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Anne Bergeret, I. Pires, M.P. Foulc, B. Abadie, Laurent Ferry, et al.. The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime. *Polymer Testing*, 2001, 20 (7), pp.753-763. 10.1016/S0142-9418(01)00030-7. hal-03254724

HAL Id: hal-03254724

<https://imt-mines-ales.hal.science/hal-03254724v1>

Submitted on 9 Jun 2021

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The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime

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Abstract

A study in an accelerated environment of the mechanical properties of glass-fibre-reinforced thermoplastic composites based on polyamide 66, poly(ethylene terephthalate) and poly(butylene terephthalate) is reported. Results showed a decrease of -90% to -50% in ultimate stress to failure and impact strength with ageing according to the nature of the matrix. Increasing the ageing temperature resulted in a faster degradation rate. Depending on the matrix nature, the mechanisms of ageing seemed to be different. Polyamide 66 and poly(butylene terephthalate) composites showed effects of both physical ageing through plasticisation and chemical degradation through chain scission. Poly(ethylene terephthalate) composites did not give evidence of any plasticisation. The extent of hydrolysis was quantified through end-group analysis and gel permeation chromatography measurements. Scanning electron microscopy observations showed that hygrothermal ageing reduced the effectiveness of the interfacial bonds.

Keywords: Hygrothermal ageing; Water; Composite; Polyamide 66; Poly(ethylene terephthalate); Poly(butylene terephthalate)

1. Introduction

In service, failures of glass-fibre-reinforced thermoplastic composites are commonly attributed to ageing of the material in its particular environment, brought about by a combination of the effects of heat, light, water and mechanical stresses on the material. Several studies have shown the important effects of absorbed water and ageing temperature on the physical and mechanical properties of composite materials [1–5]. It has been observed [6] that, above a threshold defined for a given temperature and a given ageing time, mechanisms other than simple diffusion can take place within the material, such as (1) hydrolysis of the macromolecular chains, which leads to the formation and migration of low-molecular-

weight chains; (2) hydrophilisation, which tends to increase the equilibrium water uptake through the development of local and/or overall swelling and plasticisation (or softening) of the matrix; and (3) interfacial decohesion, which induces a degradation of the composite. Most of the time, the stages of hydrolysis and hydrophilisation are not well separated in the sorption curve. Some models [6] take into account the fact that acceleration of water sorption due to hydrophilisation of the material competes with the reduction of water sorption due to hydrolysis. The purpose of this study is to improve the knowledge about these mechanisms involved in a hygrothermal environment in the case of three glass-fibre-reinforced composites with polyamide 66 (PA66), poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) matrices.

It is commonly assumed that water diffuses into the amorphous regions of the polymer where hydrolysis should occur at a rate which depends upon the crystal-

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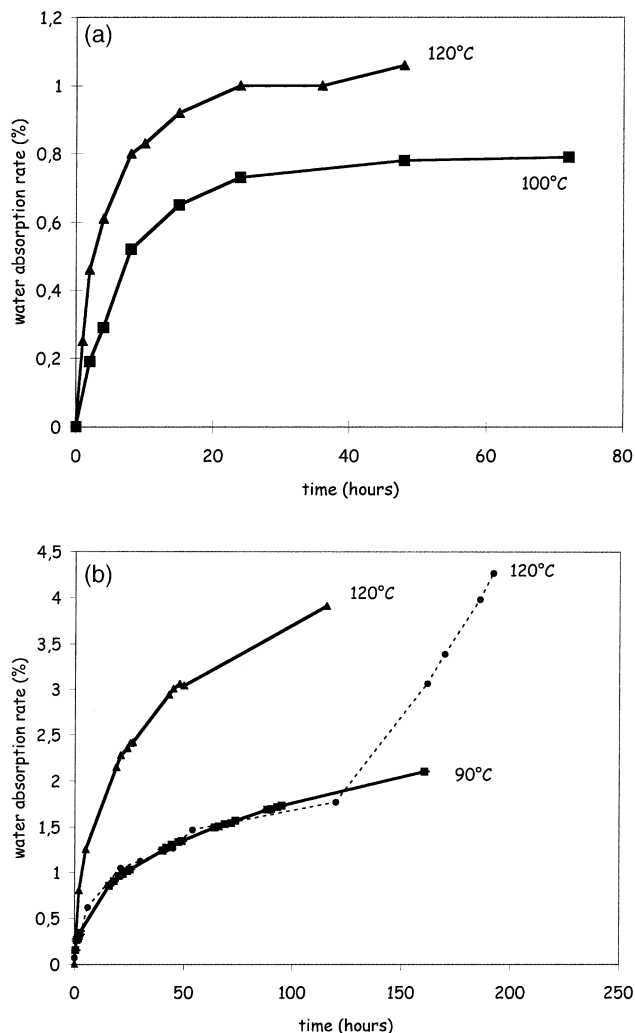


Fig. 1. Water absorption rate versus ageing time and temperature for (a) PBT composites and (b) PET composites (full line: gravimetry method; dotted line: Karl Fisher method).

linity and the initial content of end-groups [7]. Several authors [8–10] have studied the water diffusion in polyamides. Parir et al. [8] have suggested the presence of two types of water, tightly bound and loosely bound, in polyamide 6 through a study of the mechanical relaxation behaviour. According to Puffr and Sebenda [9], the first water molecule should form a double hydrogen bond between two carbonyl groups. This water may be assessed as firmly bound water. Two more molecules should join the already existing hydrogen bonds between carbonyl groups and the hydrogen atoms of amide groups. This water is classified as loosely bound water. Chaupart et al. [10] investigated ageing tests on polyamides and observed a decrease in molecular weight due to both random depolymerisation and end-group scission, leading to the migration of low-molecular-weight chains in the ageing medium.

Most of the moisture-related works on polyamides are focused on unreinforced mouldings so that there is limited work on fibre-reinforced grades. Valentin et al. [1] carried out a kinetic study of water absorption in pure polyamide 66 and short-fibre composites at different temperatures and various relative humidity levels. Results were found to obey a Fickian diffusion model. Some authors [1,4] have also studied the influence of water uptake on mechanical properties. Ultimate tensile strength decreased sharply and then stabilised as water content increased. Plasticisation induced by hygrothermal ageing increased the percentage elongation to failure for pure polyamide 66 but this result is not evident for fibre-reinforced grades.

The durability of PBT composites has not been investigated in depth, particularly with regard to hygrothermal ageing. The effect of moisture absorption on the tensile

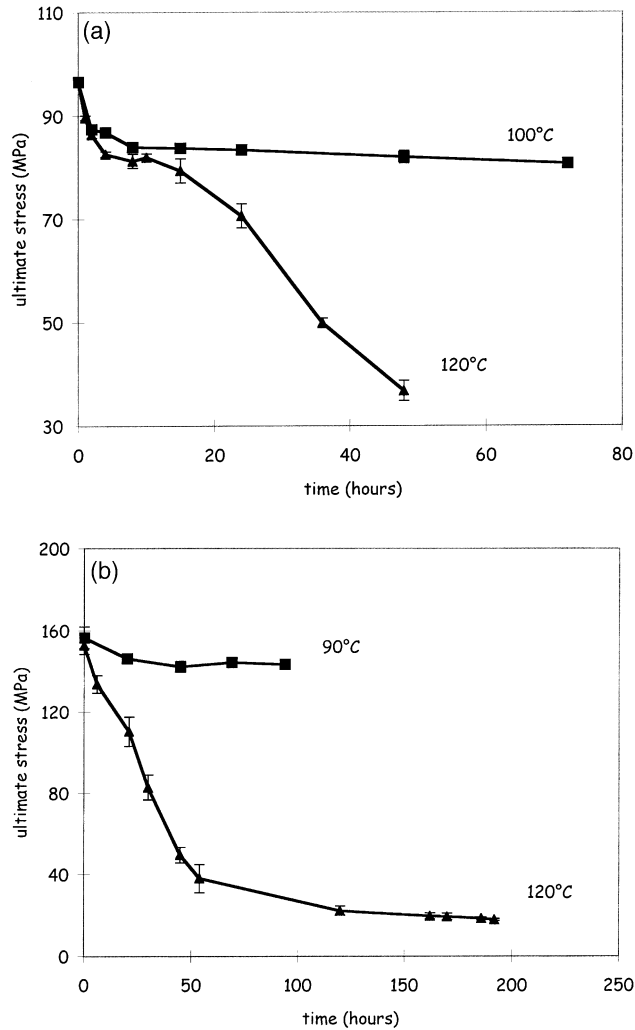


Fig. 2. Tensile properties versus ageing time and temperature for (a) PBT composites and (b) PET composites.

properties of PBT composites was reported by Mohd Ishak and Lim [3]. Ageing drastically reduced the tensile properties of both unreinforced and reinforced PBT, while there was better recoverability of the properties for the composite after redrying. The authors gave evidence of microvoid formation and no plastic deformation, which should provide for the occurrence of hydrolysis of the matrix. Czigany et al. [2] observed that key factors of the failure mode of PBT composites are interactions between matrix deformation (e.g., change from ductile to brittle failure mode because of hydrolysis of the PBT) and fibre/matrix adhesion.

The behaviour of PET and PBT on water ageing has been studied by Bastioli et al. [5]. A higher water uptake value in PET than in PBT at the same temperature was observed and attributed to the lower crystallinity in PET. Nevertheless, in both cases, swelling of the amorphous part due to water sorption should induce stresses at the

amorphous/crystalline interface, followed by microcavity formation. The impact strength data decreased with ageing time but remained higher for composite systems.

2. Experimental

2.1. Materials

A total of five materials were studied, including (1) two 30 wt% fibre-reinforced polyamide 66 composites (PA66), (2) two 15 wt% fibre-reinforced poly(butylene terephthalate) composites (PBT) and (3) one 30 wt% fibre-reinforced poly(ethylene terephthalate) composite (PET).

PA66 and PBT matrices were supplied by Dupont de Nemours Company (Switzerland) under the trademarks Zytel E101 and Crastin, respectively. Glass fibres were

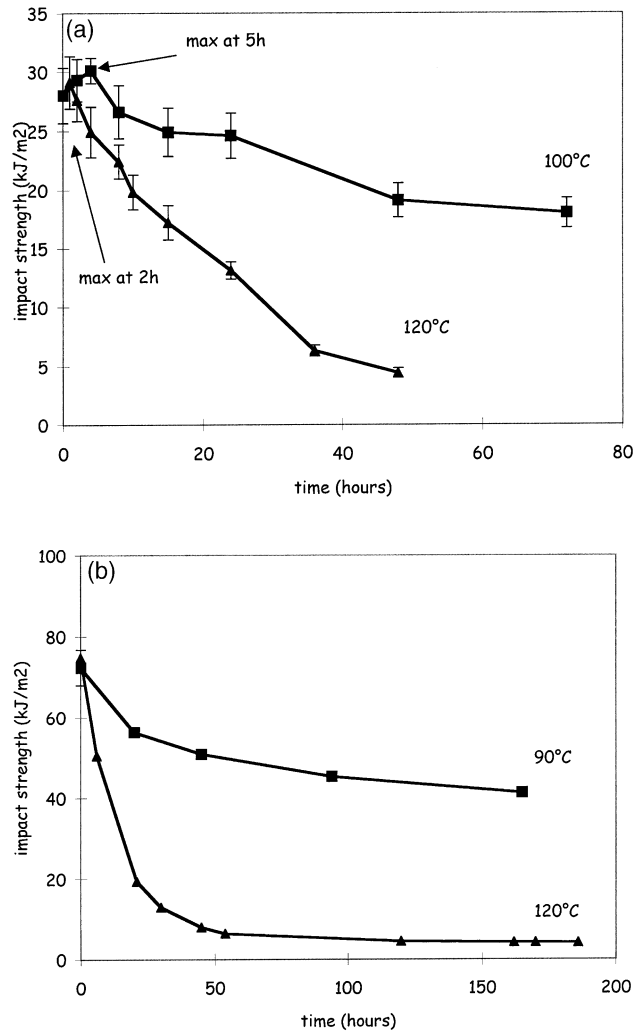


Fig. 3. Impact properties versus ageing time and temperature for (a) PBT composites and (b) PET composites.

obtained from Vetrotex Company (France). The polymer granules and the glass fibres were compounded in a twin-screw extruder (Clextral BC21) and then injection moulded (Sandretto). Materials were dried under specific conditions according to the nature of the matrix prior to extrusion, injection and ageing tests. The difference between the two PA66 composites and the two PBT composites concerns the nature of the surface treatment deposited on the glass fibre. One of the surface treatments improves the hydrothermal resistance of the composite by the presence of a specific agent in the formulation of the coating. PET composite was a commercial grade (Rynite 530) from Dupont de Nemours Company (Switzerland).

2.2. Ageing conditions

Different sets of hydrothermal conditions were chosen according to the nature of the matrix. PA66 composites were immersed in water at 135°C under pressure. Polyester-based composites were immersed in water at two different temperatures: 90°C and 120°C for PET composites, and 100°C and 120°C for PBT composites.

2.3. Mechanical properties: tensile and impact measurements

Ultimate properties were obtained in tensile mode by use of an Adamel Lhomargy DY26 testing machine. The experimental procedure as well as the sample dimensions

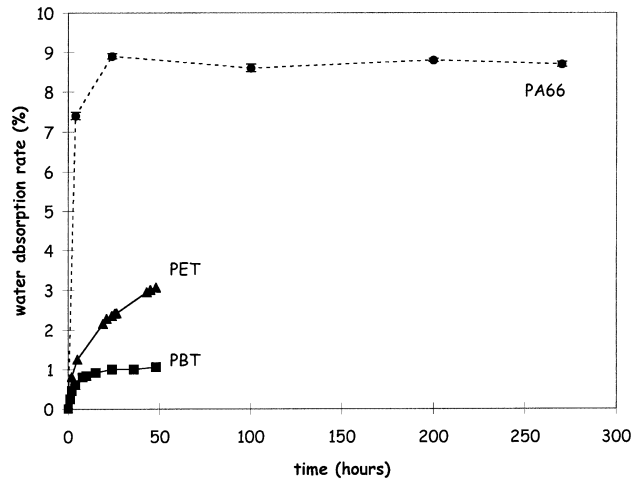


Fig. 4. Water absorption rate versus ageing time for PA66 composite aged at 135°C and for PET and PBT composites aged at 120°C: influence of the matrix.

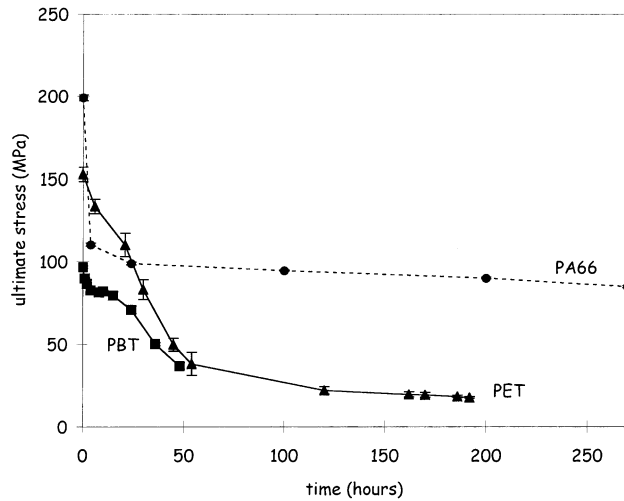


Fig. 5. Tensile properties versus ageing time for PA66 composite aged at 135°C and for PET and PBT composites aged at 120°C: influence of the matrix.

were defined according to the International Standard ISO 527.

Charpy impact resistance was measured on unnotched samples by means of a Zwick 5102 apparatus according to the International Standard ISO 75.

2.4. Water absorption rate

Water uptakes after immersion for a given time were measured through two techniques: gravimetric and titration. The gravimetric method consists of removing the samples from water and weighing them. The percentage gain at any time was determined versus the ageing time. The fibre fraction is taken into account in the calcu-

lation. The second technique is a water titration by means of the Karl Fisher method. This potentiometric titration is based on an oxidation–reduction reaction between iodine molecules in solution under a complex form and water molecules as follows:



Data are recorded after a volumetric titration on a Metrohm Titrino instrument. Samples are located in an oven at 200°C and desorbed water molecules are carried by a nitrogen flow to the titration cell. Both techniques will be compared further in this paper in the case of PET composites.

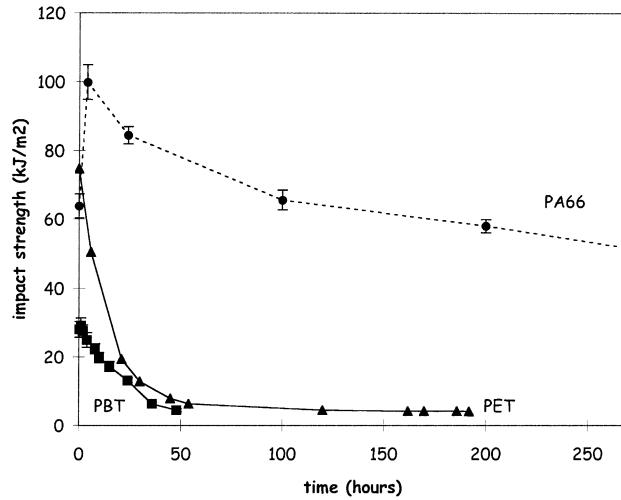


Fig. 6. Impact properties versus ageing time for PA66 composite aged at 135°C and for PET and PBT composites aged at 120°C: influence of the matrix.

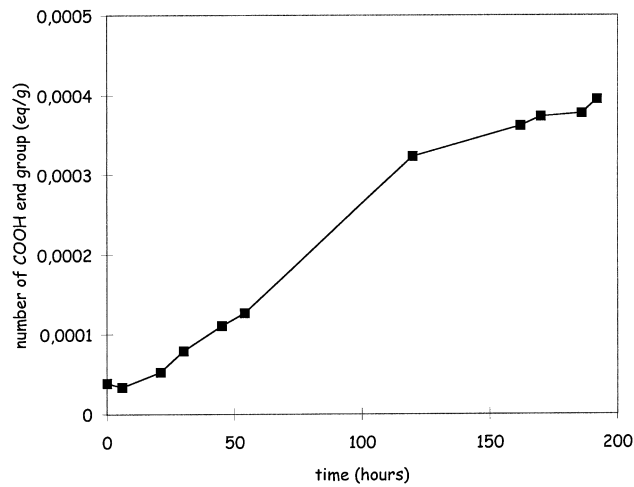


Fig. 7. Number of carboxyl ends versus ageing time for PET composites aged at 120°C.

2.5. Scanning electron microscopy (SEM) observations

Examination of the fracture surface was carried out using a Jeol JSM 35CF apparatus. The aim was to observe the mode of fracture of the samples, the interfacial adhesion between the matrix and the fibre, and the fibre length after fracture.

3. Results and discussion

3.1. Influence of the ageing temperature

The influence of ageing temperature on water sorption was studied for both PET (through gravimetry and the

Karl Fisher method) and PBT composites. It can be observed (Fig. 1) that the water sorption rate increased with exposure time and then tended towards an asymptotic value that increased with ageing temperature. This result may be due to easier diffusivity of water within the material as the temperature increased. In the case of the PET composite, the gravimetry method did not allow us to measure the water uptake at ageing times over 120 h for an ageing temperature of 120°C because the material was too degraded. Nevertheless, a determination through the Karl Fisher method showed a new rise in the water content above 120 h. Indeed, water sorption should produce hydrolysis of the polymer bonds and the formation of microvoids and microcracks. An increase in the number of microcracks can explain the new water

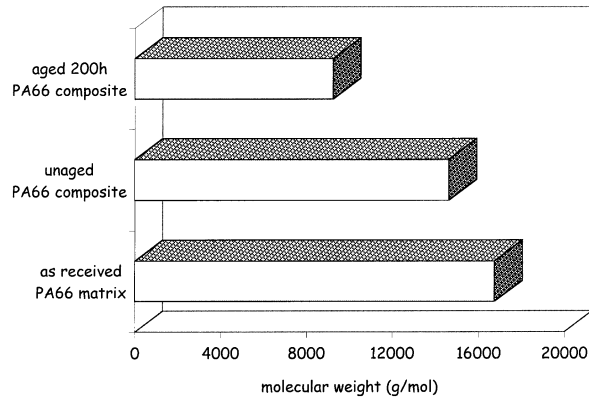


Fig. 8. Molecular weight versus ageing time for PA66 composites.

uptake. Furthermore, a greater water content has been obtained through gravimetry measurements compared with the titration data for an equivalent ageing temperature. This discrepancy could be due to the different sample preparation between the methods. Thermogravimetry tests are performed on bars of about 15 g mass. For Karl Fischer's tests samples are cut into small pieces of about 1 mm³ (total weight around 3 g) in order to increase the contact surface with air and then to optimise the water extraction rate.

Study of the mechanical properties after ageing has shown a drastic decrease in ultimate stress (Fig. 2) and impact strength (Fig. 3). For PBT composites a maximum in impact strength was observed for short times, this maximum being shifted towards longer times as the ageing temperature decreased. The decrease in ultimate stress [Fig. 2(a)] should be due to the insertion of water molecules inside the material. The maximum in impact strength may be correlated to improved polymer chain mobility induced by water and, therefore, to physical ageing through a plasticisation effect. No maximum in impact strength was evident for PET composites even at a low ageing temperature (90°C). This indicates that the rate of the plasticisation process is faster for PET than for PBT and that hydrolysis occurs at lower ageing times. The ester groups of PET seem to be more susceptible to saponification than those of PBT.

3.2. Influence of the matrix

The influence of the matrix on the water sorption rate (Fig. 4) and mechanical properties (tensile properties: Fig. 5 and impact properties: Fig. 6) was studied for both PET and PBT composites aged at 120°C and for PA66 composites aged at 135°C.

PA66 composites are more hydrophilic than polyester-based ones. Furthermore, higher water uptake values were obtained for PET composites in comparison with PBT composites at the same temperature. This result

seems to be in agreement with Bastioli et al. [5] and was attributed to the lower crystallinity of PET by these authors. Nevertheless, this result did not agree with those of Mohd Ishak and co-workers [3,11] who have observed that the equilibrium moisture content decreased with increasing fibre volume fraction because of a lower matrix fraction. In fact, PET composites have a higher fibre content (30 wt%) than PBT composites (15 wt%).

The initial impact strengths (Fig. 6) of PET and PA66 composites are similar but the latter show a better resistance after immersion in hot water. On the other hand, polyester-based composites showed a much more drastic decrease (related to chemical ageing) in ultimate stress than PA66 composites (Fig. 5), falling from 150 to 20 MPa (−86%) and from 200 to 100 MPa (−50%), respectively. Indeed, in addition to the physical ageing phenomenon, long-term ageing results in chemical ageing which is not thermoreversible as for physical ageing. The chemical changes can be characterised by the reduction in molecular weight as a result of chemical bond breakage and loss in weight associated with the migration of low-molecular-weight species.

Some authors [7] found that, for polyester materials, reactions involving chain ends occurred at a higher rate than random in-chain processes, enhancing the proportion of water-extractable products and the number of carboxyl end-groups. Knowing that each chain scission of PET chains uses up one water molecule and creates one carboxyl end-group, the hydrolytic reaction has been followed by measuring the number of carboxyl ends after various ageing times (Fig. 7). Following Pohl's method [12], samples were dissolved in boiling benzyl alcohol diluted with chloroform and titrated with sodium hydroxide. Results show an increase in carboxyl groups content with ageing time, due to chain breakage. Moreover, it is assumed that water diffuses into the amorphous regions of the polymer where hydrolysis occurs in a faster way. To complete this approach, Cagliaio et al. [13] have proposed an analysis by small-angle X-ray scattering

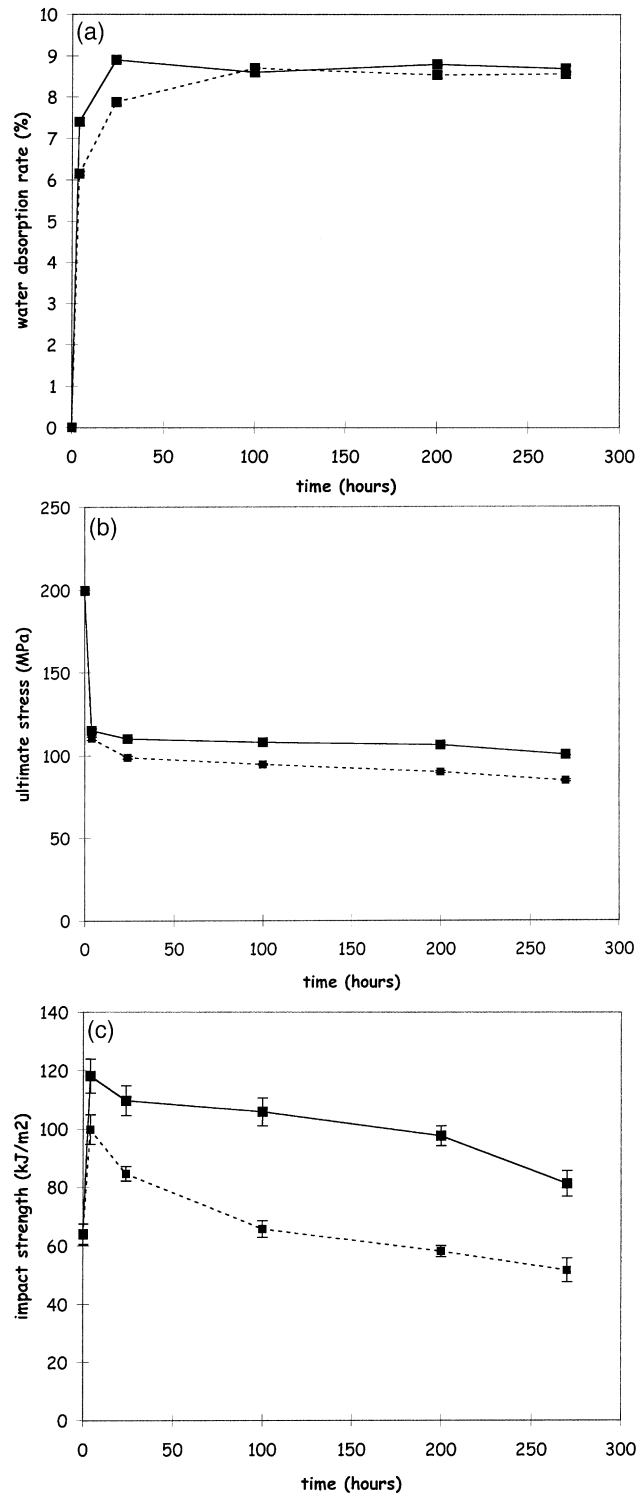


Fig. 9. Influence of the fibre coating (full line: without any specific component; dotted line: with a specific component) on the hydrothermal behaviour of PA66 composites: (a) water absorption rate, (b) ultimate stress and (c) impact strength.

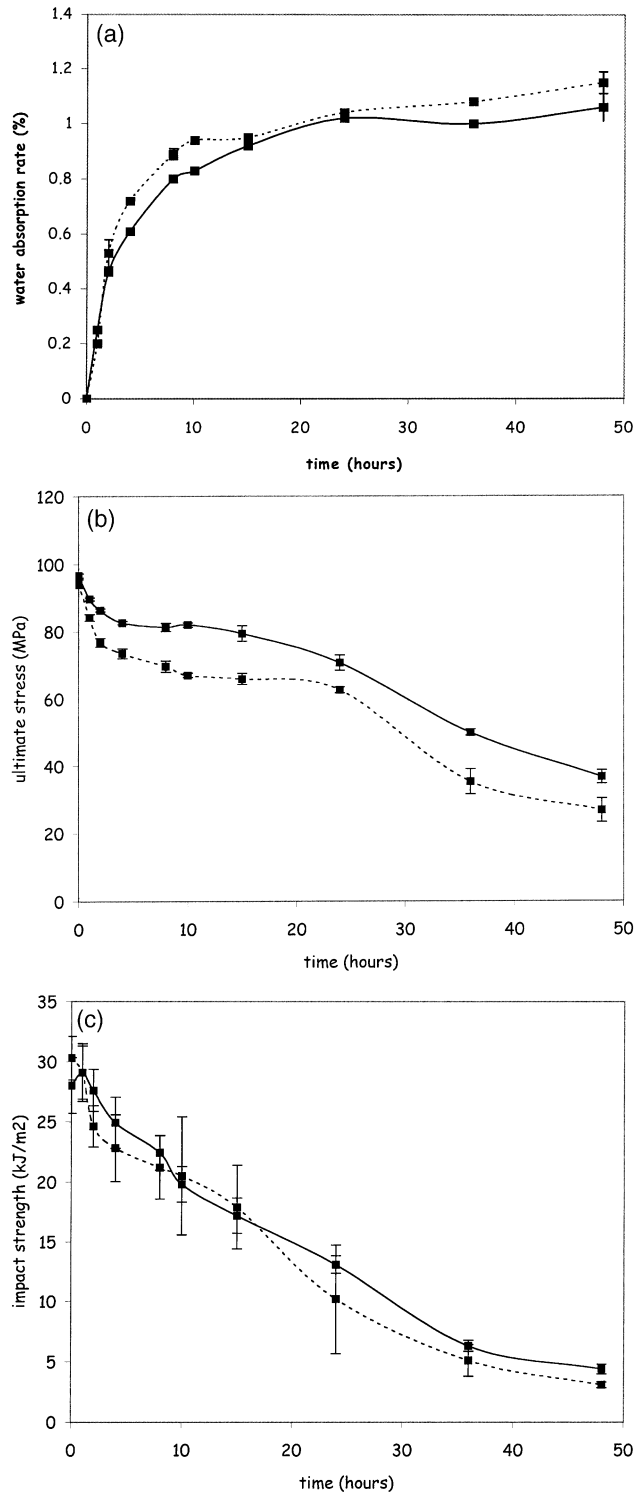


Fig. 10. Influence of the fibre coating (full line: with a specific component; dotted line: without any specific component) on the hydrothermal behaviour of PBT composites at 120°C: (a) water absorption rate, (b) ultimate stress and (c) impact strength.

(SAXS) to distinguish between amorphous regions within the material that are attacked differently by water according to the ageing time.

Concerning PA66 hydrolysis, the variations in the molecular weight according to the ageing time were determined by gel permeation chromatography (GPC). For that measurement, polyamide was functionalised [14] to become soluble at room temperature in classical solvents such as tetrahydrofuran and chloroform. Fig. 8 shows a decrease in the average molar mass from 16,000 g/mol (unaged sample) to 9000 g/mol (sample aged for 200 h at 135°C).

3.3. Influence of the fibre coating

The influence of the fibre coating has been studied for PA66 (Fig. 9) and PBT composites (Fig. 10). In both cases, a specific component was introduced into the formulation of the coating to reduce the decrease in mechanical properties due to the ageing environment.

Concerning PA66 composites, the presence of the specific agent in the coating seems to induce a lower water content at short ageing times below 100 h [Fig. 9(a)]. After this time the water mass uptake seems to be independent of the fibre coating.

Mechanical properties [Fig. 9(b) and (c)] show that the difference between both PA66 composites remains constant for ageing times longer than 100 h. It can be assumed that the chemical ageing of the matrix and the interphase is similar in both materials and is not affected by the presence of the specific component in the fibre coating. Nevertheless, only the physical ageing, i.e., the plasticisation of the matrix and/or of the interphase, should explain the difference observed at ageing times lower than 100 h. While mechanical data are distinct after an ageing time of only 2 h for the impact strength and 6 h for the ultimate stress, it can be suggested that only the plasticisation of the interphase should be delayed compared with the matrix plasticisation, because of a lower accessibility, which would explain the results. Improved interfacial adhesion and/or the existence of a network of polymer chains in the vicinity of the fibre in the presence of the specific component should explain the difference between the two PA66 composites. Moreover, Nagae and Otsuka [15] have shown that the improvement in interfacial compatibility and adhesion significantly influences the degradation of glass-fibre-reinforced plastics in water.

SEM observations of the fracture surface of PA66 samples aged for 200 h at 135°C (Fig. 11) revealed a lower fibre length after fracture in the presence of the specific agent. This observation should be related to a better interfacial adhesion. Moreover, the fibre surface is smooth when no specific component is introduced in the coating formulation, showing that hygrothermal ageing

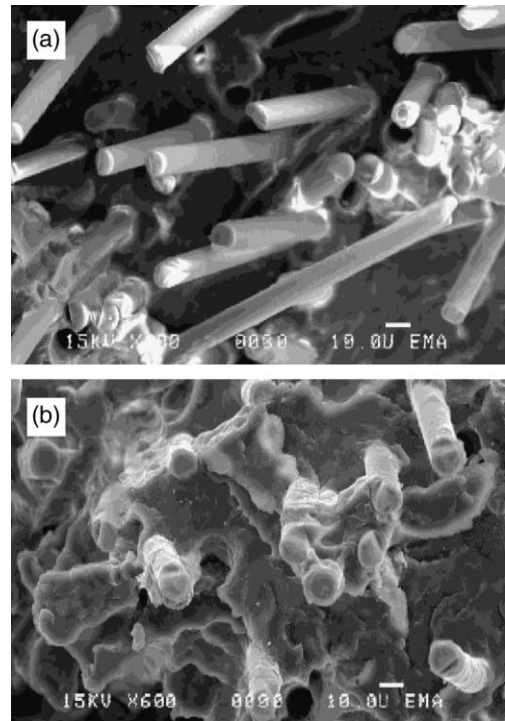


Fig. 11. Fracture surface of PA66 samples aged for 200 h at 135°C: (a) without any specific component and (b) with a specific component.

has reduced the effectiveness of the interfacial bonds in this case.

Concerning PBT composite, the presence of the specific agent in the coating lowered the water sorption rate [Fig. 10(a)] and differences in mechanical properties have been observed. Its presence seems to reduce the decrease in ultimate stress [Fig. 10(b)]. The shape of the variation in ultimate stress curve versus ageing time is different in comparison with those of the PA66 composites. In fact, after stabilisation until an ageing time of about 15 h, a more drastic fall was observed. The impact strength goes through a maximum only in the presence of the specific component [Fig. 10(c)] because of the plasticisation process. The moisture attack on the interface seems to be more serious and damaging for PBT composites when there is no specific component in the coating. Consequently, the efficiency of stress transfer is decreased.

In this way, each specific component introduced in the fibre coating seems to create a network of polymer chains that should explain the different sorption rates at the fibre/matrix interface.

4. Conclusion

Ideally, composite materials that are intended for long-term use should be tested in real time and with realistic in-service environments. This is not viable because the time involved would significantly delay product development, so that accelerated ageing tests are required. Therefore, a study of water sorption in three types of thermoplastic composite material has been undertaken which highlights a significant reduction in mechanical properties. An improvement of the hygrothermal behaviour should be obtained thanks to specific surface treatments of the fibre which induce a network of macromolecular chains at the fibre/matrix interface.

Acknowledgements

The authors are indebted to Vetrotex International Company, France, and especially to M. Michel Arpin and M. Jean Philippe Gasca, for materials, helpful discussions and financial support in carrying out a part of this work.

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