Composites Science and Technology 70 (2010) 1612–1620

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Macroscopic analysis of interfacial properties of flax/PLLA biocomposites

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ARTICLE INFO

Article history:
Received 19 December 2009
Received in revised form 31 May 2010
Accepted 2 June 2010
Available online 8 June 2010

Keywords:
A. Fibres
A. Polymer matrix composites (PMCs)
B. Interface
B. Interfacial strength
B. Delamination

ABSTRACT

This study presents results from a study of the mechanical behaviour of flax reinforced Poly(L-Lactic Acid) (PLLA) under in-plane shear and mode I interlaminar fracture testing. Slow cooling of the unreinforced polymer has been shown to develop crystalline structure, causing improvement in matrix strength and modulus but a drop in toughness. The in-plane shear properties of the composite also drop for the slowest cooling rate, the best combination of in-plane shear performance and delamination resistance is noted for an intermediate cooling rate, (15.5 °C/min). The values of G_{Ic} obtained at this cooling rate are higher than those for equivalent glass/polyester composites. These macro-scale results have been correlated with microdroplet interface debonding and matrix characterization measurements from a previous study. The composite performance is dominated by the matrix rather than the interface.

1. Introduction

The development of composite materials for large scale industrial applications, such as those in which glass reinforced polyester is currently employed, raises a number of environmental questions, particularly regarding end-of-life management. An increasing demand for materials which respect the environment has encouraged research into alternatives which are not based on fossil fuels and have a low global warming impact. One solution is to develop biocomposites such as flax fibre reinforced Poly(L-Lactic Acid) (PLLA). This type of material is recyclable [1] and bio-degradable by composting. In addition, the analysis of environmental impacts, evaluated from raw material extraction through to end-of-life, has shown that compared to glass/polyester composites their non-renewable energy consumption is divided by two. Different impacts such as global warming are also significantly reduced, though a transfer of pollution occurs towards eutrophication [2]. The quasi static tensile modulus values of biocomposites are satisfactory [1,3] but their failure stresses are lower than those of glass/polyester composites. At the micro-mechanics scale Le Duigou et al. [4], using a microdroplet test to measure Interfacial Shear Strength on flax/PLLA, showed good interface properties, comparable to those of a glass/polyester combination. The strength of the flax/PLLA interface is influenced by the morphology of the semi-crystalline PLLA matrix and by residual thermal stresses induced by thermal treatments [4].

However, in order to study the influence of interface behaviour on the mechanical properties of laminated composites a change of scale is necessary. A certain number of mechanical tests are often used to evaluate the macroscopic interface strength of composites [5]. Among these are transverse tensile, in-plane shear by tension on a ±45° laminate, short beam interlaminar shear, and interlaminar fracture tests. Few of these have been applied to biocomposites. Baley et al. [6] measured transverse tensile properties of flax/polyester composites. Their transverse strength was similar to that of glass/polyester composites (respectively 13 ± 0.6 MPa compared to 15 ± 2.5 MPa). Romhány et al. [7] used the tensile test on ±45° Materbi/flax biocomposite laminates. However, they presented their results in terms of tensile rather than in-plane shear properties as the transverse strain was not measured. There is very little data available on either interlaminar or intralaminar shear strength of biocomposites. Concerning interlaminar fracture, mode I tests on glass mat/PLLA biocomposite indicated a low G_{Ic} value of 39 ± 8 J/m^2 [8]. For comparison, the mode I fracture toughness G_{Ic} of a unidirectional glass reinforced polyester is around 90 J/m^2 [9]. Davies and Cantwell [10] and Perrin et al. [11] have shown how the microstructure of a semi-crystalline polymer matrix affects the delamination resistance of glass/PP composites. According to the cooling rate after moulding the G_{Ic} value for the composite varies from 220 J/m^2 to 1270 J/m^2. Faster cooling resulted in improved fracture energies. Herrera-Franco and Drzal [5] compared fibre–matrix adhesion measurements for carbon/epoxy with and without a fibre sizing, both at the micro-scale (microdroplet debonding, fragmentation...) and the macro-scale (tension ± 45°, Iosipescu, short beam shear...). Their study indicated similar trends for the influence of sizing at the two scales. Nevertheless

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doi:10.1016/j.compscitech.2010.06.001

some differences were seen, in particular due to the assumptions used in the calculations [5].

The aim of the present study is to evaluate the behaviour of flax/PLLA under in-plane shear and mode I delamination as a function of the parameters which influence fibre/matrix adhesion; these were previously shown in [4] to be the degree of crystallinity, the morphology of the matrix, and residual stresses. A comparison with results from the previous study, performed on the same fibres and matrix, will be made.

2. Materials and methods

2.1. Specimen manufacture

Specimens for in-plane shear were prepared according to ASTM D3518 [12] with PLLA reinforced by (±45°) flax layers. Fibre weight content is around 30%. The biopolymer is a thermoplastic Poly (L-lactic acid) or PLLA reference L9000 from Biomer®. The fibres were supplied, in the form of layers of two unidirectional tapes of untwisted yarns in a 0/90° configuration, stitched together with cotton thread, by C.R.S.T (France) with an areal weight of 500 g/m^2. The fibres were grown in France and had been dew retted before stripping and combing. The shear test standard requires a $[45/-45]_{ns}$ stacking sequence with $2 < n < 4$, and at least eight reinforcement layers to limit tension-flexion coupling [13] and increase the interlaminar area. Specimens were rectangular with the following dimensions: $(25 \times 160 \times 6.5)$ mm^3. They were prepared using the cycle shown in Fig. 1. Four conditions were examined; three different cooling cycles were applied, as shown in Fig. 2, plus an anneal below the glass transition temperature (T_g). Cooling rates were measured by insertion of thermocouples at mid-thickness of the samples. Fig. 2 shows measured values, with an almost linear cooling rate for slow cooling (A), the difference between the set moulding machine temperature and the specimen is small. At faster cooling rates the measured temperature is hyperbolic with a rapid drop to around 100 °C followed by a slower drop to room temperature. This shape can be explained by the thermal inertia of the material. The cooling rates presented subsequently are estimated using the slopes of the curves over the range of temperatures in which the polymer morphology and the residual stresses are strongly influenced by cooling rate. For semi-crystalline samples, this range is between T_{max} and melting temperature T_f. For the amorphous samples it is between T_{max} and T_g. The values of these temperatures were measured initially using Differential Scanning Calorimetry (DSC).

These three cooling rates were applied in order to obtain different morphologies in the PLLA matrix. An anneal for 72 h below T_g at 50 °C enables residual stresses, generated by rapid cooling (quench in water) to be released without developing crystalline structure. The annealing time is determined using DSC. An endothermic peak appears at T_g corresponding to the delayed reorganisation necessary to reach equilibrium.

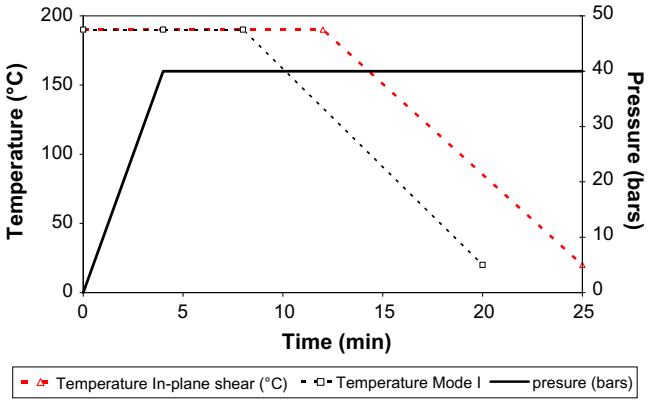

Fig. 1. Film stacking manufacturing cycle for in-plane shear and mode I specimens with water cooling (~15.5 °C/min).

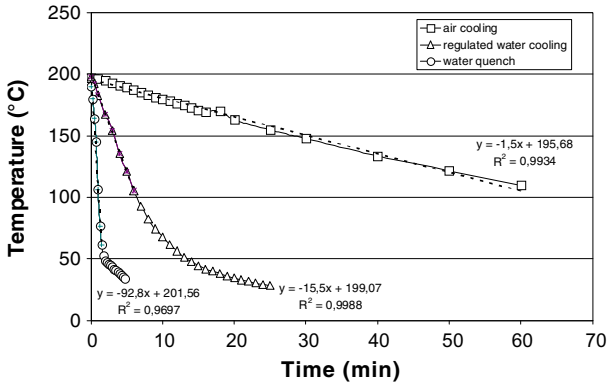

Fig. 2. Cooling kinetics for biocomposites.

The procedure to produce specimens for delamination resistance tests was similar to that described above, but with a shorter time at 190 °C (Fig. 1) as the thickness is less (4 mm compared to 6.5 mm). The fibre content is the same, but here the biocomposite tested is reinforced by flax in the form of mat. The ISO 15024 [14] standard is applied, although it is primarily intended for testing delamination of unidirectionally reinforced composites,

The flax mat is produced using a paper-making route. This results in a quasi-isotropic in-plane fibre distribution which is interesting as it minimizes the weaknesses of natural fibres, their poor transverse and shear properties [15]. The mat also allows fibres with 9 ± 1 mm length and a high aspect ratio ($L/d \approx 470$) to be used, as fibre bundles are separated during the mat production process. The mats used here have an areal weight around 150 g/m^2 and have not undergone any chemical or physical surface treatment.

A Teflon film 20 μm thick is inserted at mid-thickness during manufacture to provide a starter crack. This is slightly thicker than the ISO 15024 [14] standard recommends (<13 μm). It is also not possible to measure G_{Ic} values on these mat reinforced composites directly as their flexural properties are too low, so they are bonded to machined aluminium reinforcements of dimensions $(200 \times 20 \times 4)$ mm^3 (Fig. 4). Ten specimens with different initial starter crack lengths a_0 ($40 < a_0 < 75$ mm) were tested for each material.

2.2. Mechanical tests

2.2.1. Tension ±45°: in-plane shear

The in-plane shear specimens underwent similar thermal treatments to those applied to microdroplets previously [4] in order to be able to compare results. This tensile test on ±45° laminates was chosen as it is sensitive to interface and matrix properties. Tests were performed according to ASTM D 3518 [12] on an Instron 8803 machine with a 50 kN load cell, at a crosshead displacement rate of 2 mm/min. An MTS biaxial extensometer was used to measure longitudinal and transverse strains. This test provides shear stress τ_{12}, shear strain γ_{12} and shear modulus G_{12} values. Modulus G_{12} was determined from the slope of the plot of shear stress Eq. (1) versus shear strain (Eq. (2)) in the range γ_{12} range between 0% and 0.2%.

$$\tau_{12} = \frac{\sigma_x}{2} \tag{1}$$

where σ_x is the applied stress.