Self-reinforced poly(lactic acid) nanocomposites of high toughness

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ABSTRACT

Self-reinforced poly(lactic acid) (SR-PLA) nanocomposites have been developed for the first time by using electrospun PLA fibre mats as a starting material followed by hot-compaction. During hot-compaction, the temperature was set while hot-pressing time was varied from 10 to 60 s to optimize processing conditions. The resulting transparent SR-PLA nanocomposite films were characterized using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and tensile testing. SEM observations confirmed that SR-PLA nanocomposites can be successfully prepared under the right conditions with hot-pressing time significantly affecting the composite microstructure. DSC results revealed that all SR-PLA films had considerably higher crystallinity with more stable crystallites and also a higher glass transition temperature when compared to bulk isotropic PLA film. Furthermore, a substantial improvement in both strength and ductility of these SR-PLA nanocomposites was observed in tensile testing. Of particular interest was the notable increase in toughness of the SR-PLA nanocomposite films as a result of their unique microstructure and related failure mechanisms.

1. Introduction

Agricultural-based poly(lactic acid) (PLA) has become increasingly popular because it has great potentials for a wide range of uses; for instance, as a commodity and an engineering plastic. PLA has numerous benefits, such as biodegradability, transparency, good strength, and is easier to process than most other biopolymers. However, its high brittleness and low heat distortion temperature (HDT) need to be significantly improved in order to fully gain market acceptance and further extend applications of PLA. For these reasons the reinforcement of PLA by ligno-cellulose based fibres such as flax, hemp or kenaf [1,2] or nanofillers like clays or carbon nanotubes [3,4] has been a very active area of research over the past decade.

An interesting alternative to traditional composites based 'foreign' fillers from an end-of-life and recycling point of view is the concept of "single polymer", "all-polymer" or "self-reinforced (SR) polymer" composites [5–8]. The concept was pioneered in the 1970's for polyethylene [9], and has later shown to be highly effective for other polymers such as polypropylene (PP) and poly(ethylene terephthalate) (PET). The preparation route for self-reinforced polymer composites typically relies on selective surface melting of oriented fibres or tapes, either mono- or bi-component to enhance the processing window, which upon cooling recrystallizes to form the matrix that binds the fibres or tapes together. The result is a fully recyclable, single polymer composite material with greatly enhanced mechanical properties as a result of remaining oriented fibre cores embedded in a recrystallized matrix.

More recently the concept has also proven itself as another effective way to create PLA-based materials with greatly improved mechanical and thermal properties as reported by Mai et al., Bocz et al., and Gao et al. [10–12]. In these works, SR-PLA or all-PLA composites were created by different techniques, including PLA tape extrusion followed by solid-state drawing and hot-pressing [10], filament winding, film-stacking and compression [11], or PDLLA solution impregnation followed by filament winding and hot-pressing [12]. Because of its ability to be absorbed into the human body and its non-toxic biodegradation products, the uses of SR-PLA composites, fabricated by melt spinning, drawing, and hot

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compaction, have also been previously investigated for medical applications such as sutures and fracture fixation plates [13,14].

Fully bio-based and biodegradable self-reinforced composites with remarkably high mechanical performance, toughness and/or transparency were introduced by a number of researchers based on all-cellulose nanocomposites [15–22] and/or cellulose nanopaper [23]. These all-cellulose nanocomposites were typically produced by means of partial dissolution of microcrystalline cellulose, cellulose nanofibrils, or bacterial cellulose in solvents like lithium chloride/N,N-dimethylacetamide or ionic liquids [15–22].

Inspired by previous works on SR-PLA and all-cellulose nanocomposites, here we aim to combine the advantages of self-reinforcement and nanofibre structures to create SR-PLA nanocomposites with a significant improvement in toughness and thermal properties. For this purpose, we developed a novel procedure consisting of two main steps; (i) electrospinning to prepare PLA fibre mats as a starting material and (ii) hot-compaction of these mats to create SR-PLA nanocomposites. The structure, morphology, and mechanical and thermal properties of these SR-PLA films were investigated using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and mechanical tests.

2. Experimental

2.1. Electrospinning of PLA fibre mats

PLA fibre mats were prepared by an electrospinning technique for later use in the fabrication of SR-PLA nanocomposites. PLA pellets (PLLA) with the intrinsic viscosity of 1.28 dL g^{-1} and crystallinity of 36.7% (determined by DSC analysis in the current work) from NatureWorks (USA) were used as-received and converted into electrospun mats using a PLA solution of 8% w/v in 7:3 v/v dichloromethane (DCM) and dimethylformamide (DMF) as a solvent system. Each PLA solution was poured in a 10-mL glass syringe, the open end of which was connected to a blunt 20-gauge stainless steel hypodermic needle (OD = 0.91 mm), used as the nozzle. Then each PLA solution was electrospun under a fixed electric field of 20 kV/18 cm. The feeding rate of the solution was controlled by solution gravity. It was not controlled by feeding pump. Yet, from the solution volume added in the glass syringe and electrospinning time, the estimated feeding rate of the PLA solution were around 4 ml/h. Relative humidity was controlled in the range of 55–60% RH. The collection time was ~2.5 h, resulting in fibre mats of 400 ± 10 μm in thickness.

2.2. Fabrication of SR-PLA nanocomposite films

PLA fibre mats with the size of 70 × 70 mm were cut from these electrospun mats. Next, four plies of PLA fibre mats were placed in a porcelain filter funnel connected to a vacuum system and then 30 ml of ethanol (absolute for analysis, supplied by Merck KGaA, Germany) was poured onto the stacked PLA mats to replace and remove any residual water from the mats since PLA has a tendency to absorb moisture from the air. It should be noted that if this ethanol rinsing step was not performed, PLA discoloration or degradation would occur in subsequent hot-pressing steps. Next, the stacked PLA mats were removed from the funnel and left at an ambient temperature for 30 min and then further dried in a hot air oven at 50 °C for another 15 min to ensure complete removal of the ethanol. The dried PLA mats were then cut into 16 rectangular samples and all were stacked into a square mould (30 mm × 30 mm × 150 μm) for composite film fabrication. The mould was then placed in a compression moulding machine (Scientific LP-S-80, Labtech Engineering) operated at a set temperature of 165 °C. Normally, in order to maximize the reinforcing effect of fibres in self-reinforced composites, the processing temperature window has to be carefully controlled for an adequate selective surface melting of the fibres, leading to a perfect interface as well as high degree of self-reinforcement [6,8]. However, for the hot-compaction of the electrospun nanofibres in this study, temperature was not varied as the processing temperature window in the case of polymer nanofibres will be even narrower than in the case of traditional hot-compaction. In traditional hot-compaction of mono-component micron-sized fibres selective the processing temperature window is around 1 °C [6], which would require a highly precise temperature control well beyond the capability of common hot-pressing equipment. Therefore, in the current study the hot-pressing temperature was fixed at 165 °C and was selected on the basis of the endset melting temperature of electrospun PLA mats as revealed by DSC analysis since then all crystals of different phases or lamellae thicknesses at the fibre surface will be melted. Therefore, instead of using temperature as the main hot-compaction parameter, here selective surface melting of the PLA fibres was achieved by varying the hot-pressing time from 10 to 60 s. Hence, the resulting nanocomposites were denoted as SR-PLA-10s to SR-PLA-60s, respectively. The hot-compaction process was set as follows: (1) preheating; 1 min 45 s, (2) venting; 2 s, (3) pressing at pressure of ~6 MPa; 10–60 s, and (4) cooling; 10 min. After this processing cycle, the film sample was removed from the mould and a SR-PLA nanocomposite was obtained. An isotropic PLA film was also prepared by hot-pressing PLA pellets (PLA) and used for comparison.

2.3. Thermal analysis

Thermal transitions of the film samples were studied using Differential Scanning Calorimeter (DSC) (Mettler Toledo 822e). A sample of 5–7 mg was heated from 40 °C to 250 °C with a heating rate of 10 °C/min. The corresponding glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m), and cold crystallization enthalpy (ΔH_{cc}) were determined. The crystallinity (χ_c) of each sample was calculated by comparing its melting enthalpy to that of the 100% crystalline PLA ($\Delta H_m°$ of 93.0 J/g) [24] through the following equation:

$$\chi_c[\%] = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100 \tag{1}$$

2.4. Mechanical testing

Tensile tests were carried out using a universal testing machine (Instron 5560), operating with an extension rate of 1 mm/min at 50% RH and room temperature (RT). The film tensile specimens were 3 mm in width and 15 mm in gauge length. The reported Young's modulus (E), tensile stress at yield (σ_y), tensile strength at break (σ_b), elongation at yield (ε_y), elongation at break (ε_b), and tensile toughness (U_T) as depicted by the area under the stress-strain curve were evaluated from five repeats for each sample.

2.5. Morphological observation

After tensile testing, the fracture surfaces of the film specimens were observed under a Scanning Electron Microscope (SEM) (LEO 1450 VP) at an accelerating voltage of 10 kV. The specimens were mounted vertically on aluminum stubs using aluminum adhesive tape. Prior to the examination, the specimen surfaces were sputter coated with a thin layer of gold.