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Preparation and properties of self-reinforced poly(lactic acid) composites based on oriented tapes

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ABSTRACT

The inherent brittleness and poor thermal resistance of poly(lactic acid) (PLA) are two main challenges toward a wider industrial application of this bioplastic. In the present work, through the development of self-reinforced PLA (SR-PLA) or "all-PLA" composites, the high brittleness and low heat deflection temperature (HDT) of PLA have been overcome, while simultaneously improving the tensile strength and modulus of SR-PLA. The obtained composites are fully biobased, recyclable and under the right conditions compostable. For the creation of SR-PLA composites, first a tape extrusion process was optimized to ensure superior mechanical properties. The results show that SR-PLA composites exhibited enhanced moduli (2.5 times) and tensile strengths (2 times) and showed 14 times increase in impact energy compared to neat PLA. Finally, the HDT of SR-PLA was also increased by about 26 °C compared to neat PLA, mainly as a result of an increase in modulus and crystallinity.

1. Introduction

Growing public concern and new environmental legislations have created a substantial driving force for manufactures to consider the environmental impact of their products at all stages of the life cycle. For this reason, biobased and biodegradable polymers have been the subject of many studies during the past decade. Poly(lactic acid) (PLA) is one of the most promising thermoplastic biopolymers because of its attractive mechanical properties, low emission of greenhouse gases, low amount of energy used for production, potential biodegradability and high industrial production capacity [1]. However, due to its high brittleness and low heat deflection temperature (HDT), PLA has not yet gained full market acceptance as an engineering resin. One possible strategy to improve the mechanical and thermal properties of PLA has been through the addition of natural fibres to make so-called "green composites" [2]. To optimize the composites' mechanical properties, a large number of research papers have dealt with different fibre modification methods, plasticizers, and combinations of different fibre types. Graupner et al. [3] gave a thoroughly overview comparing the influence of various fibres on mechanical characteristics of PLA based composites. Improved HDTs are often observed in natural fibre reinforced PLA composites, often due to an increase in modulus as well as crystallinity. Although the use of natural fibres to reinforce PLA seems at first to be an environmentally sound approach as they are renewable, there are some issues with respect to end-of-life scenarios for these composites. In the case of mechanical recycling their relatively poor thermal stability may lead to severe additional thermal degradation of the composites during subsequent reprocessing steps [4].

A promising approach to composite recycling is the concept of "self-reinforced polymer" composites (SRPs) or "all-polymer" composites, in which a polymer matrix is reinforced with oriented fibres or tapes of the same polymer. The absence of "foreign" reinforcements means enhanced fibre–matrix interfacial adhesion and more importantly, full recyclability without the need for separation of fibre and matrix. The concept was first presented by Capiati and Porter using oriented polyethylene (PE) reinforcement and PE matrix with different melting temperatures [5]. This film/fibre stacking technique, where using similar polymers with different melting temperatures to achieve melting of one phase to yield matrix, while retention of another phase to yield reinforcement, became a most frequently used technology that was subsequently published when creating SRPs based on other polymers [6]. In following several decades, it has been successfully transferred to a range of polymers using various consolidation technologies [6–9].

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In the early 2000s, Peijs and coworkers developed a co-extrusion technique based on polypropylene (PP) through which the processing temperature window could be widened to as much as 30 °C [6]. The volume fraction of reinforcement in these composites based on co-extruded tapes was extremely high (~90%), while various parameters could be used to adjust mechanical and interfacial properties [10]. Because of the large processing window, a wide range of composite fabrication techniques were demonstrated by Cabrera et al., including filament winding [11], non-isothermal stamping [12] and the creation of sandwich panels [13]. These SR–PP or all-PP composites are currently marketed under the trade name of PURE®. Following on from these successes, research into SRPs has moved towards other polymer systems such as PE [14], poly(ethylene terephthalate) (PET) [15], cellulose [16] and aramid [17].

In present work, another family of SRPs is being presented based on the biopolymer PLA. The main advantages of using biopolymer are to create performance products from sustainable resources, competing with fossil hydrocarbon sourced polymers, at the same time leaving open the possibility of composting as an alternative end-of-life option in addition to recycling. A flow diagram summarizing the life cycle of SR-PLA composites is shown in Fig. 1. PLA pellets can be synthesized from corn through a series of chemical routes. From these pellets, oriented PLA tapes are processed by extrusion and solid-state drawing. These tapes can be woven into fabric and subsequently consolidated into sheets. Finally, finished articles can be produced by thermoforming of these sheets. At the end of the products' life, they can be collected and mechanically recycled into other PLA based products such as packaging or even new SR-PLA composites. At the end of their life-time these PLA materials can finally be composted in a commercial composting facility.

To date, SR-PLA composites have been studied mainly for clinical use such as sutures, rods screws and plates. Improved strength and rigidity have been reported. Törmälä [18] manufactured SR-PLA by sintering of PLA fibres and studied the biodegradation of these composites *in vivo*. The initial flexural strength and shear strength of SR-PLA are 2.1 times and 1.4 times higher than the corresponding values of injection moulded PLA materials. This Finnish group developed a few other self-reinforced bioresorbable materials based on polyglcolides (PGA) and PLA for surgical implants [19]. Other groups also studied various physical and thermal treatments and their effects on widening the processing window [20]. Jia et al. [21] reported SR-PLA composites and PLA reinforced polybutylene succinate (PBS) (PLA–PBS) composites based on commercial textile grade Ingeo™ PLA yarns from NatureWorks®. Despite the fact that these Ingeo™ have rather limited mechanical performance, improved tensile strength and modulus were observed for both types of SRPs, with the highest improvements reported for SR-PLA. They explained this by the better properties of the PLA matrix compared to PBS and better interfacial adhesion in the case of SR-PLA. However, until now, impact behaviour and HDT of SR-PLA composites, which both limit the majority of applications of PLA, have not been studied. In the current work, highly oriented PLA tapes, with high tensile strength and modulus achieved by solid-state drawing, were combined with isotropic PLA films using a film-stacking technique into a "brick-and-mortar" structure. The optimization of a tape-manufacturing route for the creation of bio-based fully recyclable and potentially compostable composites is presented, together with an investigation of interfacial, mechanical and thermal properties of resulting SR-PLA composite laminates.

2. Experimental

2.1. Materials

NatureWorks® Ingeo™ PLA 4032D and 3051D polymers were used for the reinforcing tapes and the matrix phase, respectively. Both grades are poly(L-lactic acid) (PLLA). Unless otherwise specified, PLA in this paper always refers to PLLA. The weight average molecular weight (M_w) of PLA 4032D and 3051D are 133,500 and 72,633 g/mol respectively, as determined by means of gel permeation chromatograph (GPC) in chloroform with an AGILENT Technologies 1200 series, equipped with 2× Agilent PLgel Mixed D column and a pre-column. The melting temperatures (T_m) of the PLAs used are approximately 169 °C for the oriented tapes and 154 °C for the matrix phase, as measured by differential scanning calorimetry (DSC).

2.2. Manufacture of PLA tapes and SR-PLA composites

A Collin single screw extruder was employed to obtain a PLA extruded film. This extruded film was quenched by winding on a chill roll, followed by post-drawing on heated rollers to create an

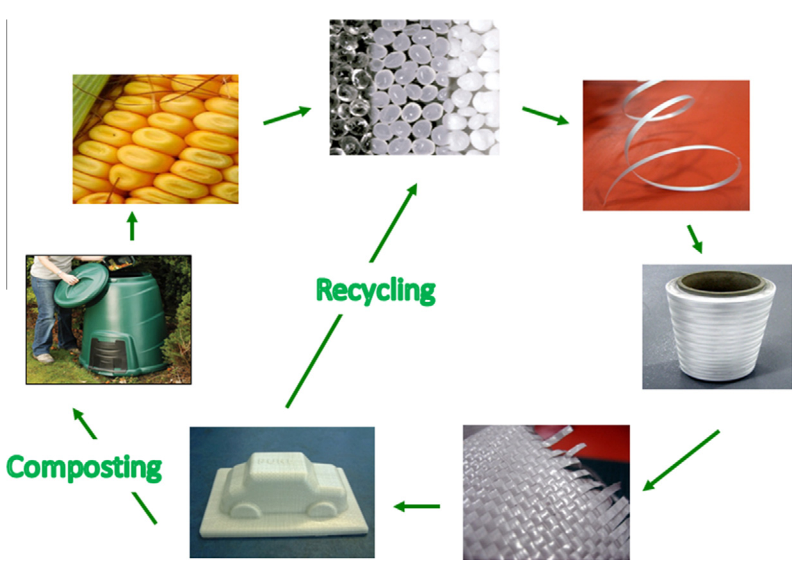

Fig. 1. Life cycle of SR-PLA composites. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)