Woven Glass Fabric/Polyester Composites: Effect of Interface Tailoring on Water Absorption

S. Pavlidou, K. Krassa, C. D. Papaspyrides

Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou, Athens 157 80, Greece

ABSTRACT: An experimental investigation was carried out to study the effect of different surface treatments on the moisture absorption behavior of glass fabric/polyester composites. The materials under study included composites containing clean glass fabrics, fabrics treated with a silane coupling agent, and fabrics coated with a poly(dimethylsiloxane) elastomer. Weight gain data versus time of immersion were collected at three immersion temperatures and water uptake at equilibrium as well as apparent diffusion coefficients were calculated. The interlaminar shear strength was also measured at the initial dry state and at different stages of the absorption process to estimate the interfacial contribution to sorption behavior. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 843–851, 2005

Key words: glass fibers; polyester-based composites; poly-(dimethylsiloxane); water absorption; interlaminar shear strength

INTRODUCTION

Hygrothermal aging research on composites has increased over the last few decades, because these materials are being increasingly utilized for structural applications that almost invariably entail contacts with liquids or vapors and where their long-term properties are of primary importance.[1–4] Generally, polymer-based materials are not water soluble but, unlike metals or ceramics, are capable of absorbing varying amounts of water from their surroundings, depending on their chemical nature and formulation, as well as on the humidity and temperature of the environment to which they are exposed.[5–7] Such water absorption affects both the short-term and long-term properties of the material, especially at high temperatures.[2,7] Therefore, understanding the molecular mechanisms of moisture diffusion and moisture-induced damage is very important to improving the long-term durability of advanced composites.[8]

Moisture penetration into composite materials is governed by three mechanisms. The first involves direct diffusion of water molecules into the matrix, and in some cases into the fibers. The second is capillary flow of water molecules along the fiber/matrix interface followed by diffusion from the interface into the bulk resin. It is activated when debonding between the fibers and the matrix occurs, often as a result of water attack at the interface. The third mechanism is the diffusion through microcracks, pores, and so forth in the material.[9]

Fortunately, it has been pointed out that, although moisture absorption is governed by three different mechanisms, the overall behavior can usually be treated as Fickian (i.e., diffusion coefficients can be measured experimentally). However, several hygrothermal aging studies involving unsaturated polyester resins revealed that the existence of the two additional absorption mechanisms (i.e., capillarity and transport by microcracks) resulted in non-Fickian behavior, whereby a stable equilibrium moisture content was not attained. At high immersion temperatures, hydrolysis of the ester groups resulted in the formation of microvoids, which were filled with water. According to Mohd Ishak et al., positive deviations from Fick's law may be attributed to processes such as microcrack formation or leaching of matrix constituents.[10]

In our studies, water absorption experiments were conducted on woven glass fabric/polyester composites to investigate the effect of the interface on the sorption behavior. Because the rapid diffusion along the fiber–matrix interface represents a main transport mechanism for conveying water to the interior of composites, it becomes obvious that the interphase plays a key role in determining moisture absorption behavior and greatly affects the response of the composite in humid environments.[2,11] Fabrics with alternative surface treatments were considered. These included material treated with a commercial silane coupling agent, a heat-cleaned material, and a material coated with a

Correspondence to: C. D. Papaspyrides (kp@softlab.ece.ntua.gr).

poly(dimethylsiloxane) (PDMS) elastomer or a poly-amide layer. The former is known to chemically bond to the polyester matrix, thus hindering further water absorption, whereas the others lead to the formation of composites with weak interfacial adhesion.[12] A previous study[13] found that a PDMS coating greatly enhances the impact strength when deposited on clean glass fabrics. The same behavior was also observed when polyamide coatings were alternatively applied.[14] Moreover, the effect on water absorption motivated significant interest, because silicones are widely used in water-repellent applications and polyamides comprise typical hydrophilic materials. In this article, the case of PDMS-coated fabrics is presented versus clean and commercially coated ones.

In order to determine the interfacial contribution to sorption behavior, the interlaminar shear strength (ILSS) was chosen here as the most appropriate mechanical property to characterize interfacial degradation. Specimens were immersed in water at the relatively low levels of 25, 35, and 45°C, because absorption and degradation mechanisms at higher temperures would not be the same as those under the actual service conditions.[15]

EXPERIMENTAL

Materials

Plain-woven fabric E-glass cloth (HK WR 500-A, C. Chronis SA) was used with 1/1 warp/weft strands. Each strand consisted of 22 μm diameter filaments, and the linear density of the glass was 1150 tex. The matrix material was an unsaturated polyester resin (Norpol 410-900, C. Chronis SA), which was cured with a suitable amount of methyl ethyl ketone peroxide. PDMS (Silopren C-70, Bayer AG) was used as a coating material. It was crosslinked by the addition of a crosslinking agent (blend of alkoxisilanes and tin catalysts, 1% v/w), forming an elastomer with a 3-dimensional network structure.

Alternative fiber surface treatments

Fibers with three alternative surface treatments were used in this study. These included as-received fibers (i.e., coated with a silane-based sizing at the time of manufacture), desized fibers, and fibers coated with PDMS after removal of the commercial sizing.

Desizing involved pyrolyzing the size by heating the fabrics at 600°C for 2 h. This "heat-cleaning" treatment is sufficient to remove presizing and organic impurities from the glass fiber surface, according to Tillie et al. and Larena et al.[16,17]

PDMS deposition was performed by the dip-coating technique, using toluene as a solvent. The desized fabric was fixed on a frame and was immersed into the

elastomeric solution (0.5% w/v) at room temperature. It was then dried in an oven (120°C, 10 min) to effect solvent evaporation. The amount of PDMS deposited on the fabrics was gravimetrically found to be 0.29 phr (parts per 100 parts of clean fibers).

Specimen preparation

Woven E-glass fabric/polyester composites were fabricated by resin transfer molding. After placing six cloth pieces in the mold and degasing the resin to avoid air entrapment in the composite, the mold (32-cm diameter, 3-mm thickness) was closed with two flat metal plates. All injections were carried out under a pressure of 2 bar. To prepare neat polyester specimens, the resin was simply cast in a 3-mm thickness mold. All materials were cured for 24 h at room temperature and postcured at 60°C for 4 h and 80°C for 4 h before specimens were cut. Because ILSS measurements were to be conducted immediately after the absorption tests, specimens dimensions were those dictated by ASTM D 2344, the standard method for short beam shear tests. The weight fraction of the fibers in the composites, as determined by the matrix burn-off technique (600°C, 3 h), was approximately 55%.

Moisture absorption tests

Prior to absorption experiments, the specimens were dried in an oven at 35°C until constant weight was reached and then stored in a desiccator. Dry specimens were weighed with an analytical balance and then immersed in a water bath, which was fixed at three temperatures: 25, 35, and 45°C. To monitor weight changes, the specimens were removed from the liquid environment, wiped gently with a tissue, immediately weighed, and then immersed again in the water. At least five specimens per condition were tested.

Short beam shear test

The ILSS was determined for the initial dry state using a tensile testing machine (model 4466) with a crosshead speed of 1.3 mm/min, as recommended by ASTM D 2344. Short beam shear tests were also conducted at different stages of the absorption process, both on wet specimens and on specimens that were removed from the water bath and dried to constant weight at 35°C, in order to examine to what extent water absorption causes irreversible changes. At least five specimens of each composite were tested.

RESULTS AND DISCUSSION

ILSS

Figure 1 presents the ILSS values as determined at intermediate and equilibrium stages of the absorption

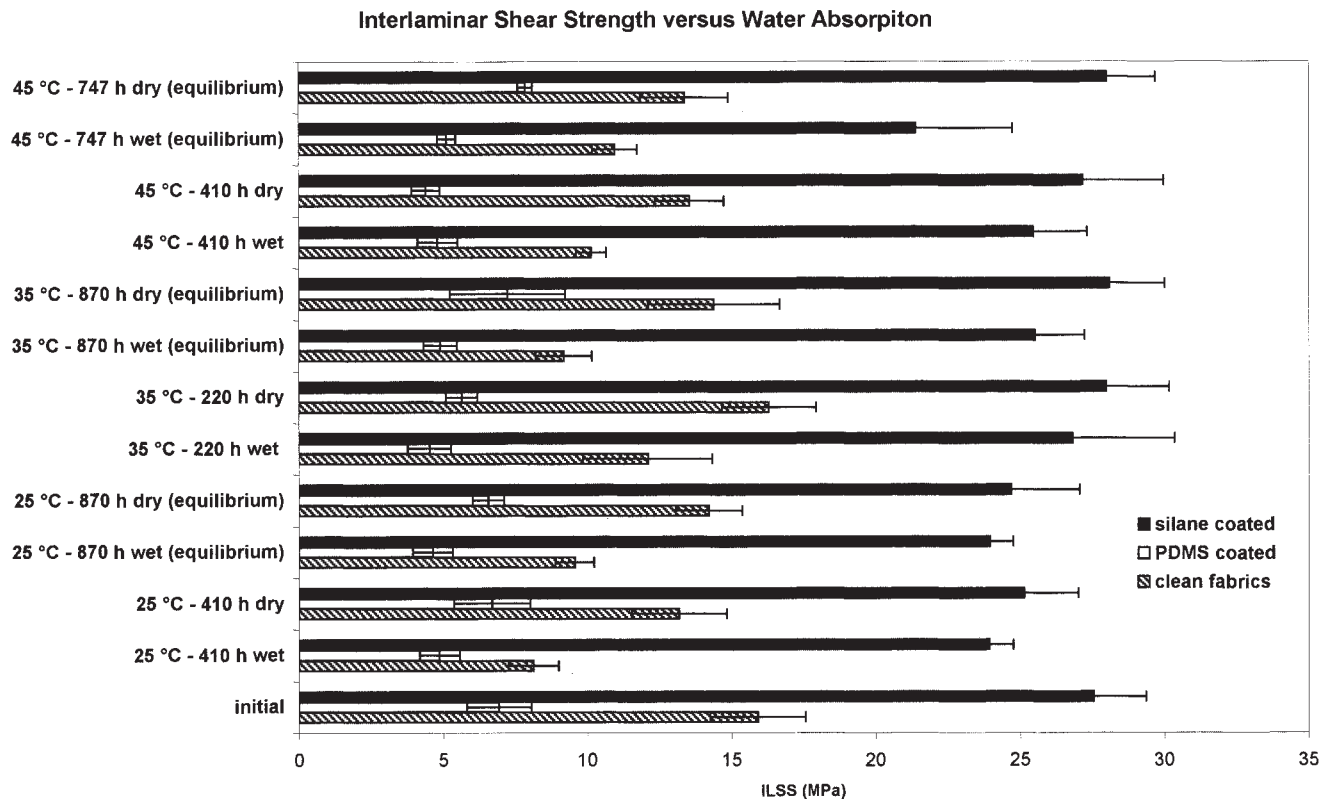**Interlaminar Shear Strength versus Water Absorpiton**

Figure 1 The interlaminar shear strength and retained interlaminar shear strength at different stages of water absorption for silane, PDMS-coated, and clean fabric based composites at 25, 35, and 45°C.

process for each composite and for the three temperatures. All specimens failed in an interlaminar shear manner.

It is readily observed that at the initial, dry state, the composite containing fabrics treated with silane (designated hereafter as silane treated) have superior ILSS compared to the other two composites (designated as clean and PDMS treated). Removal of the silane causes a large decrease in the ILSS, which is further reduced by insertion of a PDMS interphase. This is not surprising because, as already mentioned in the Introduction, the silane coating is introduced to ensure chemical bonding at the interface whereas in the clean and PDMS-treated fabrics the matrix bonds to the reinforcement only through mechanical anchoring. Moreover, in the presence of the PDMS coating, apart from the bad affinity between PDMS and the polyester resin, the ability of the polyester resin to penetrate through the fabric is hindered.[13,18,19]

To compare dry and wet specimens, it seems that, in the case of the silane-treated composite, water absorption does not seriously affect the ILSS. It is anticipated that the chemical bonds established through the silane coating prevent moisture penetration at the interface, that is, finishes are effective against molecular water penetration by diffusion along the glass–resin interface.[20] Actually, it is well known that once water

reaches the interface, the siloxane bonds between the silane coupling agent and the glass surface are easily hydrolyzed.[21] However, even a small amount of remaining covalent bonds prevents liquids from deteriorating the joint under wet conditions.[20] Moreover, it has been demonstrated that the fiber–resin bond is reversible on redrying wet specimens.[18,22] Thus, specimens that have been subjected to water absorption recover some of their ILSS on redrying.

In the case of clean and PDMS-treated composites, water absorption has a more pronounced impact on ILSS values, because the weak interface offers an easy path for water molecules to penetrate and thus degrade the interface. In the presence of water the ILSS is reduced, because water acts as a lubricant and facilitates debonding. Upon redrying the water diffuses readily out of the composite, the frictional bond reforms, and ILSS recovery is observed.[22]

Moisture absorption

Maximum water uptake

The temperature dependence of the maximum water uptake at equilibrium (M_∞) is not well established in the literature. Many authors have reported the equilibrium moisture content to be independent of tem-
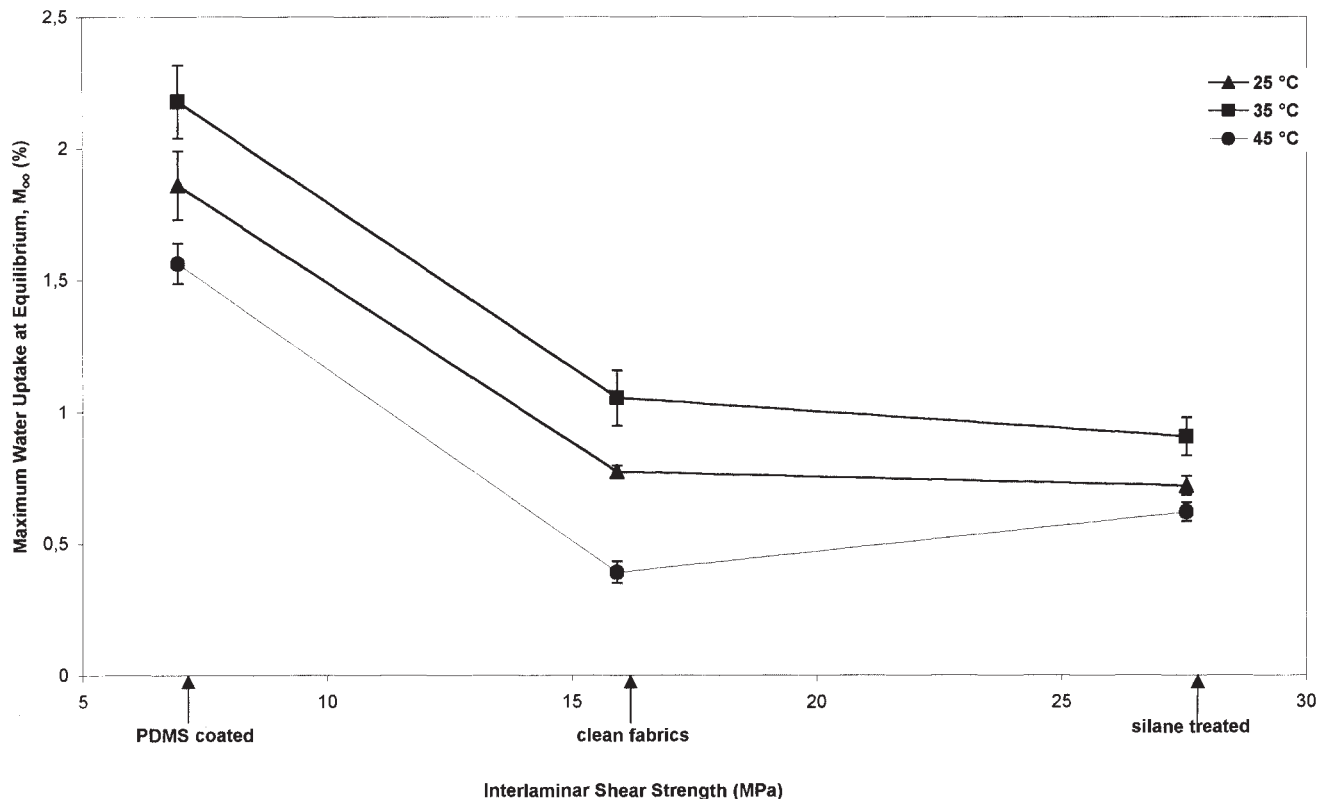
Figure 2 The maximum water uptake at equilibrium versus the interlaminar shear strength.

perature, whereas others observed either positive or negative temperature dependencies.[10,15,23] For example, M_∞ has been reported to be an increasing (e.g., in polyesters), decreasing (e.g., in certain polyimides), or independent (e.g., in certain epoxy–amine networks) function of temperature.[24] It seems that no consistent explanation has been given for these trends.

In this study an increase of M_∞ is observed for all three composites with a temperature rise from 25 to 35°C, but the equilibrium water uptake values significantly decreased at 45°C (Fig. 2).

This behavior can be easily attributed to the hydrolysis of the polyester matrix, taking into account that the time required to reach equilibrium is approximately 1 month. In fact, it is well known that the aging of fiber reinforced polyester composites in wet conditions is essentially dominated by polyester hydrolysis.[25] The water interferes with the esteric bonds of the resin and destroys the structure of the polymer, breaking the polymeric chain.[26,27] Hydrolysis becomes more severe as the temperature increases. Consequently, at elevated temperatures, one should expect a loss of polyester weight competing with the weight increase from water absorption and leading eventually to lower M_∞ values. The weight loss due to hydrolysis was determined at the end of the experiment by reconditioning the specimens after immersion and reweighing them. The reconditioned weight was lower

than that at the initial dry state and the difference was considered as water-soluble matter lost during the immersion test. The percentage of soluble matter lost during immersion was calculated as

soluble matter lost (%)

$$= [(\text{initial weight} - \text{recond. weight})/\text{initial weight}]$$
$$\times 100 \quad (1)$$

The results are presented in Table I and certify that hydrolysis is much more severe at 45°C than at the lower temperatures, in agreement with the aforementioned mechanism.

Figure 2 also certifies the existence of a distinct relationship between ILSS and M_∞, which should be expected as improved interfacial bonding between the matrix and the fibers is believed to hinder further water absorption in composite materials.[10] In contrast,

TABLE I
Percentage of Soluble Matter Lost During Immersion

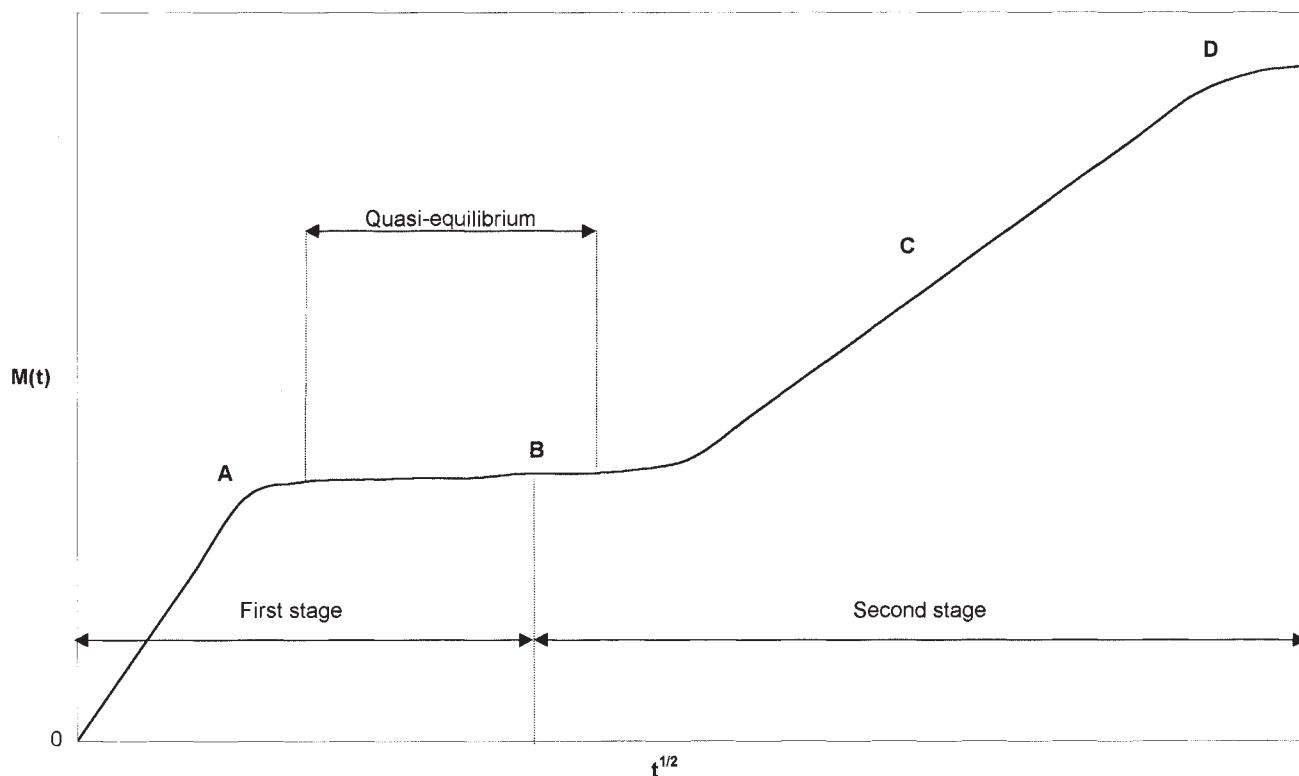|	25°C	35°C	45°C
Silane treated	0.0406	0.0308	0.2799
Clean fabrics	0.0276	0.0332	0.4599
PDMS coated	0.0432	0.0480	0.4571

Figure 3 A schematic presentation of the two-stage type of sorption.[28]

easy debonding of the fibers from the matrix and delamination provides more free space and induces localized water entrapment. In other words, weaker adhesion provides more pathways to the water and allows more water to be absorbed by the composite. Furthermore, in a previous study,[26] we clearly demonstrated that the insertion of a hydrophilic material [poly(hexamethylene adipamide)] into the composite interface lowers the ILSS of the composite and accounts for severe water accumulation. However, it is worthwhile to observe that even the PDMS coating, although it comprises a typical hydrophobic material, leads to identical behavior because it deteriorates the adhesion of the fibers to the matrix.

It should be noted that the M_∞ values found in this study agree with typical solubilities encountered in thermoset composites.[11]

Absorption curves

Figure 3 shows a non-Fickian sorption case called the two-stage sorption type (2SS). The material initially absorbs moisture rather quickly up to a concentration corresponding to point A, then the absorption becomes very slow and follows a sigmoid curve until the final true equilibrium is reached. Detailed studies have demonstrated that absorption from points O to B via A not only looks Fickian but actually obeys various criteria for Fickian sorption, whereas the process from point B to the final equilibrium via C is decidedly non-Fickian. It should be noted that the initial "Fickian" absorption proceeds as if the concentration corresponding to B is its final equilibrium. However, because this concentration is by no means the true equilibrium to be reached under given conditions, it is called the quasiequilibrium level.[9,26] It is well established that a distinct separation between the two stages exists when the relaxation process is much slower than diffusion.[8] In other words, this non-Fickian sorption behavior is related to the case of a glassy polymer and vanishes above its glass-transition temperature.

This type of two-stage behavior is encountered at 25 and 35°C (e.g., Fig. 4). That is, at these temperatures the absorption process consists of two separate stages. The first stage of the absorption curve appears to be Fickian, so it can be treated as such mathematically. However, the second stage is associated with other phenomena, such as the advancement of the slow relaxation process of polymer chains,[8] microcrack formation,[10] and fiber/matrix debonding with subsequent formation of liquid films around the surface of the fibers.[23] All these phenomena result in additional water absorption.

Regarding the effect of the surface treatment on the absorption curves, a "smoothing" of the 2SS curves is
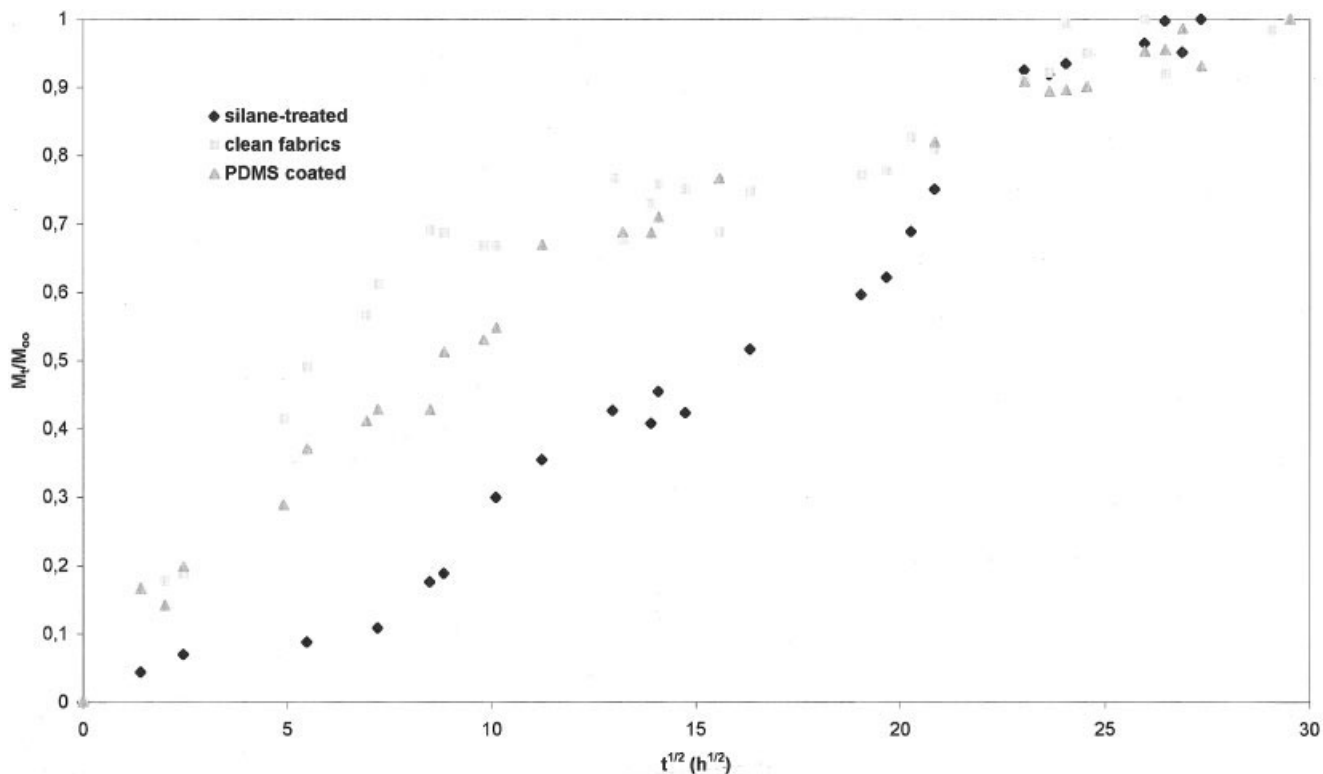
Figure 4 Absorption curves for silane, PDMS-coated, and clean fabric based composites at 25°C.

observed for composites with lower ILSS values. It is postulated that the low interfacial adhesion promotes autocatalytic debonding between the fibers and the matrix as a result of water attack at the interface. Therefore, it seems that at low temperatures the higher ILSS composites exhibit matrix dominated behavior with a typical 2SS profile. However, this is not true for the low ILSS composites, where the 2SS absorption is not so evident because of the interphase dominated performance. In contrast, at high temperatures, as can be seen in Figure 5 at 45°C, all composites display Fickian behavior. This could be attributed to a faster relaxation of the polyester matrix.

An interesting observation concerning the low ILSS composites is that the insertion of the PDMS interphase (and thus the insertion of a second interface) doubles the water uptake with respect to the composites containing clean fabrics throughout the absorption process. In other words, the absorption curve for PDMS-coated fabrics coincides with the doubled absorption data of composites with clean fabrics, which is shown in Figure 6 at 35°C. This is also true for 25°C, but not for 45°C, because at that relatively high temperature the whole process is dominated by the Fickian behavior of the matrix. That is, as previously mentioned, at low temperatures absorption takes place mainly through the interface, because the slow relaxation of the polymer chains does not allow much water to penetrate through the glassy matrix. The

doubling of absorption with the insertion of an interlayer indicates this dominating role of the interface. Conversely, at relatively high temperatures water molecules can diffuse through the matrix because of the faster relaxation process of polymeric chains from the very beginning of the immersion. In this case it is the matrix rather than the interface that controls the shape of the absorption curve.

Diffusion coefficients

The diffusion coefficients presented in Figure 7 were determined following the 1-dimensional approach. The ratio of the amount of water sorbed by the specimen at time t $(M_t)/M_\infty$ was plotted versus $t^{1/2}$/the specimen thickness (l) and the diffusion coefficient (D) was calculated from the slope of the initial linear part of the diffusion curves by[2]

$$M_t/M_\infty = 4(Dt/\pi l^2)^{1/2} \qquad (2)$$

As already discussed, for short time intervals typical Fickian diffusion behavior is encountered and diffusion coefficients can be computed from the slope of the initial linear part of the curves by means of eq. (2).

Hydrolysis of the polyester matrix is not expected to have any effect on the calculation of D because this calculation corresponds to very short immersion times, when hydrolysis has not commenced. It is
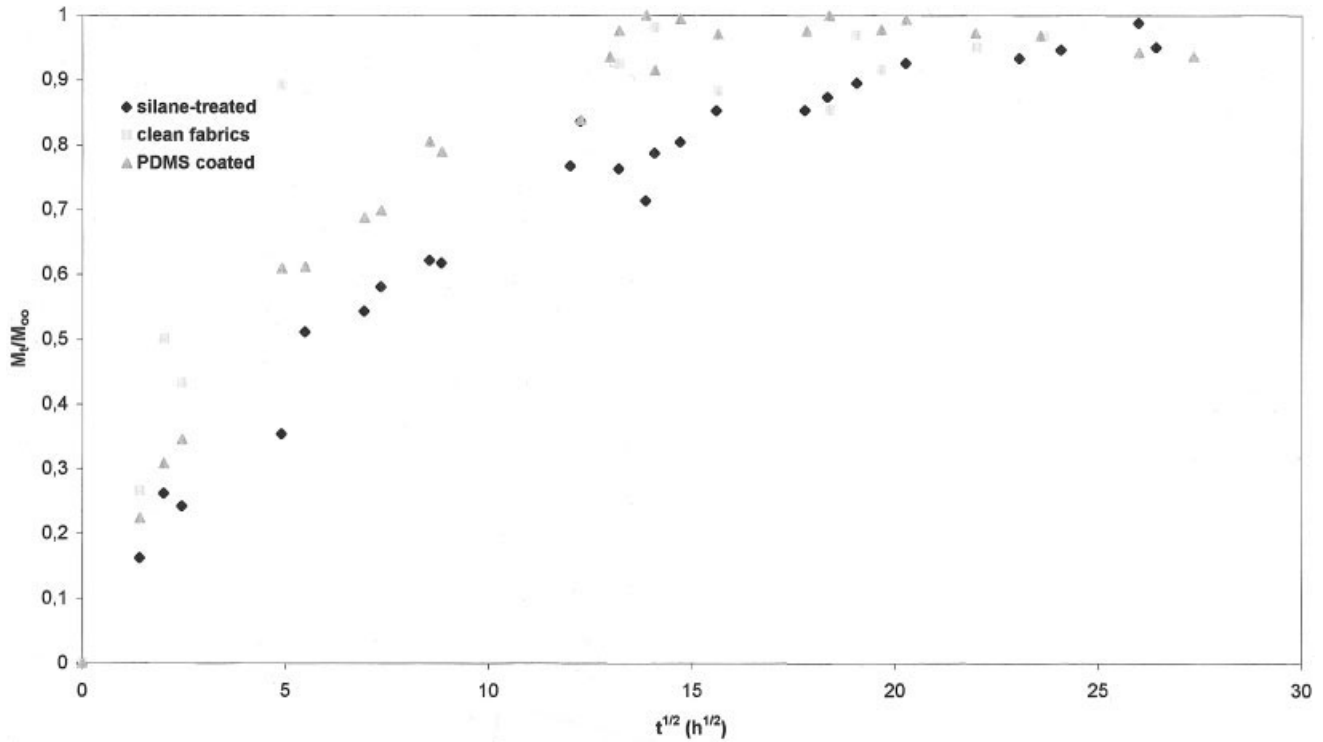
Figure 5 Absorption curves for silane, PDMS-coated, and clean fabric based composites at 45°C.

readily observed from Figure 7 that the diffusion coefficients of the same order of magnitude were found for all three composites, with slightly lower values

encountered for the silane-treated ones. In other words, not only the strong adhesion of this composite causes a decrease of M_∞ (Fig. 2), but also it seems that,
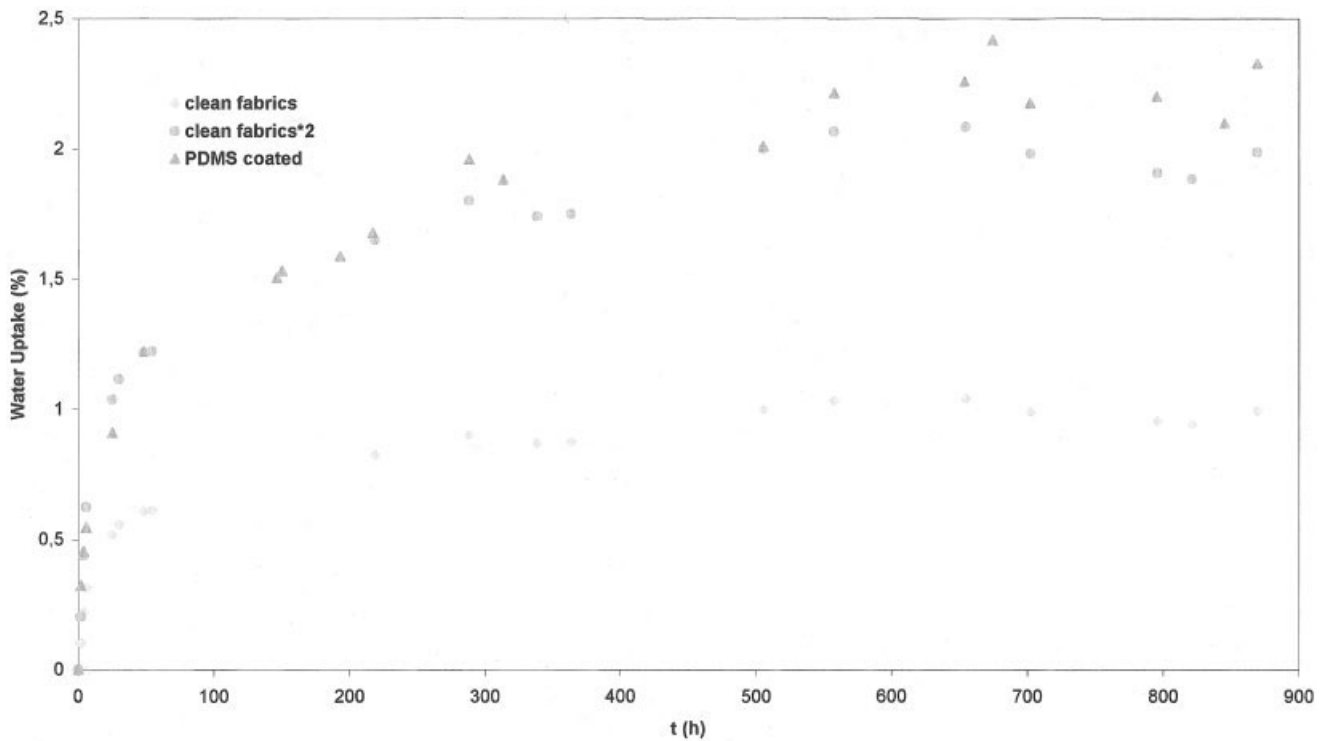

Figure 6 A comparison of the moisture uptake at 35°C for composites containing clean and PDMS-coated fabrics.
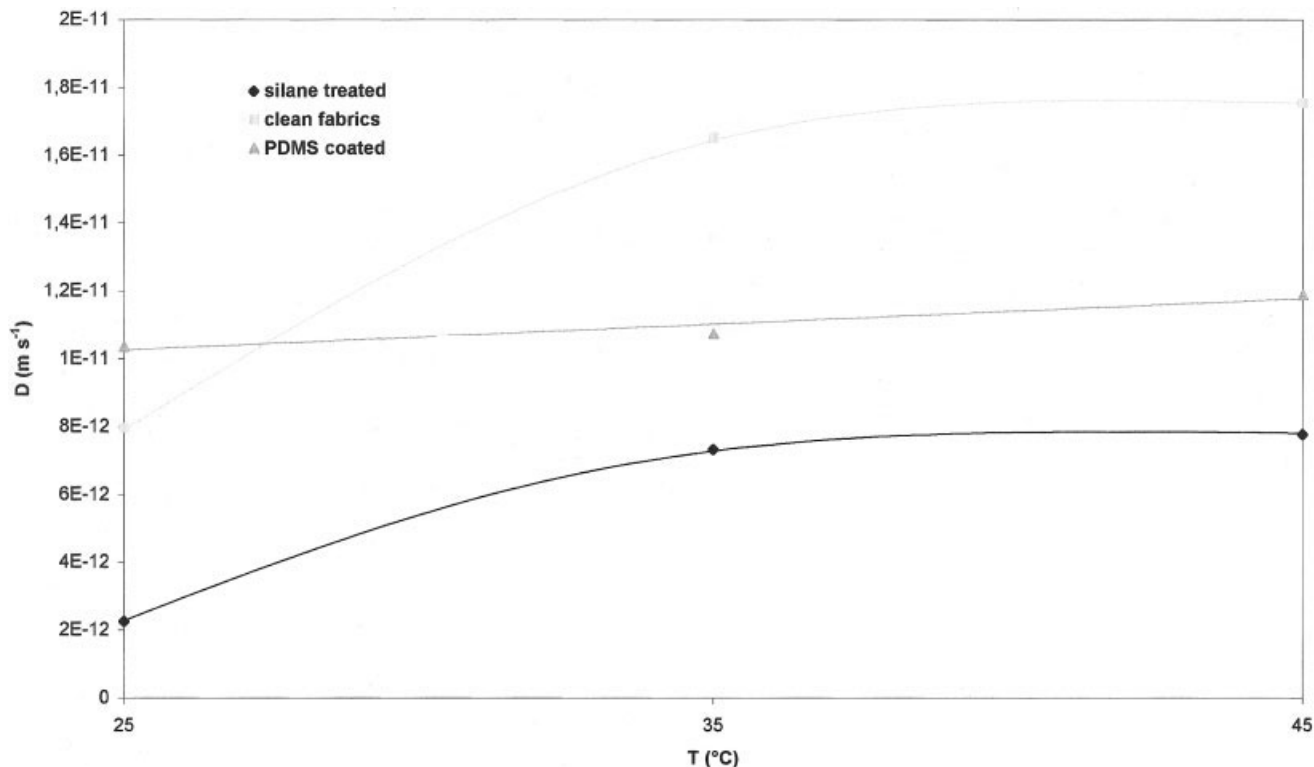
Figure 7 Diffusion coefficients for silane, PDMS-coated, and clean fabric based composites at 25, 35, and 45°C.

because there are fewer pathways for water to start diffusing into the composite, this inhibits and retards the diffusion process from the very beginning. It should be noted that the diffusion coefficient values found in this study agree with typical ones reported for most plastics and their related composites.[10]

The temperature dependence of diffusion coefficients can be expressed by the Arrhenius equation:

$$D = D_0 \exp(-E_a/RT) \qquad (3)$$

where the preexponential term D_0 is the permeability index, E_a is the activation energy of the diffusion process, and R is the gas constant.[9,15] The D_0 and E_a values determined here are listed in Table II. If the only mechanism of moisture penetration was diffusion through the matrix, the activation energy would have been the same for all three composites. Thus, the discrepancies found here indicate the presence of highly

diffusive paths for composites with weak interfaces. Note that the calculated activation energies are in agreement with typical values for thermosets.[15]

CONCLUSIONS

We studied water absorption in glass fabric/polyester composites, characterized by different interfacial strengths, using short beam shear tests to reveal interfacial degradation and strength retention. The diffusion curves at 25 and 35°C follow a 2SS form, especially for the high ILSS material, whereas all diffusion curves at 45°C follow typical Fickian behavior. Concerning the effect of the different surface treatments of reinforcing agent, maximum water uptake was found to increase as the ILSS decreased. On applying the PDMS coating, even though it is a typical hydrophobic material, water absorption was enhanced because of easier debonding of the fibers from the matrix. An interesting observation was that at low temperatures, where relaxation phenomena of the polymeric chains are slow and hinder the diffusion through the matrix, the insertion of the PDMS layer doubled the water uptake values in comparison to composites with clean fabrics. This was attributed to the formation of a second interface and points out the prevailing role of the interface in moisture absorption at low temperatures. In contrast, a temperature increase accelerated the re-

TABLE II
Permeability Indexes (D_0) and Diffusion Activation Energies (E_a)

	D_0	E_a (kJ/mol)
Silane treated	1.1 E-03	49.0
Clean fabrics	2.9 E-06	31.4
PDMS coated	9.1 E-11	5.4

laxation of the matrix. Therefore, at higher temperatures water molecules readily diffused through the polyester network and it was the matrix rather than the interface that controlled the absorption process.

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