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Hydrothermal Ageing of GF/PP Composites: When Glass/Polymer Adhesion Favours Water Entrapment

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This study aims to assess the effects of ageing in boiling water on the transverse tensile mechanical properties of unidirectional commingled GF/PP composites, as well as the influence of the fibre/matrix adhesion on the water absorption and desorption mechanisms. For this purpose, different interfacial qualities were obtained by a modification of the fibre reinforcement sizing (polypropylene specific sizing, or no sizing), and of the matrix (with or without coupling agent). A very good retention of the mechanical properties was observed for those composites which had been treated so as to improve the fibre/matrix adhesion. It is also shown that the better the adhesion, the longer the water remained inside the composite material. This induced effect appears to be the counterpart of the protecting role against moisture of a strong interface. The interfacial interactions act as barriers both during absorption and during desorption. This leads to water molecule entrapment. Hence, the persistence of water trapped at the interfaces in the case of sized glass fibres composites leads us to recommend investigations on the long term effects on longitudinal tension properties, since the effects of zero-stress ageing are known to reduce fibre strength.

1. INTRODUCTION

The quite recent introduction to the market of continuous glass fibre thermoplastic composites has provided a technological and cost-effective solution to a number of composite problems, including their storage, processing, brittleness, and even recycling. While the demand has been driven by a variety of applications in aerospace (the fixed leading-edge nose on the wings of the Airbus A340-500/600) and automotive (bumper beams) industries, these new materials are finding their way into furniture, medical and marine applications¹. Nevertheless, extensive research efforts are still required on the analysis of their short and long term behaviour, and on reliability models for part design and dimensioning optimisation. The scientific and technical literature contains extensive data about continuous glass fibre reinforced thermoset composites^{2,3} and chopped glass fibre based thermoplastic composites^{4,5,6}, but very few data are available about continuous

glass fibre/thermoplastic composites made from commingled yarns. For these new materials, where the thermoplastic matrix is derived from the thermoplastic fibres in the commingled yarn, most studies have focused on the processing conditions and their influence on the mechanical performances of the material^{7,8,9}.

The processing of commingled yarn glass/thermoplastic composites is considerably hindered if the glass fibres are not sized, due to the repulsive electrostatic interactions that take place between glass fibres and thermoplastic fibres. Glass fibre sizings generally contain organosilanes to protect the silica fibres against attack by moisture, and to enable the polymeric coating to react chemically with the surface of the glass in order to improve the adhesion¹⁰. To achieve these tasks, organosilanes are bifunctional and they react at one end of their molecules with the substrate mineral surface and at the other end with the matrix. However, the deposition of an aminosilane coating onto the glass fibres is not sufficient in the case of an unreactive

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matrix such as polypropylene. Therefore a maleic anhydride grafted polypropylene is dispersed into the matrix and/or added to the sizing in order to link the matrix to the silanized glass surface by reaction with the amine group of the silane. Besides favouring the creation of chemical bonds and intermolecular interactions between the reinforcement and the matrix, the silane based sizing may generate a specific polymeric structure close to the surface (the so-called interphase). It may also induce a more perfect wetting of the polymer on the treated surface¹¹. The contribution to fibre/matrix adhesion in the case of thermoplastic composites made by each of these three mechanisms is still being debated.

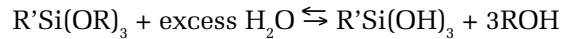
Studies concerning the role of the fibre/matrix interface and the fibre sizing in the performance of continuous yarn glass thermoplastic composites are quite rare¹²⁻¹⁴. In particular, the effects of boiling water are still not well documented, although these materials may be exposed to aggressive environments in service. Moreover, the chemical bonds generated by the silane chemistry between the glass and the polymer matrix are generally subject to hydrolysis. Hence, a focus is needed on the hydrothermal behaviour of these materials in order to improve their water resistance and overall performance.

The purpose of this paper is to highlight the effects of hydrothermal ageing on the mechanical behaviour in transverse tension of commingled polypropylene/glass fibre yarn composites with different interfacial qualities. The choice of this loading mode is justified by the fact that it is one of the most sensitive to interfacial effects. Moreover, the low transverse tensile strength of unidirectional laminates remains a major issue in the design of composite structures submitted to complex and coupled loading modes. Another aim was to investigate the influence of a silane based glass sizing and of a PP-g-MAH (i.e. polypropylene grafted with maleic anhydride) matrix coupling on the water absorption level and on the desorption rate of these materials.

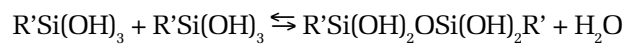
2. FUNDAMENTALS

Considering the (organo)silane chemistry effects on glass/polymer adhesion, organosilanes have the general bifunctional form X_3SiR' where X stands for an hydrolysable group (typically either chlorine, alkoxy or amine) to react with the surface, and R' is a non-hydrolysable organofunctional group which reacts with the polymer (e.g., vinyl, epoxy, amino,

mercapto...)^{15,16}. Before or during the application and bonding processes, the organosilanes are hydrolysed, initiating a complex cascade of reactions. Silanes first undergo hydrolysis to form silanol-containing species $R'Si(OH)_3$, which are responsible for bond formation with the substrate¹⁷:



Then, the silanetriols $R'Si(OH)_3$ self-condense to form siloxanes $-SiOSi-$ and interact with the silanols of the glass surface through hydrogen bonding:



Finally, condensation takes place between the silanol of the oligomer and the surface silanols:

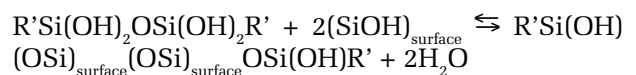


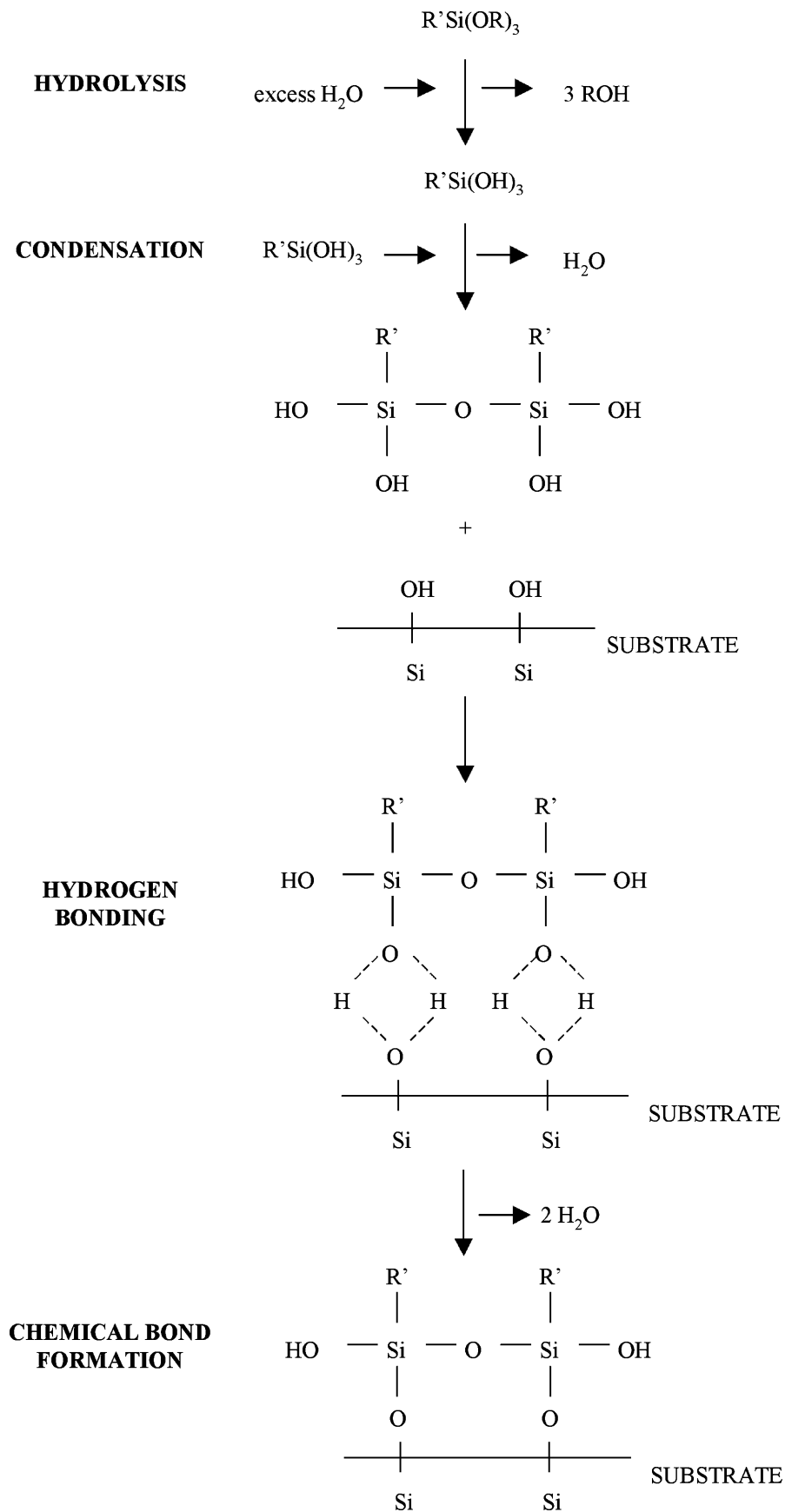
Figure 1 depicts a simplified view of the reactions involved, for the case of alkoxy-silanes¹⁸. The scheme points out that alkoxy-silanes condense with the glass surface to form chemical linkages but they can also interact with the surface silanols through hydrogen bonding.

3. EXPERIMENTAL

The investigations have been carried out on 4.6 ± 0.2 mm thick unidirectional glass fibre/polypropylene composite plates, manufactured by the filament winding of commingled yarns on a flat mandrel and then consolidated by compression and high temperature. The rovings supplied by Saint-Gobain -Vetrotex International had different sizings, and some but not all composite samples had a coupling agent in the matrix. Also, all the rovings were produced from a common basis: glass fibres (60% in weight)/homopolymer polypropylene filaments with a narrow distribution of molecular weights. Four materials were obtained, with different interfacial qualities:

- Specific sizing with or without coupling agent (referred to as S/C and S/N respectively)
- No sizing with or without coupling agent (referred to as N/C and N/N respectively).

Figure 1. Reaction and bonding mechanism of alkoxy silanes (from ref. 18)



The *specific* sizing was made up of an aminosilane and PP-g-MAH. The PP-g-MAH was added to ensure a chemical linkage between the amine part of the silane and the polypropylene matrix. The *no sizing* based composite was simply water-sized, with 1% of lubricant added during the glass fibre drawing. The coupling agent blended into the PP matrix (about 2% in weight) to make it more polar was a PP-g-MAH with a weight-average molecular weight very close to that of the PP matrix.

The ageing conditions consisted of immersion for 72 hours at 100 °C in demineralized water. Once the samples were extracted from the ageing bath, they were stored at 24 °C, 50%RH, and the mass fraction of absorbed water still remaining in the composite was measured regularly. The mechanical testing in transverse tension was carried out 450 hours after the extraction of the samples from the ageing bath. Transverse tensile tests on standard test specimens were performed on an Instron 1185 tensile machine at a crosshead speed of 1 mm/min.

3. RESULTS

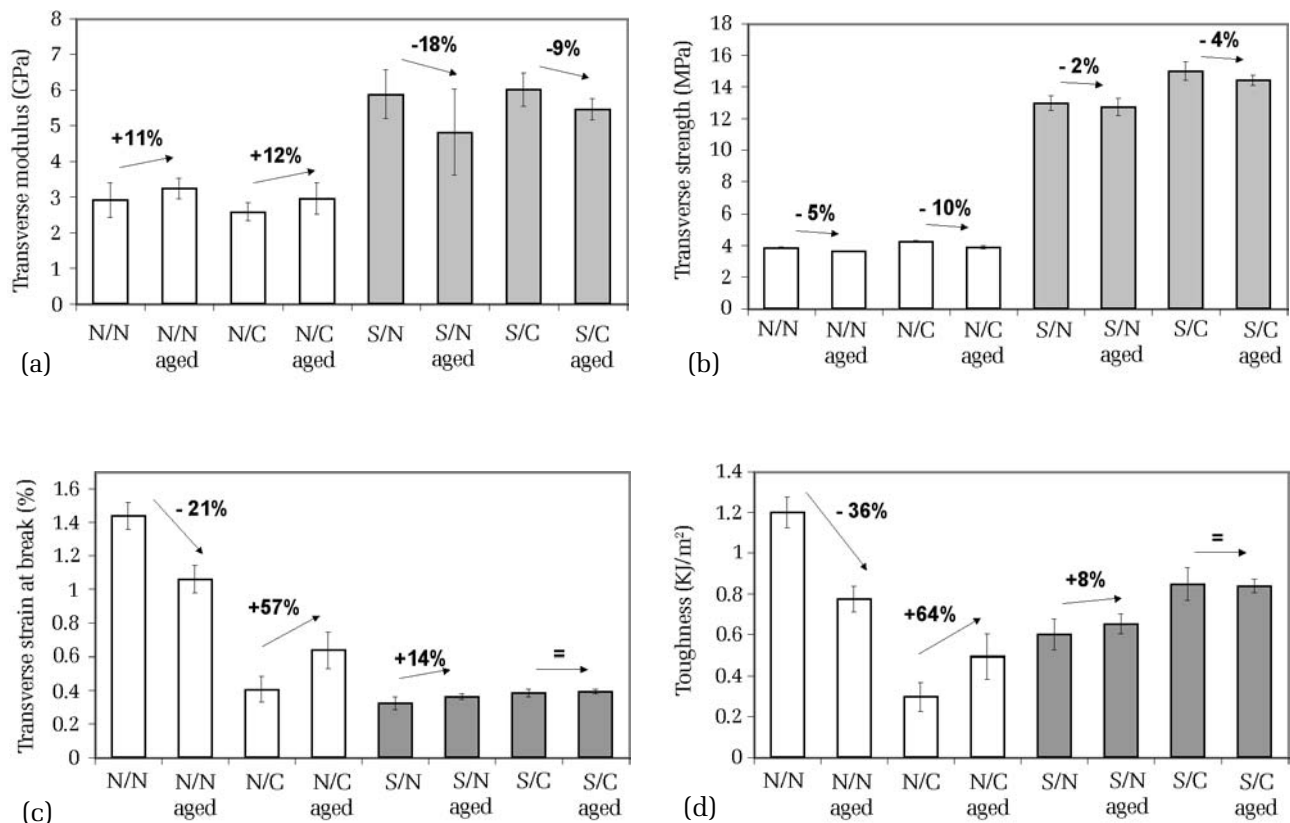
3.1 Mechanical Properties Before and After Ageing

The mechanical properties in transverse tension are reported in Figure 2 for each composite material type, before and after ageing in boiling water.

Considering the data scattering (standard deviations are indicated on the graphs), the ageing-induced variations observed for the ultimate properties of the sized composite materials (S/N, S/C) were hardly significant. The tensile strength, elongation at break and toughness (calculated as the area under the stress/strain curves) remained unchanged before and after ageing in boiling water. A more significant lowering of the elastic modulus was however noticed for both sized types after ageing.

The behaviour of the unsized composite materials (N/N, N/C) was quite different. The tensile strength

Figure 2. Transverse tensile properties of UD glass/PP composites with different interfacial qualities (N/N, N/C, S/N, S/C) before and after 72 h aging in boiling demineralised water – a) Modulus – b) Strength – c) Elongation at break – d) Toughness



remained unaffected and the elastic modulus was slightly improved by ageing in boiling water (within the limits of data scattering). On the other hand, the ageing effects on the elongation at break (and thus, logically, on the toughness) were much more important. In the case of the unsized composites with a pure PP matrix (N/N), the ageing caused a 21% decrease in the elongation at break and a corresponding 36% diminution of the toughness. Adding PP-g-MAH to the matrix (N/C) however induced a 57% increase in the elongation at break and 64% increase in toughness.

3.2 Water Absorbed Fraction and Water Desorption Rate

Figure 3 reports the desorption curves (absorbed water, mass fraction vs. time) for the previously hydrothermally aged unidirectional glass/PP composites. The highest mass fraction of absorbed water was observed in the case of the unsized type, without a coupling agent in the matrix (1.25%; N/N). Adding a PP-g-MAH coupling agent to the matrix resulted in a decrease in the mass fraction, which reached 0.98% (N/C). Finally, the sized composites presented the lowest mass fraction of absorbed water, with a value slightly higher for the uncoupled type S/N (0.8%) than the coupled one (0.65%; S/C).

The untreated composite N/N was also the type which desorbed water fastest. The mass fraction of absorbed water in that case reached zero in less than 50 hours whereas 250 hours were necessary to totally extract the absorbed water in the case of the unsized material with matrix coupling (N/C).

The water mass fraction characterising the sized materials first significantly dropped after about 50 hours and then decreased more gradually. The sized composites still contained more than 0.1% of water after 500 h storage. Finally, the sized samples with matrix coupling showed the lowest amount of absorbed water, together with the lowest desorption rate.

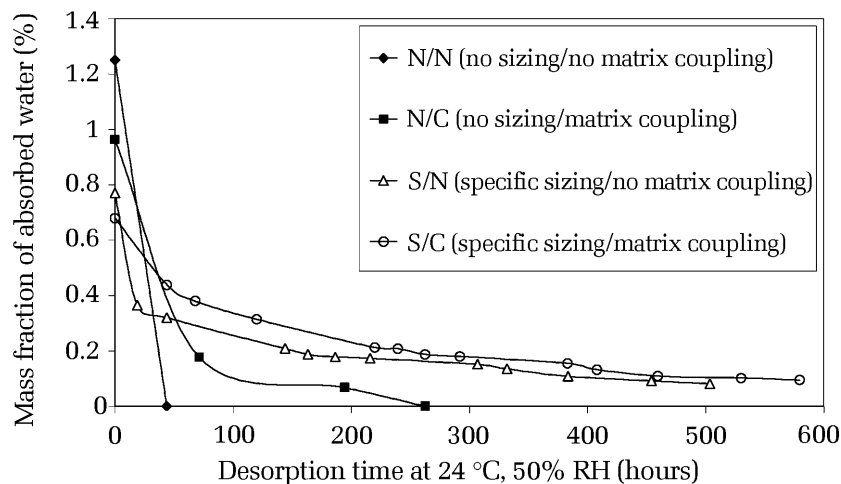
4. DISCUSSION

4.1 Glass/Polymer Adhesion

In order to discuss the influence of ageing on the mechanical properties, the absorbed water mass fraction and the desorption rate, it is necessary to consider the quality of the glass/polymer adhesion for the four different composite materials. Their characterisation in transverse tension coupled with acoustic emission and fracture surface analysis¹⁹ has previously allowed us to discriminate between adhesion levels and to suggest the nature of the bonding mechanisms involved between the polymer matrix and the substrate:

The unsized samples (N/N and N/C) appeared to be difficult to separate in terms of adhesion intensity. However there was evidence to suppose that the introduction of a PP-g-MAH coupling agent to the matrix (type N/C) induced intermolecular forces (Van der Waals, hydrogen linkage) that bond the matrix and the reinforcement, as well as chemical bonds which may have resulted from the hydrolysis of some of the PP-g-MAH molecules after the manufacture of the composite. Also, an interfacial superstructure

Figure 3. Desorption curves for UD glass/PP composites for different interfacial qualities



has been observed for the N/C category, suggesting a transcrystalline structure.

The types treated with an aminosilane based sizing (S/N and S/C) presented the highest level of adhesion, considerably higher than that of the 'unsized' adhesion. They were characterised by a rigid, strong and thick interphase (made up of a mixture of the matrix and the sizing components) between the pure PP matrix and the continuous reinforcement, and many chemical bonds (siloxane linkages) were supposed to exist at the surface of the glass. The addition of a PP-g-MAH coupling agent to the matrix slightly improved the glass/PP adhesion by reinforcing the link between the pure matrix and the interphase, and by providing additional physical and chemical bonds between the interphase and the glass surface.

4.2 Influence of Ageing on the Short Term Mechanical Behaviour in Transverse Tension

The analysis of the transverse tensile mechanical properties of these commingled polypropylene/glass fibre yarn composites led to the following assumptions:

- The absence of any treatment for the PP matrix and the glass fibres results in a significant reduction in the transverse elongation and toughness due to ageing (type N/N). A first hypothesis might be that the degradation is localised within the bulk matrix. In that case, the effect should however also be observed for the sized composites. The fact that ageing does not affect the properties of these materials suggests that the ageing phenomenon mainly takes place at the glass/polymer interface. It is hence possible to assume that the degradation mechanism of the untreated category N/N is a failure of the anchorage bond sites between the polymer and the glass surface.
- The opposite effect is observed when the pure PP matrix is functionalised by a PP-g-MAH coupling agent (category N/C). It is known that the modified matrix is better bonded to the glass as a result of the occupation of some surface hydroxyl groups –OH by the carboxylic part of the maleic acid. Hence, the interface is better preserved from ageing and the increase in the toughness can be attributed to modifications occurring within the bulk matrix. As the properties of the sized composite

remain unchanged, it can be assumed that the ageing effects are confined to a region very close to the glass surface. Some studies report changes in the PP matrix microstructure caused by the modified polypropylene²⁰⁻²⁴. It has also been observed that the PP-g-MAH/PP blend may recrystallise at high temperature in the presence of moisture²⁵. Nevertheless, it is difficult to use these results directly to explain why the composite N/C becomes more ductile after ageing. The question remains open and requires further investigations, focusing especially upon the specific interfacial matrix structure (*a priori* transcrystalline) induced by the co-crystallisation of the PP-g-MAH coupling agent with the PP matrix and upon the consequences of the PP-g-MAH hydrolysis on this superstructure.

- The sized materials (S/N, S/C) show excellent retention of their properties after ageing. This can be attributed to the presence of a strong interphase with strong chemical bonds, which protects the glass/polymer interface from water degradation. The slight decrease noticed in the elastic modulus can be attributed to a plasticisation effect, due to the water remaining trapped in those materials at the testing time (450 h, cf. Figure 3). The functionalisation of the PP matrix by the PP-g-MAH coupling agent has no additional significant effect, contrary to the unsized composites, and the composite behaviour remains stable after ageing.

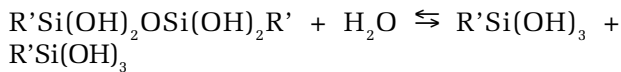
4.3 Relationship Between Adhesion and Water Entrapment

The lack of affinity between the hydrophobic polypropylene matrix and water leads to consider absorption and desorption as phenomena which take place at the glass/polymer interface. This is consistent with the results reported in Figure 2, which clearly indicate that water absorption and desorption mechanisms were strongly influenced by the glass fibre surface treatment. It is also possible to establish an inverse relationship between the number of interactions between the polymer and the glass surface (and hence the adhesion intensity of the four composite materials N/N < N/C < S/N < S/C), and both the mass fraction of absorbed water and the water desorption rate. The higher the number of glass/polymer interactions, the lower the water absorption level and desorption rate.

It is quite consistent to observe that the mass fraction of absorbed water decreased with improving

adhesion intensity. Each interfacial bond is indeed an obstacle for the migration of water molecules along the glass/polymer interface. Either the water molecules are simply blocked or they move as a consequence of capillarity effects, but the hydrolysis of the chemical bonds encountered, or the ‘screening’ of the physical interactions, hinder their progression along the surface

However, the results also highlight the fact that the better the adhesion, the longer the water persists inside the composite material (slower desorption). This is the counterpart of the ‘barrier’ effect due to the interfacial interactions acting as guardians with more or less resistance with respect to water. In the case of silanized glass fibres, one has to consider chemical bonds and the reaction between a siloxane bond and water:



where the siloxane linkage is dissociated into two silanetriols $R'Si(OH)_3$. The reaction is reversible, a fact which implies that once the siloxane bond has been forced by the water, it can reform to play the same barrier role with respect to the desorption. Thus, the sizing can trap the water, which explains its persistence within the sized composites. The mechanism is similar in the case of an intermolecular interaction between the polymer and the glass substrate. It is broken by the water molecules, but easily reformed.

What could be the consequences of this water entrapment in terms of material integrity and reliability? It is well known that the strength of a glass fibre is a matter of stress concentrations when cracks are present on its surface. Griffith developed a fracture mechanics model expressing the strength S of a fibre having one surface crack of depth a as a function of the surface energy γ :

$$S = \frac{1}{2} \sqrt{\frac{2\gamma E_0}{\pi a}} \quad (1)$$

where E_0 is the Young’s modulus of the glass fibre. France *et al.*²⁶ and Cameron^{27,28} showed that the surface energy of glass decreases as a function of time because of corrosion induced by the environment. Hence, from Equation (1) a decrease in the surface energy results in a weakening of the fibre. This process is called zero-stress ageing and, concurrently with static fatigue, leads to fracture as a function of time²⁹.

The persistence of water trapped at the interfaces for the sized composites highlights the question of the degradation of the treated glass surface. Zero-stress ageing is thus to be specifically considered in the evolution over several months or years of the mechanical behaviour of sized glass fibres composites. Further research work is in progress, focusing on their behaviour in longitudinal tension where the composite strength is governed by the fibre strength.

5. CONCLUSIONS

The effects of hydrothermal ageing on commingled yarn glass fibres/polypropylene composites has been investigated in terms of transverse tensile properties and water absorption and desorption. It has been observed that an aminosilane fibre sizing protects these materials against water very well (as judged by a good retention of the mechanical properties). It has also been noticed, and is a well-known phenomenon, that the fibre sizing results in a diminution of the amount of absorbed water. However, it has been pointed out that the better the adhesion, the longer the water stays inside the composite material. This appears to be the counterpart of the protecting role against moisture of a strong interface. The interfacial interactions act as barriers during absorption and also during desorption. This leads to water molecule entrapment. The persistence of water trapped at the interfaces justifies further investigation into the effects of this zero-stress ageing on the long term behaviour in longitudinal tension of composites with sized glass fibres, even if no major modification of the short term behaviour is expected.

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