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Review article

Influence of the fibre/matrix interface on ageing mechanisms of glass fibre reinforced thermoplastic composites (PA-6,6, PET, PBT) in a hygrothermal environment

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ABSTRACT

A study of the properties of short glass fibre reinforced thermoplastic composites based on poly(ethylene terephthalate), poly(butylene terephthalate) and polyamide-6,6 in an aggressive environment is reported. The influence of the fibre/matrix interface on the composite behaviour in a moist environment is especially studied. Competitive phenomena may explain differences observed according to the nature of the fibre surface treatment. Among them these characteristics may be an intrinsic fragility of some chemical interfacial bonds, the hydrophilicity of some chemical groups, the presence of long macromolecular chains neighbouring the interface or of a transcrystalline interfacial area.

1. Introduction

Owing to their excellent mechanical properties, composite materials have been widely used throughout the last four decades. Their use in hostile environment has given rise to studies devoted to the durability of their properties. In fact, as those materials are subjected to:

- environmental stresses such as high and/or low temperatures, moisture/water attack, UV exposure, saline atmosphere, presence of micro organisms;
- mechanical stresses due to long term mechanical stresses.

Different mechanisms may occur simultaneously according to the severity of the exposure conditions and led to a decrease in the composite lifetime:

- physical ageing inducing mechanical degradation including plasticization of the matrix and swelling and release of internal stresses,
- chemical ageing inducing an irreversible chemical degradation such as hydrolysis of the matrix and the interphase and interfacial de-cohesion due to osmotic cracking.

This paper deal with the hygrothermal resistance of three commonly industrially used glass fibre reinforced thermoplastic composites: poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and polyamide-6,6 composites. In the literature most of studies have been focused on thermoset composites such as epoxies and unsaturated polyesters used for marine applications [1,2]. In this last case, the authors especially discussed interfacial de-cohesion induced by osmotic cracking damage. Nevertheless during this last decade considerable efforts have been devoted to understand the hygrothermal behaviour of glass fibre reinforced thermoplastic composites, such as polyimide [3,4], polyetheretherketone (PEEK) [5], poly(phenylene sulfide) (PPS) [5], polyamides [6–8], and saturated polyesters (PET, PBT) [9–17].

In these studies authors generally focus either on one property (for example mechanical properties) or on one ageing factor (for example moisture) so that the extrapolation to industrial cases should be considered with caution as well as models proposed for lifetime prediction.

Moreover investigations mainly concern only two approaches: a macroscopic (millimetre) approach that gives information on macroscopic mechanical behaviour of the composite materials as

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a function of ageing time and a microscopic (nanometre) approach that gives details on molecular, morphological and microstructural evolutions with ageing time. Most of the time no relationship has been established between these two approaches.

Finally the prediction of the long term behaviour of composite materials remains difficult due to the lack of knowledge of the long term behaviour of the interface/interphase between the matrix and the fibre because of the small scale involved. Different approaches have been investigated through macroscopic samples representative of the interfacial zone [18,19], through dynamic mechanical analyses [20] and through micromechanical tests such as pull-out, micro bond test [21–23], single fibre fragmentation test [24–26] and nano-indentation [27], but the extrapolation of the microscopic results to macroscopic behaviour should be considered in many cases with caution.

Therefore it is proposed in this paper to present a new multi scale approach. The objective of this approach is to create a link between the classical macroscopic (millimetre) approach (which gives information on macroscopic mechanical behaviour of the composite materials as a function of ageing time) and the microscopic (nanometre) approach (which gives details on molecular, morphological and microstructural evolutions with ageing time) by introducing an intermediate scale called mesoscopic (micron) scale that gives results on the local damage and potential stress accommodation.

2. Materials and techniques

2.1. Materials

Polymers used in this study were the following:

- terephthalate polyethylene PET 2153 ® supplied by Dolder Co. (Basel, CH),
- terephthalate polybutylene PBT Crastin ® supplied by Dupont de Nemours Co. (Geneva, CH),
- polyamide-6,6 PA-6,6 Zytel E101 ® supplied by Dupont de Nemours Co. (Geneva, CH).

Two kinds of glass fibres were incorporated in each polymer. The first was a glass fibre with a standard surface treatment which is compatible with the nature of the polymer matrix in which this fibre would be introduced. This fibre would be named ST_{PET}, ST_{PBT} or ST_{PA66} according to the nature of the polymer matrix. The second glass fibre is a glass fibre with a specific surface treatment which was formulated for an increased water resistance of the global composite in which the fibre will be incorporated. This fibre would be named SP_{PET}, SP_{PBT} or SP_{PA66} according to the nature of the polymer matrix. All the glass fibres were supplied by Saint Gobain Vetrotex International Co. (Chambéry, France).

For this study, simplified surface treatments were used for glass fibres based only on two components, i.e. a coupling agent and a film former agent. It is well known through a huge amount of literature showed that the coupling agent which is in mainly cases an organosilane will react, on one side with the glass surface through siloxane functions, and on the other side, with the other components of the glass fibre sizing or with reactive groups of the matrix. A very small number of papers [28,29] are published on film former agents, probably because of the reluctance of the glass fibres manufactures to reveal the composition of glass fibre surface treatments. Nevertheless it well known that the main role of film former agents is to protect the glass fibres during the fibre processing, to stick together the elementary filaments that form the glass fibre and to create chemical and/or physical linkages between the coupling agent and the polymer matrix. The composition of the different surface treatments used for this study are presented on Table 1.

The composite materials samples (ISO 527 type 1A dumbbells) were obtained through extrusion (Clextral BC21 twin screw extruder) and injection moulding (Sandretto Serie Otto AT). The glass fibres contents are in weight: 45% for PET composites, 15% for PBT composites and 30% for PA-6,6 composites.

2.2. Ageing tests

Different sets of hygrothermal conditions were chosen according to the nature of the polymer matrix and to the final industrial applications of the composite materials. Indeed as polyester composites would be used for electronic households devices, the corresponding ageing condition for these composites is the immersion in water at 120 °C in an autoclave under a pressure of 1.6 bars. Polyamide composites are used in some automotive applications such as under-the-hood devices, and especially anti-freeze containers of the cooling automotive system. Therefore the ageing condition is the immersion in water at 135 °C in an autoclave under a pressure of 2.8 bars. Samples were hung vertically in a Sanoclav MCS autoclave (20 l) and taken off at the chosen ageing time for the different characterisations. It can be noticed that these experimental ageing conditions are oxygen-free whereas real-life ageing will involve oxygen. Therefore following results may be lowered compared to the reality in some cases. The evolution of ageing as a function of oxygen concentration will be presented in a future paper.

2.3. Techniques

2.3.1. Static and dynamic mechanical techniques

Ultimate tensile properties (Adamel Lhomargy DY26 testing machine) and un-notched Charpy impact strengths (Zwick 5102) were investigated according to ISO 527 and ISO 75 International Standards respectively. Tensile tests were performed by using photomechanical techniques which lead to non-intrusive local and macro-homogeneous measurement of kinematic fields.

The dynamic mechanical properties were studied with a VA 815 Metravib RDS apparatus at a heating rate of 5 °C/min over a temperature range from −150 to 230 °C. The samples ($60 \times 10 \times 4$ mm^3) were tested using an imposed frequency of 10 Hz and an oscillation amplitude of 10 μm in the bending mode. The purpose of this analysis consisted in the determination of the main α relaxation characteristics for different ageing times.

2.3.2. Photomechanical techniques

The photomechanical technique is an optical method (white light source; high resolution CCD camera Kodak Megaplus 1.4 1024×1024 scared and joined pixels) which allows the evaluation of in-plane kinematic field without contact with a surface geometrical pattern during a uniaxial tensile test (Dartec M1000/RE 100 kN). A digital image correlation software (CinEMA ®, Ecole des Mines d'Alès, France) allows the quantification of the Green Lagrange strain tensor at any point of the surface of the tested

Table 1
Surface treatments of the different glass fibres used in this study.

	Glass fibres	Coupling agents	Film former agents
Standard glass fibres	ST_{PET}	Aminosilane	Polyurethane
	ST_{PBT}	Epoxysilane	Epoxy resin/amine agent
	ST_{PA66}	Aminosilane	Polyurethane
Water resistance glass fibres	SP_{PET}	Aminosilane	Mixture of two epoxy resins
	SP_{PBT}	Aminosilane	Epoxy resin/epoxy agent
	SP_{PA66}	Aminosilane	Polyurethane/acrylic agent