Materials and Design 66 (2015) 473–485

Contents lists available at ScienceDirect

Materials and Design

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

Thermo-mechanical performance of poly(lactic acid)/flax fibre-reinforced biocomposites

Elias Nassiopoulos [a], James Njuguna [b,*]

[a] Centre of Automotive Technology, Cranfield University, Cranfield, UK
[b] Institute for Innovation, Design and Sustainability, School of Engineering, Robert Gordon University, Aberdeen AB10 7GJ, UK

ARTICLE INFO

Article history:
Received 27 January 2014
Accepted 23 July 2014
Available online 1 August 2014

Keywords:
Polymer–matrix composites
Mechanical properties
Mechanical testing
Thermal analysis
Biocomposites

ABSTRACT

In this study, the thermo-mechanical performance of flax fibre reinforced poly lactic acid (PLA) biocomposites was investigated for the potential use in load bearing application such as body-in-white and body structures in the automotive sector. Focus was given into the relationships between the thermal and mechanical properties, and the material response under different loading and environmental conditions. The strength (72 MPa) and stiffness (13 GPa) of flax/PLA composites investigated indicate a very promising material to replace traditional choices in load bearing application. The PLA's crystallinity was measured to approximately 27%. Annealing above 100 °C for an hour decreased that value to 30%, but analysis of tensile results of annealed specimens reveals a significant reduction of both the tensile strength and modulus. This reduction is associated with micro-cracking that occurred on the surface of PLA during the heating as well as deterioration of the flax properties due to drying. The study results show that strength and modulus increased with increasing strain rates, while elongation at break reduces respectively. A modulus of 22 GPa was recorded in 4.2 m/s crosshead velocity. Further, flax/PLA showed significantly higher modulus than flax/epoxy for the composites studied. Improvement of the interfacial bonding and the temperature characteristics, combined the thermoplastic nature of PLA, demonstrates that flax/PLA composites is ideal for use in structural automotive applications.

1. Introduction

Natural fibre composites are fast emerging as viable alternative to traditional materials and synthetic composites. Their low cost, lightweight, good mechanical performance and their environmentally friendly nature makes them an ideal choice for the automotive [1]. The automotive industry has already embraced these composites for several years for the production of non-structural components and their use is predicted to constantly increase in coming years. On-going efforts are aimed at developing 100% structural composites utilising bio-sourced polymers as a matrix for natural fibres reinforcement as an alternative to synthetic fibres.

Flax fibres are considered to be one of the strongest and commercially available plant fibres. Its strength varies between 350 and 1500 MPa whilst its modulus can be as high as 80 GPa [2–8]. These properties combined with its very low density and excellent damping properties make flax fibres a very good alternative to glass fibres in structural applications. To date, research has shown that flax fibre reinforcements considerably improve the stiffness and strength of the matrix, whether thermoset or thermoplastic [9–11], with the performance being affected by the fibre length, volume fraction within the composite and the interfacial adhesion between the fibres and the matrix [11,12].

One of the most promising and suitable bio-sourced polymers is poly(L-lactide) (PLA). It is an aliphatic thermoplastic polyester derived from lactic acid found in renewable resources, such as corn, wheat, barley, cassava, and sugar cane [13]. Lactic acid is then polymerised to PLA, either by gradual polycondensation or by ring-opening polymerisation. Due to the chiral nature of lactic acid, several distinct forms of PLA exist: poly-L-lactide (PLLA) is the product resulting from the polymerisation of L,L-lactide (also known as L-lactide), while poly-D-lactide is produced from D-lactide. Polylactic acids are hydrophobic in nature and are among the few polymers in which the stereochemical structure can easily be modified by polymerising a controlled mixture of the L- or D-isomers to yield high molecular weight amorphous or crystalline polymers that can be used for food contact applications.

Recent research has shown that PLA is a highly suitable polymer matrix for natural fibres – reinforced composites. For instance, Tokoro et al. [14] mixed three types of bamboo fibres into a PLA

* Corresponding author. Tel.: +44 (0) 122 426 2304.
E-mail address: j.njuguna@rgu.ac.uk (J. Njuguna).

http://dx.doi.org/10.1016/j.matdes.2014.07.051
0261-3069/

matrix to improve its impact strength and heat resistance. Their studies resulted in good quality composite materials with the presence of the bamboo fibres increasing greatly the impact performance and thermal properties. Ochi [15] investigated kenaf/PLA composites with different fibre proportions. He reported that the Young's modulus, tensile and bending strength linearly increased up to a 50 wt.% fibre content in the composite. The study observed that unidirectional biodegradable composites fabricated using an emulsion-type PLA resin and kenaf fibres at a fibre content of 70 wt.% had high tensile and flexural strengths of 223 MPa and 254 MPa respectively. Shibata et al. [16] study prepared composites with PLA/lyocell fabric by compression moulding. The tensile modulus and strength of lyocell/PLA composites improved with increasing fibre content. Impact strength was considerably higher than that of pure PLA. Pan et al. [17] also produced PLA/kenaf composites by injection moulding with kenaf fibre contents ranging between 0% and 30%. At 30% a tensile strength improvement of 30% was observed.

The extended use of bio-composites for the manufacturing of vehicle components would benefit largely the industry, but to date their low mechanical properties associated mainly to the thermal stability and the interactions between the fibres and the matrix, restrict their use. Although studies report the properties and potential improvements of biocomposites, the overall mechanical behaviour from a structural point of view is not completely understood and mechanical performance is below the target. The properties of the biocomposites and their mechanical performance under different environments and their effect of different loading conditions are still not understood well enough for adoption in mass products in the transport industry.

In this work, therefore, we focused on developing further understanding on thermo-mechanical behaviour of PLA/flax biocomposites manufactured using compression moulding. The primary aims were to determine the phenomena dominating their mechanical behaviour and their potential use in structural automotive applications. The mechanical properties were evaluated through tensile testing in varying environmental and loading conditions simulating typical operational conditions. Thermal studies including dynamic mechanical thermal analysis and calorimetry were conducted. Microscopy was employed in order to investigate fracture surfaces and fibre/matrix interactions.

2. Materials and methods

2.1. Materials

A commingled/pre-impregnated PLA/flax fabric (mixed flax and PLA fibres) was used to manufacture the specimens. The poly(L-lactide) acid (PLA) was based on lactides acquired from corn starch fermentation (supplied by Natureworks@) and had 1.25 g/cm^3 density. The reinforcement used was a 2 × 2 twill flax weave with an approximate unconsolidated thickness of 0.8 mm (once consolidated the thickness is around 0.3 mm). All samples were prepared using a hot press moulding process with 12 layers of the fabric for the 3 mm samples and 16 layers for the 4 mm samples. The parts were moulded at 180 °C, 15 bar pressure and held there at maximum temperature for 5 min before cooling stage. The manufacture plates had 1.4 g/cm^3 density and they were then machined to produce test specimens. The manufacturing was tuned to result in samples with 40 vol.% flax. The volume fraction has a critical effect on the properties of natural fibre bio-composites. A value between 30% and 40% has been used in numerous studies and was proven to give natural fibre composites of high quality and thermo-mechanical properties [2,3,14,21,24]. It was observed that the properties will generally improve with an increased volume fraction, up to a certain value, after which further increase result in weaker components.

For PLA/fibre reinforced composites to be successful for structural applications, they will have to perform as well appreciated epoxy-based fibre reinforced composites presently used in the automotive industry. Hence good reference material for performance evaluation in this study.

Epoxy resins are widely used as structural adhesives in the aerospace and automotive, the aerospace and a wide range of products where high strength bonds are required. Epoxy resins are also very commonly selected from the automotive industry [1] for the manufacturing of natural fibre bio-composites, and are among the most studied resins to be combined with natural fibres [24] in the literature. Further, there is today a wide range of available bio-sourced epoxy resins (extracted from natural sources such as epoxidised vegetables oils (EVOs) like pine oil waste and soya oil, or waste streams of other industrial processes, such as wood pulp and bio-fuels production) in the European market and an increasing number of companies with extended knowledge on the production of natural composites using these resins. All epoxy/flax composite samples were manufactured by MaHyTec (France). In a typical process, a 0/90° balanced woven fabric (FlaxPly BL300) provided by LINEO was combined with a bio-sourced epoxy resin based on epoxidised pine oil waste (Epobiox LV with hardener Ca23) supplied by Amroy with a 50 vol.% fibre fraction. The plate samples (1.274 g/cm^3) were manufactured through compression resin transfer moulding (RTM) process. A pressuring force of 10 kN was used, with a sequential cycle of 2 h in 800 °C and 3 h with a temperature of 1250 °C. Finally the test samples were then cut out using a milling machine to meet the ASTM 3039 standard.

2.2. Characterisation

2.2.1. Microscopy

For the study of fracture surfaces obtained as a result of mechanical testing of samples and the morphology of the composite, a Scanning Field Emission scanning electron microscope (FE-SEM) was used; model XL30 from FEI, with an acceleration voltage of 15 kV. Before examination all samples were sputtered coated with gold/palladium for 2 min to avoid charging.

2.2.2. Dynamic mechanical analysis

To assess the temperature of decomposition and the rate of degradation of the materials DMA testing was performed. The DMA instrument used was a Q800 from TA Instruments equipped with a dual-cantilever bending fixture. The frequency was constant at 1 Hz and the temperature was set at 25 °C and then linearly increased by 1 °C per minute until 150 °C. The samples were cut into rectangles of 35 mm × 13 mm × 3 mm to accommodate the DMA. At least three samples per material were tested.

2.2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a TA instruments Q200 with aluminium sample pans, to evaluate the degree of crystallinity of the PLA in the composite. The glass transition temperature (T_g), cold crystallization and melting temperatures (T_m) were also determined. PLA was pulverized using a blade to scratch from composite panels' surface. The powdered samples, between 5 and 10 mg in weight, were packed into a stainless steel high volume DSC pan and sealed. Five samples were tested and heated between 25 °C and 200 °C with a rate of 1 °C/min in a nitrogen atmosphere. Two of the samples were also tested in cooling with the same rate for better understanding of the materials transitions.