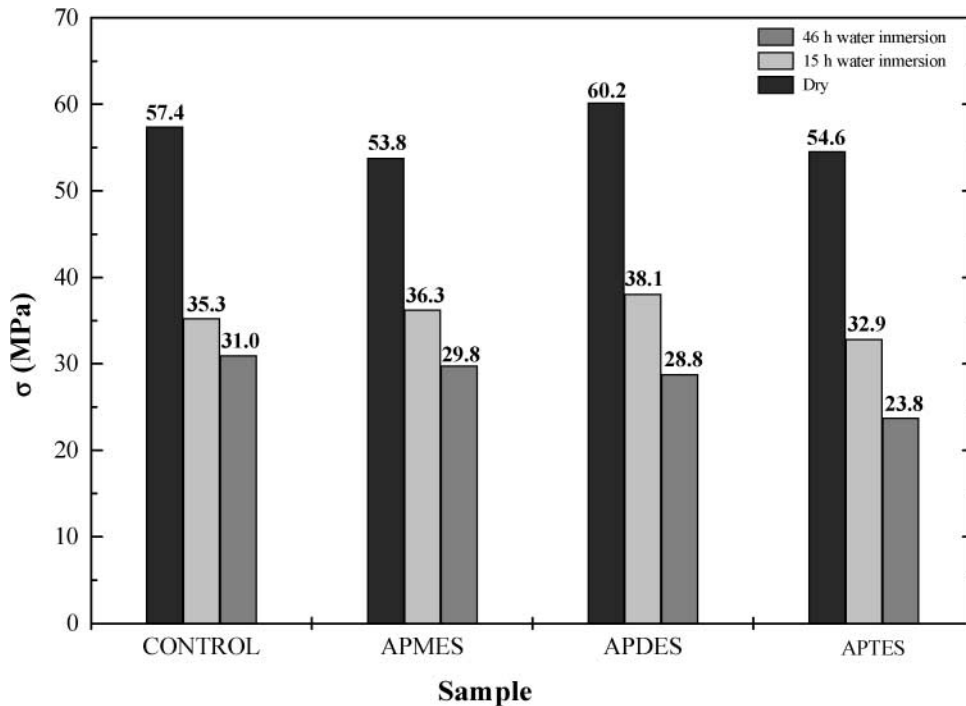

FIG. 5. Bar graph showing tensile strength values as a function of sample and water immersion time.

fiber coating. This means that the more accessible the amine groups are, the higher the crossliking density is, and therefore the greater rigidity is.

b. Tensile strength. Although there is almost no difference between tensile strength values when the errors are taken into account (Table 1), the following tendency can be seen: APDES ≥ CONTROL > APTES = APMES.

When an ideal join between the reinforcement and the matrix takes place, the absence of interface sliding is assumed, and the interfacial transmissibility has to be 100%. Therefore, the tensile strength must be the highest. From this argument one could say that the tendency for interfacial transmissibility should be: APDES ≥ CONTROL > APTES = APMES.

In order to explain these results, we could take into account different adhesion mechanisms in each system:

1. *Electrostatic adhesion for CONTROL sample.* There must be strong interaction between highly polar silanol groups of the glass surface (≡Si−OH) and hydroxyl groups of the resin (=CH−OH). In addition, due to a very high surface free energy of the fibers (24), 112 mN/m, their wettability by the polymer and, therefore, the surface contact between them, must be quite significant. When glass fibers are silanized, the surface free energy greatly decreases (24), by about 30%, and electrostatic adhesion must be lower. Therefore, if there is no other contribution to compensate this loss of adhesion, the interfacial strength will not be improved.

2. *Chemical adhesion for APMES sample.* This contribution comes from the addition reaction of hydrogen from silane amine groups to the epoxy ring of the matrix system. For this composite, this contribution does not seem to be very important; probably due to the low concentration of amino groups.

3. *Chemical and interpenetrating network adhesion mechanism for APDES sample.* As epoxy polymer chains can easily diffuse through the silane coupling layer formed by linear oligomers, many amine groups are accessible to react with epoxy groups.

4. *Chemical and chain interdiffusion adhesion mechanism for APTES sample.* In this case, chemical bonds are restricted to the outer region of the coupling layer because APTES can yield a highly crosslinked structure. This argument would explain similar tensile strength values for APMES and APTES samples.

In conclusion, for the system under study, an interpenetrating network adhesion mechanism seems to be the most important contribution to the adhesion and, therefore, to interfacial strength.

2. Fractographic Analysis

Figure 2 shows representative images of the breakage region for different specimens tensile testing. All of them have the same overall characteristics: cylinders, which are debonded glass fibers from the epoxy resin. Nevertheless, it is possible to observe clear differences between samples under study. For example, after failure some epoxy polymer remains all around

the fibers as for APTES as for APDES samples, with even more remaining in the latter. These observations suggest a cohesive failure in the matrix. On the other hand, the glass fibers on the CONTROL and APMES samples show very clean surfaces, although for the APMES samples a small amount of polymer can be seen between fibers. These observations suggest an adhesive failure in the interface.

Although the CONTROL sample shows adhesive failure (Fig. 2), its relatively high tensile strength (Table 1) can be
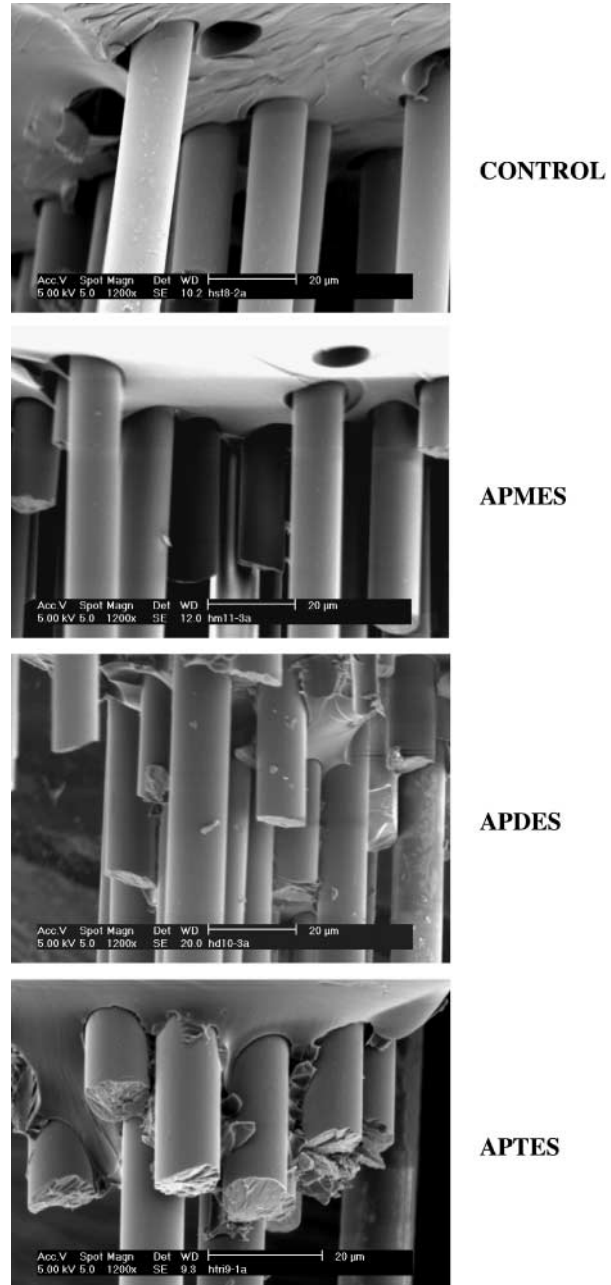

FIG. 6. Representative SEM images of the breakage region for different specimens tensile tested at equilibrium water content.

explained assuming high electrostatic interactions along the f ber debonding process, while when chemical breakage takes place there is a more brittle fracture. In fact, the CONTROL sample showed the largest elongation.

3. Effect of Different Glass Fiber Surface Treatments in the Hydrolytic Degradation of Glass Fiber/Epoxy Composites

The moisture absorption process in polymer composites can often be described by Fick's law of diffusion, which can be expressed as (6, 25)

$$\frac{M - M_0}{M_{eq} - M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)} \exp\left[\frac{-D(2n + 1)^2 \pi^2 t}{h^2}\right],$$

[2]

where M_0 is the initial water content and h is the sample thickness. The coeff cient of diffusion, D, is given by (6, 26)

$$D = \pi \left(\frac{h}{4M_{eq}}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2,$$

[3]

where $(M_2 - M_1)/(\sqrt{t_2} - \sqrt{t_1})$ is the slope of the initial part of the water uptake curve.

The percentage mass increase for four composite materials and TRIEPOX epoxy polymer is shown as a function of the square root of time in Fig. 3. All of the samples nicely followed

Sample	M_{eq} (%)	$D \times 10^8$ (cm^2 s^{-1})
CONTROL	6.85	0.66
APMES	6.09	0.71
APDES	5.92	0.67
APTES	5.87	0.70
TRIEPOX	5.98	0.67

Fick's law of diffusion. Values of the diffusion coeff cient, D, and equilibrium water content, M_{eq}, are given in Table 2. Nearly the same values of D were obtained in all cases. This may be due to the very small volume fraction of f bers (0.3%). However, although the equilibrium water content indicates that the APMES, APDES, APTES, and TRIEPOX samples absorb nearly the same amount of water, the CONTROL sample has about 0.9% higher water content. In this case, water can be strongly adsorbed on the intensely hydrophilic surface of nonsilanized glass f bers.

In order to study the effect of moisture on mechanical properties, two water immersion times, 15 and 46 h, were selected. Figure 3 shows that, in the f rst immersion time, the absorption of water is diffusion controlled process, while the second immersion period ref ects equilibrium water content.
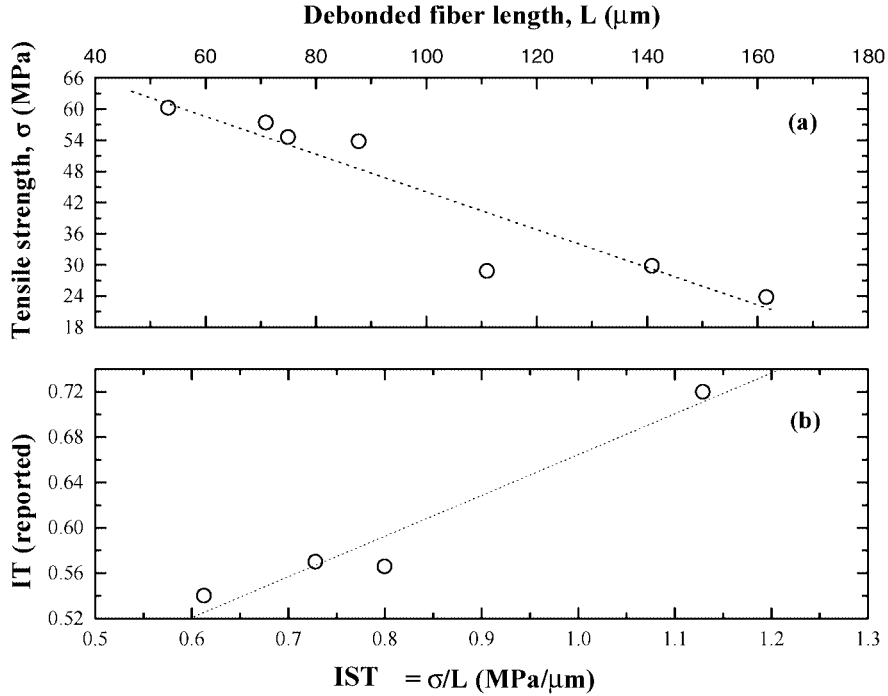

FIG. 7. (a) Tensile strength as a function of the number average debonded glass length (data obtained from the different reinforced specimens tested) and (b) interfacial transmissibility def ned by Ikuta *et al.* (15), IT, vs tensile strength per length unit of debonded f ber, IST.

7

The bar graph in Fig. 4 shows the Young's modulus values as a function of the different samples. All composites with silanized glass fibers seem to have lower rigidity when equilibrium water content is reached. This result suggests plastification of the epoxy matrix at the interface due to hydrolyzed silane residues and water molecules.

The bar graph in Fig. 5 shows tensile strength values as a function of the samples. It is observed that, after 15 h of immersion, sufficient water can diffuse at the interface to completely change sample properties. However, due to the low volume fraction of fibers, tensile strength does not seem to be sensitive enough to clearly appreciate the influence of different glass fiber treatments. On the other hand, if one compares composites with the silanized glass fibers in Fig. 5, the hydrolytic damage rate seems to follow this order: APMES < APDES < APTES. This result is in accordance with other results regarding hydrolysis rates of the same silane-coupling coatings (27), in which it was concluded that the hydrolysis rate of the glass–silane siloxane linkages, $Si_{(glass)}-O-Si_{(silane)}$, is greater than that of silane–silane linkages, $Si_{(silane)}-O-Si_{(silane)}$.
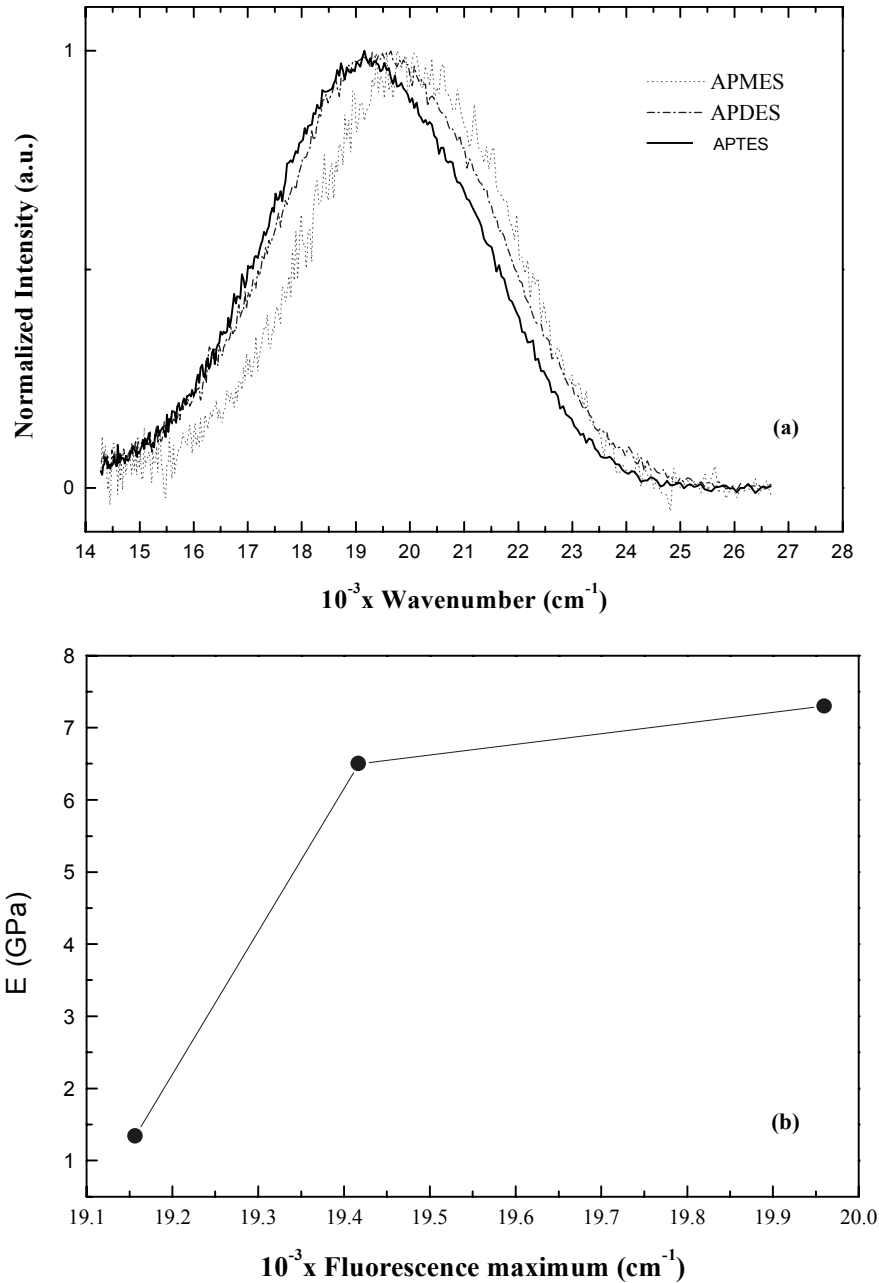

FIG. 8. (a) Fluorescent spectra of dansyl group labeled to three different glass surface coatings (APMES, APDES, and APTES) in epoxy-based composites. (b) Young's modulus, E, vs fluorescent emission maxima, ν.

SEM images (Fig. 6) show that after 46 h of exposure to water (equilibrium), all of the samples have a similar aspect. They show f bers having a very smooth surface without adhered polymer. It can therefore be concluded that all of the samples have adhesive failure at the interface when equilibrium water content is reached.

4. Quantitative Fractographic Analysis

Figure 7(a) shows tensile strength as a function of the mean debonded glass length. A linear correlation can be observed. This correlation suggests that both f ber length at the breakage region and interfacial strength are proportional, as the single-f ber tests showed (28). Therefore, one might conclude that interaction between longitudinal f bers in a composite is not a critical factor for the interfacial strength. In fact, it could be def ned as a new parameter called "interfacial stress transmissibility," IST, as the tensile strength per length unit of debonded f ber, since this parameter shows the ratio between tensile strength of the composite and the ability to slide f bers and polymer matrix against each other.

Actually, this parameter is not the interfacial transmissibility that was def ned by Ikuta *et al.* (17) using a single f lament coupon test, but it gives us similar information. In fact, if the IST values are represented versus the IT values that they obtained for the same system (8), Fig. 7b, a nearly linear correlation is followed.

5. Fluorescence

Finally, we studied the f uorescent response of dansyl moiety directly attached to the coupling region. It is known that f uorescence from dansyl group is very sensitive to its environment, for example, polarity and rigidity. Therefore, we thought that observing f uorescence response would be a good *in situ* analytical method to f nd the rigidity of the interface on a molecular scale. Figure 8a shows f uorescent spectra of the dansyl group labeled to three different glass surface coatings (APMES, APDES, and APTES) on epoxy-based composites. It can be seen that there is a clear shift depending on the sample. It is known that the dansyl f uorescence band undergoes a blue shift when rigidity increases (23, 29). Therefore, we can conclude that rigidity at the interface increases in the following order: APTES < APDES < APMES.

In fact, if the Young's modulus (gives an idea of material rigidity) is represented versus the f uorescent emission maxima, Fig. 8b, an ascending correlation is obtained which is in accordance with the discussion above.

SUMMARY

The inf uence of different aminosilanes f ber coatings on the strength of epoxy-based composite materials has been studied using a very easy fractographic test. In addition, we tried a new f uorescence method to get information on a molecular level precisely at the interface. Three silanes: γ-aminopropyl-triethoxysilane, γ-Aminopropylmethyldiethoxysilane, and γ-Aminopropyldimethylethoxysilane were used to obtain different molecular structure at the interface. The main conclusions that can be extracted from this work are summarized as follows:

• The mechanical properties of glass f ber reinforced epoxide composite materials are strongly dependent on the molecular structure of the coupling region. Crosslinking density and, therefore, rigidity, increase as the accessibility of the functional groups of the coupling layer increases.

• The interpenetrating network adhesion mechanism seems to be the most important contribution to the adhesion and, therefore, to interfacial strength.

• The hydrolytic damage rate depends on the surface reinforcement treatment. This damage rate increased as the $Si_{(silane)}-O-Si_{(silane)}$ siloxane bonds increased.

• The f ber length at the breakage region in glass f ber/epoxy matrix composites, and interfacial strength, are nearly proportional.

• By using f uorescent labels, rigidity could be easily monitored *in situ* at the interface.

REFERENCES

1. Plueddemann, E. P., "Silane Coupling Agents." Plenum Press, New York, 1982.
2. Ishida, H., *Polym. Comp.* **5,** 101 (1984).
3. Suzuki, N., and Ishida, H., *Macromol. Symp.* **108,** 19 (1996).
4. Dibenedetto, A. T., and Lex, P. J., *Polym. Eng. Sci.* **29,** 543 (1989).
5. Walker, P., *J. Adhesion Sci. Technol.* **4,** 279 (1991).
6. Adams, R. D., and Singh, M. M., *Compos. Sci. Technol.* **56,** 977 (1996).
7. Viña, J., García, E. A., Argüelles, A., and Viña, I., *J. Mater. Sci. Lett.* **19,** 579 (2000).
8. Hamada, H., Ikuta, N., Nishida, N., and Maekawa, Z., *Composites* **25,** 512 (1994).
9. Mittal, K. L., "Silanes and Other Coupling Agents." Utrech, New York, 1992.
10. Ishida, H., "Controlled Interphases in Composites Materials." Elsevier, New York , 1990.
11. Wang, D., and Jones, F. R., *Sur. Inter. Anal.* **20,** 457 (1993).
12. Schutte, C. L., Mcdonough, W., Shioya, M., Mcauliffe, M., and Greenwood, M., *Composites* **25,** 617 (1994).
13. Jang-Kyo Kim and Yin-Wing Mai, *in* "Engineered Interfaces in Fiber Reinforced Composites," Chap. 5. Elsevier, New York, 1998.
14. Park, J. M., and Subramanian, R. V., *J. Adhesion Sci. Technol.* **5,** 459 (1991).
15. Park, J. M., Shin, W., and Yoon, D., *Comp. Sci. Tech.* **59,** 355 (1999).
16. Park, J. M., Kim, J., Goda, K., *Comp. Sci. Tech.* **60,** 439 (2000).
17. Ikuta, N., Maekawa, Z., Hamada, H., Ichihashi, H., Nishio, E., and Abe, I., *in* "Controlled Interfaphases in Composite Materials," p. 757. Elsevier, Amsterdam, 1990.
18. González-Benito, J., Cabanelas, J. C., Aznar, A. J., Bravo, J., Vigil, M. R., and Baselga, J., *J. Appl. Polym. Sci.* **62,** 375 (1996).

19. González-Benito, J., Cabanelas, J. C., Aznar, A., Vigil, M. R., Bravo, J., Serrano, B., and Baselga, J., *J. Luminiscence* **72–74,** 451 (1997).
20. González-Benito, J., Cabanelas, J. C., Vigil, M. R., Aznar, A. J., Bravo, J., and Baselga, J., *J. Fluorescence* **9,** 51 (1999).
21. González-Benito, J., Aznar, A. J., Lima, J., Baiao, F., Maçanita, A. L., and Baselga, J., *J. Fluorescence* **10,** 141 (2000).
22. Li, Y., Chan, L., Tyer, L., Moody, R. T., Himel, C. M., and Hercules, D. M., *J. Am. Chem. Soc.* **97,** 3118 (1975).
23. Mikeš, F., González-Benito, J., and Baselga, J., *in* "Book of Abstracts of the XVIII IUPAC Symposium on Photochemistry," Dresden, July 2000, p. 428.
24. González-Benito, J., Baselga, J., and Aznar, A. J., *J. Mater. Process. Technol.* **92–93,** 129 (1999).
25. Jiménez, B. M., González Benito, J., Aznar, A. J., and Baselga, J., *Bol. Soc. Esp. Cerám. Vidrio* **39,** 425 (2000).
26. Crank, J., "The Mathematics of Diffusion." Clarendon Press, Oxford, 1975.
27. Springer, G. S., *in* "Environmental Effects on Composites Materials" (G. S. Springer, Ed.), Vol. 3. Technomic, Lancaster, 1988.
28. Jang-Kyo Kim and Yiu-Wing Mai, "Engineered Interfaces in Fiber Reinforced Composites." Elsevier, New York, 1998.
29. González-Benito, J., Aznar, A. J., Maçanita, A. L., and Baselga, J., *Bol. Soc. Esp. Cerám. Vidrio* **39,** 396 (2000).