Reactive & Functional Polymers 85 (2014) 193–200

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

The effect of cellulose nanowhiskers on the flexural properties of self-reinforced polylactic acid composites

Kazi M. Zakir Hossain [a], Reda M. Felfel [a,b], Chris D. Rudd [a], Wim Thielemans [c,d,*], Ifty Ahmed [a,*]

[a] Division of Materials, Mechanics and Structures, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom
[b] Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt
[c] School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom
[d] Process and Environmental Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 17 September 2014
Accepted 17 September 2014
Available online 28 September 2014

Keywords:
PLA fibre
Self-reinforced composite
Cellulose nanowhiskers
Flexural properties

ABSTRACT

Self-reinforced polylactic acid (SR PLA) composites incorporating cellulose nanowhiskers (CNWs) were produced by coating orientated PLA fibres with a polyvinyl acetate (PVAc)–CNW mixture as a binder prior to hot compaction at 95 °C. PLA fibres were produced with an average diameter of 11 (±0.9) μm via a melt-drawing process at 180 °C. Scanning electron microscopy (SEM) images revealed that the CNWs imparted roughness to the PLA fibre surface. Cross-sectional examination of the SR PLA composites after hot-pressing confirmed that the PLA fibres had maintained their morphology. Incorporation of 8 wt% CNWs within the SR-PLA composites revealed an increase in their flexural strength (48%) and modulus (39%) compared to the control composite (flexural strength ~82 MPa and modulus ~3.9 GPa). In addition, whilst the control SR-PLA composite revealed quite brittle characteristics, the addition of CNWs and PVAc gave the self-reinforced composite a more ductile behaviour.

1. Introduction

Self-reinforced composites (SRCs) have found widespread use for applications in the biomedical, construction and packaging industries [1,2]. The concept of self-reinforced composites was first developed by Capiati and Porter [3] who demonstrated that the orientation of aligned chains within the same polymer significantly improved their initial mechanical and fracture failure properties. In this process, fibres derived from the same polymer were heated above the glass transition (T_g) temperature but below their melting temperature (T_m) and compressed to produce composite plates using high pressure where the ultimate mechanical properties of the prepared composites depended on the molecular weight of the polymer and the fraction of aligned chains within the self-reinforced composites [4,5]. The selection of temperature, pressure and time are very important in order to maintain optimum reinforcing effect of the fibres in SRC processing [6]. Various techniques such as hot compaction [7], partial dissolution [8], cool drawing [9] and chemical modification [10] have been employed to manufacture self-reinforced composites. Several studies have reported on the successful production of SRCs using a wide variety of polymer fibres, including polyethylene (PE) [11–14], polypropylene (PP) [15,16], polyethylene terephthalate (PET) [17], polyamides [18,19], polylactic acid (PLA) [4,20,21], polyglycolic acid (PGA) [22,23] and polymethylmethacrylate (PMMA) [24,25].

For biomedical applications, fibres derived from biopolymers such as polylactic acid (PLA), polyglycolic acid (PGA), and their copolymer PLGA have been the most widely investigated for SRC processing [21–23]. Amongst them, PLA is one of the most common bioresorbable polymers utilised for internal bone fixation implants due to its favourable degradation and mechanical properties, and availability with different lactide contents (i.e. L/D ratio) [26,27]. In order to produce SRCs with superior mechanical properties, it is desirable to develop high modulus and high strength fibres. The mechanical properties of PLA fibres have been shown to be improved with aligning/orientation of the molecular chains during fibre spinning [28] and drawing processes [29–31]. For example, Mezghani and Spruiell [28] reported increased tensile strength and modulus of as-spun Poly(L-lactic acid) (PLLA) filaments from 80 MPa to 385 MPa and from 3.7 GPa to 6 GPa respectively, by decreasing the fibre diameter from 67 μm to 13 μm utilising a high speed winder drum (100–4700 m min^{-1}). They suggested that the improvement of tensile properties was attributed to an increase in crystallinity

* Corresponding authors at: Renewable Materials and Nanotechnology Research Group, KU Leuven, Campus Kortrijk, Etienne Sabbelaan 53, 8500 Kortrijk, Belgium (W. Thielemans).
E-mail addresses: wim.thielemans@kuleuven.be (W. Thielemans), ifty.ahmed@nottingham.ac.uk (I. Ahmed).

http://dx.doi.org/10.1016/j.reactfunctpolym.2014.09.012
1381-5148/

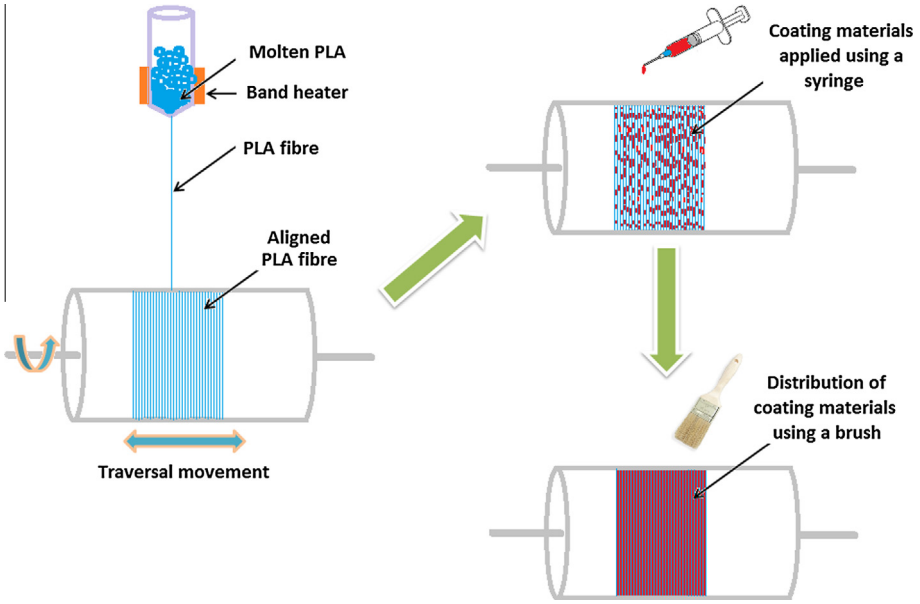

Fig. 1. Schematic of PLA fibre drawing and coating procedure employed to produce aligned fibre mat.

from 5% to 43% as a result of strain induced chain orientation within the polymer fibres.

For self-reinforced PLA composite processing, use of highly crystalline PLA filaments also showed significantly improved interfacial bonding due to the similar chemical structure of both matrix and reinforcing elements [32]. For example, Li and Yao [33] produced 0.5 mm thick single PLA composites using amorphous PLA sheets (5% crystallinity) and crystalline PLA yarn (40% crystallinity) via a compression moulding process at 140 °C, and reported that the self-reinforced PLA composite containing 25 wt% unidirectional PLA yarns (consisting of 135 continuous fibres with average diameter of around 20 μm) had improved the tensile strength by 31% and modulus by 48% when compared to the control PLA sheet (tensile strength ~44.8 MPa and modulus ~2.5 GPa). The flexural properties of a 3.2 mm thick self-reinforced PLLA composite produced via a hot compaction process at 95 °C were investigated by Wright-Charlesworth et al. [20] and reported that SR-PLLA had higher initial flexural properties (strength ~139.2 MPa and modulus ~5.4 GPa) when compared to non-reinforced PLLA (strength ~110.8 MPa and modulus ~3.9 GPa).

Although SRCs have shown a higher strength and modulus compared to the non-reinforced polymer, recent studies have also focused on the enhancement of the material properties through modification of the processing techniques [7] as well as through the incorporation of fillers [34–36]. For instance, Foster et al. [35] investigated the incorporation of carbon nanofibres (CNF) into hot compacted polypropylene (PP) woven tapes and also the addition of other nano and micro-sized fillers, such as talc, nanoclay, fly ash and carbon black. It was reported that all of the fillers improved the interlayer adhesion properties compared to the pure PP tape/film, which was confirmed via SEM images and peel testing.

Natural polymers such as chitosan [38], alginate [39] and cellulose [40,41] both in nano and microfibre form have also been incorporated in PLA for use in tissue engineering and biomedical applications. Cellulose nanowhiskers (CNWs) have widely been investigated in nanocomposites [40–44] processing due to their biodegradability [45–47], biocompatibility [48,49] and superior mechanical properties (tensile modulus ~105 GPa for cotton based nanocellulose) [50].

In this study, PLA fibre mats were prepared using melt-spun PLA fibres coated with a blend of cellulose nanowhiskers (CNWs) and polyvinyl acetate (PVAc). Recently, we investigated the blend of CNWs and PVAc as a coating material on individual PLA fibre surfaces, which demonstrated that a PVAc/CNW blend was beneficial by imparting surface roughness as well as increasing the mechanical properties of the fibre [51]. A composition of 75 wt% CNW and 25 wt% PVAc was found to have the greatest improvements, and this blend was used in the work presented here. The attachment of nanowhiskers onto the fibre mats was examined via scanning electron microscopy (SEM). The self-reinforced composites investigated in this study were produced via a hot compression process by laminate stacking the PLA fibre mats and the effect of CNWs and PVAc on the structural and mechanical properties of the composites are reported.

2. Materials and methodology

2.1. PLA fibre drawing

PLA fibres were produced via a melt-drawing process [52]. Briefly, vacuum dried (at 50 °C for 48 h) PLA beads (NatureWorks LLC, Ingeo™ Grade 3251D, average M_w ~90,000–120,000 g mol^{-1}, Density = 1.24 g cm^{-3}) were melted at 180 °C in air using a steel mould, which was heated with a band heater, and comprising a 2 mm hole at its base. Molten polymer exited through the base of the mould via the hole under the effect of gravity and was drawn downwards and collected on a drum using traverse mode at 0.025 mm spacing and rotating at 400 m min^{-1}, which was found optimal for the production of higher strength PLA fibres (Table 1) [51,52]. The drum had a diameter of 1 m with a collector distance of 50 cm from the steel mould.

2.2. Preparation of cellulose nanowhiskers (CNW)

CNWs were produced via acid hydrolysis of cotton (purchased from Fisher Scientific, UK) in aqueous H_2SO_4 (64 wt%) (Fisher Scientific, UK) for 45 min at 45 °C [40,53]. The hydrolysed cotton was washed with de-ionised water followed by centrifugation at 10 °C (three cycles, each at 10,000 rpm for 15 min) and then dialysed under running tap water for 48 h to ensure removal of free acid. Sonication was then carried out to homogenise the