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Polylactide single-polymer composites with a wide melt-processing window based on core-sheath PLA fibers

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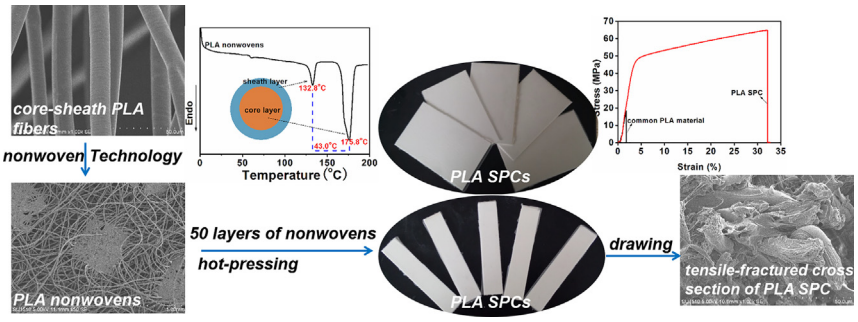
HIGHLIGHTS

- PLA single polymer composites are prepared using PLA nonwovens made of core-sheath PLA fibers as raw materials.
- PLA single polymer composites can be prepared on industrial scale.
- The melt processing window of PLA single polymer composites is more than 40 °C.
- PLA single polymer composites have excellent mechanical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Polylactide (PLA) single polymer composites (SPCs) were prepared using PLA nonwovens made of core-sheath PLA fibers as raw materials by hot-pressing. The core and sheath materials were poly(L-lactide) (PLLA) and PLA with D-lactide of about 10 mol% (PLA90), respectively. The melt processing window of PLA SPCs reached more than 40 °C. The effects of hot-pressing temperature on the crystallinity, the size distribution of crystallites, the lamellar thickness and mechanical property of PLA SPCs were significant while those of hot-pressing pressure were small. The strong interfacial adhesion between matrix and reinforcement led to high mechanical properties of PLA SPCs. For pure PLA materials prepared at 180 °C, the tensile strength (σ_b), elongation at break (ε_b), the work of rupture (W) and impact strength (α_{cU}) were only 19 MPa, 1.8%, 0.15 J, and 2.8 kJ/m^2, respectively while those of the SPCs prepared at 130–160 °C were 47–65 MPa, 15–32%, 9–22 J, and 14.9–67.2 kJ/m^2, respectively. With the increase of hot-pressing temperature, the σ_b, W and α_{cU} decreased.

1. Introduction

The matrix and reinforcement of single polymer composites (SPCs) are derived from the same polymer so that SPCs can be recycled and have strong interfacial bonding between matrix and fibers [1]. An increasing number of SPCs have been manufactured from various polymers, for example, polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), poly(lactic acid) (PLA), polyamide (PA), and poly(methyl methacrylate) (PMMA) [1].

PLA is a biocompatible, biodegradable and thermoplastic polyester synthesized from renewable resources [2–4]. Among the family of

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biomass-derived biodegradable polymers, PLA has relatively high strength and modulus [2,4]. It has been widely used as the matrix of fiber-reinforced composites. Work has also been reported on PLA SPCs. Törmälä et al. prepared PLA SPCs using PLLA fibers as reinforcement and poly(D,L-lactic acid) (PDLLA) as matrix [5]. They also prepared PLLA SPCs by partially fusing together softened PLLA fibers in pressurized cylindrical mold [5]. Jia et al. [6] and Wu et al. [7] also prepared PLA SPCs using a similar method. However, the precursor of both the matrix and reinforcement was PLA fiber so that the melt processing window of PLA SPCs was very narrow.

Li et al. [1] proposed that PLA as a slowly crystallizing polymer could be processed into physical forms with different crystallinity, from amorphous films to highly crystalline fibers. The amorphous PLA could be used as a matrix material. However, for amorphous PLA, two competing processes, fusing and crystallizing, exist during heating. It is well known that during preparing PLA SPCs, the fusion should be promoted while the crystallization in the matrix should be restricted. During the preparation of PLA SPCs by this method, the amorphous PLA should be rapidly heated to a suitable temperature between glass transition temperature (T_g) and melting temperature (T_m) so that it does not have time to crystallize. PLA SPCs with large thickness cannot be manufactured by this method because of the long time needed for thermal energy transfer from the SPC surface to its center.

Mai et al. [8] used highly oriented PLA tapes as the reinforcement and isotropic PLA film as matrix to prepare PLA SPCs. The highly oriented PLA tapes were pre-tensioned during hot-pressing to restrict the relaxation of molecular chain so that T_m of the PLA tape shifted to a higher temperature. This method widened the melt processing window of PLA SPCs. However, it is difficult to prepare PLA SPCs by normal hot-pressing device using this method because the additional tensioning device is required.

Kriel H et al. [9] prepared PLA SPCs using mats of core-sheath fibers of semi-crystalline PLLA (core) and amorphous PDLLA (sheath) through coaxial electrospinning. The T_m of semi-crystalline PLLA was high so that the melt processing window of PLA SPCs was wide. As the matrix (sheath layer) and reinforcement (core layer) were combined in the same fiber, the reinforcement was distributed evenly in the matrix. However, the crystallinity and orientation of the PLA fiber prepared by electrospinning was relatively low because of low tensile stress [10]. During hot-pressing process, shrinkage and disorientation of the reinforcement PLLA fiber happened easily. The matrix PDLLA was completely amorphous, which made physical aging of PDLLA happen easily. The above factors were probably the reasons why the obtained PLA films were brittle. In addition, the maximum end-use temperature of the amorphous PLA matrix was less than T_g (about 60 °C). Moreover, solution electrospinning usually involve toxic organic solvents, which are harmful to the environment. The low throughput of electrospinning also makes it difficult to produce PLA SPCs on an industrial scale by this method.

In order to overcome the shortcomings of the above methods, a new method of making PLA SPCs based on hot-pressing PLA nonwoven fabrics of core-sheath PLA fibers is investigated in this paper. The structure and mechanical properties of the obtained PLA SPCs were studied by differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), scanning electron microscope (SEM), tensile and Charpy impact tests. In the core-sheath PLA fibers, the core and sheath materials were PLLA and PLA with D-lactide of about 10 mol% (PLA90), respectively. The melting temperature of PLA90 and PLLA was about 130 and 170 °C, respectively, so that the melt processing window was able to reach more than 40 °C. The highest end-use temperature of the obtained composites was the melting temperature of PLA90. In addition, the matrix (sheath layer) and reinforcement (core layer) were combined in the same fiber so that the reinforcement could be distributed evenly in the matrix. Therefore, this method could prepare PLA SPCs with high fiber volume content. The core-sheath fibers were prepared by common melt spinning and the resultant nonwoven fabric was manufactured by thermal-calendaring, in which no solvent was involved. Commercially available devices were used during the preparation of PLA SPCs. The output of core-sheath PLA fibers and corresponding nonwoven fabrics was high so that PLA SPCs could be prepared on larger scale.

2. Experimental

2.1. Materials

The thermal-calendared nonwovens made of core-sheath polylactide (PLA) fibers with the diameter of about 14 μm were supplied by Hengtian Changjiang Biological Materials Co. Ltd (China). The area density of the PLA nonwoven fabrics was 19.4 g/m^2. The core and sheath materials were poly(L-lactide) (PLLA) and polylactide with D-lactide of about 10 mol% (PLA90), respectively. The weight ratio of core and sheath layers was 65:35.

2.2. Preparation of PLA SPCs

Firstly, the nonwoven fabrics were cut into rectangular specimens with a dimension of 100 mm × 20 mm. The length direction is the machine direction. Secondly, 50 layers of the PLA nonwoven specimen were placed in each hole of the mold. The diagram of the mold is shown in Fig. 1. Each mold contains five holes of the dimensions 100 mm × 20 mm × 1 mm. Thirdly, the mold with the nonwoven specimens was put on the holder of a CARVER 4128 hot-pressing machine (Carver Inc., Wabash, IN) and was hot pressed to make the PLA SPC samples. Finally, the mold containing the PLA SPCs was taken out from the hot-pressing machine and cooled to room temperature naturally. To study the effects of hot-pressing temperature and pressure on the structure and mechanical properties of PLA SPC, samples were made under 6 temperatures (120, 130, 140, 150, 160 and 180 °C) and 5 pressures (1, 2, 3, 4 and 5 MPa). The hot-pressing time was 15 min for temperatures of 120, 130, 140, 150 and 160 °C, but it was reduced to 5 min for 180 °C because intact samples could not be prepared by hot-pressing for 15 min. The PLA SPC samples were named in the form of PLA SP*C-P*, in which *T* and *P* stand for hot-pressing temperature and pressure, respectively.

Samples with 100 mm × 160 mm × 3 mm were also prepared by hot-pressing using 150 layers of the PLA nonwoven specimen to test impact properties of PLA SPCs.

2.3. Differential scanning calorimetry

The glass transition, physical aging, crystallization and melting behaviors of the samples were characterized by differential scanning calorimetry (DSC) with a DSC Q200 (TA Instruments®, Inc.). Nitrogen was used at a flow rate of 50 mL/min. The instrument was calibrated with In and Pb. The sample (4.0–6.0 mg) was heated from 0 to 200 °C at 10 °C/min.

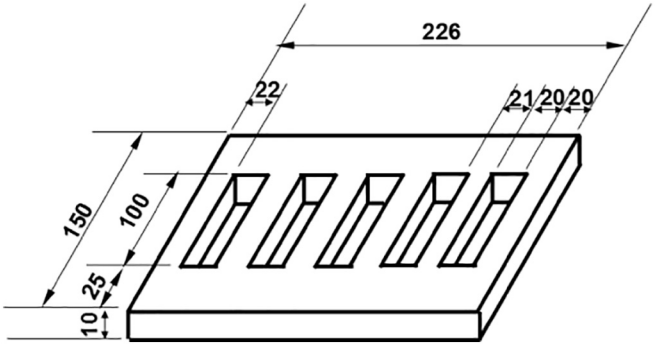

Fig. 1. The diagram of the mold.