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Thermal degradation of Polylactide/Poly(ethylene glycol) fibers and composite fibers involving organoclay

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ABSTRACT

In this study, electrospun fibers of melt blended poly(lactic acid) and poly(ethylene glycol), (PLA)-PEG blends involving 10, 15 and 20 wt% PEG and their corresponding composites with organically modified montmorillonite, Cloisite 30B were prepared and characterized by x-ray diffraction, differential scanning calorimetry, thermogravimetry and direct pyrolysis mass spectrometry techniques. The narrower fiber diameters observed for the PLA-PEG fibers involving organoclay compared to the corresponding neat fibers were associated with the presence of quaternary ammonium salt as organic modifier increasing electrical conductivity. Strong evidence for phase separation during the electrospinning process was detected for PLA-PEG fibers. On the other hand, for PLA-PEG composite fibers, as a consequence of the diffusion of both PLA and PEG chains from the bulk polymer into the galleries between the silicate layers of the organoclay, the interactions between PLA and PEG chains were enhanced and both components showed similar thermal characteristics, indicating lack of phase separation. These interactions further inhibited the interactions between the PLA chains and organic modifier of the organoclay

1. Introduction

Being biodegradable and biocompatible polymer the use of polylactide (PLA) has gained significant interest due to the environmental and economic concerns. Yet, due to the limited thermal and mechanical characteristics a great attention is given on the enhancement of thermal and mechanical properties of polylactides [1–11]. Among the several plasticizers used to improve properties of PLA, due to its miscibility, biodegradability, and food contactable application, poly(ethylene glycol), (PEG), is almost the most suitable material [12–23]. Yet, both miscibility and brittleness characteristics were found to depend upon the plasticizer content and molecular weight [14,15]. Although, different approaches were used for the incorporation of PEG in PLA such as physical blending, synthesis of copolymers (end functionalized, branched or block copolymers), coatings etc, the physical blending was the most widely used method of choice due to its simplicity. Nanocomposites of PLA/PEG blends were also prepared to improve physical characteristics further [24–27]. It has been determined that PEG molecules co-intercalate the silicate layers of Cloisite 30B, together with PLA, allowing better parallel stacking of the silicate layers and the interaction between them. With an increase in the PEG content, the decrease in the glass transition temperature and crystallization temperature of PLA nanocomposites were detected indicating the double role of PEG as a plasticizer and as a compatibilizer during the preparation of PLA nanocomposites [25,26].

In addition, preparation of PEG containing PLA fibers via electrospinning has been reported in several studies [28–32]. In a recent study micro- and nano-fibrous mats from PLA and PEG were prepared by electrospinning. PEG incorporation achieved using either physical blending, or chemical grafting did not significantly modify the surface wettability of the mats, yet showed a plasticizing effect on PLA as evidenced by DSC [28]. This effect was more pronounced in the case of the physically blended fibers in agreement with the higher PEG mobility.

In the present study, we report preparation and characterization of electrospun PLA-PEG fibers and composite fibers via X-ray diffraction, (XRD), Scanning Electron Microscope, (SEM), Differential Calorimetry, (DSC), and Thermogravimetry Analyses, (TGA) and Direct pyrolysis mass spectrometry, DP-MS analyses. As evidenced by direct pyrolysis mass spectrometry, PLA-PEG fibers containing organically modified montmorillonite resulted in thinner fibers with significant improvement in thermal stability.

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2. Experimental

2.1. Materials

Polylactide, PLA, (Mn ~ 190000), and poly (ethylene glycol) (Mn ~ 8000), were purchased from Cargill Dow. Polymer samples were dried at 60 °C overnight under reduced pressure prior to the mixing processes. The methyl tallow bis-2-hydroxyethyl ammonium modified montmorillonite, Cloisite 30 B (C30B), with cation exchange capacity of 90 meq/100 g clay, and interlayer distance d_{001} = 1.85 nm, was provided by Southern Clay Products Inc. All the materials were used as received.

The mixtures of PLA-PEG with appropriate blend ratios, (90/10, 85/15 and 80/20 wt/wt) and their composites involving 3 wt% C30B were melt-compounded using a DSM Xplore twin screw micro compounder at 190 °C, with a screw speed 100 rpm for 8 min. Solvents $CHCl_3$ (99%) and dimethylformamide, DMF, (99%) were obtained from Sigma Aldrich.

2.2. Preparation of fibers

Recent experiments done by changing the concentration of PLA from 3% to 20% (w/v) in $CHCl_3$/DMF solvent systems having varying compositions (v/v 100:0, 50:50, 60:40, 70:30, 80:20 and 90:10) indicated longer average distance between the beads on the fibers with the increase in the volume ratio of DMF in the solvent system, and reduction in beads and beaded fibers but with the increase in concentration of PLA [34]. However, as the DMF and PLA concentrations were increased thicker fiber diameters were generated. The optimum concentration of PLA in $CHCl_3$/DMF solvent system was determined as 15% (w/v) PLA in 90:10 v/v $CHCl_3$/DMF and these concentration values were selected for generation of PLA-PEG and PLA-PEG composite fibers by electrospinning.

The solutions of PLA/PEG blends and PLA/PEG-C30B composites prepared in 90:10 v/v in chloroform/DMF mixture solvent systems were taken into 1 mL syringes with metallic needle of 0.6 mm inner diameter. The syringe was positioned horizontally on a syringe pump (New Era Pump Systems, Inc NE 300) and the positive electrode of the high voltage power supply (was clamped to the metal needle (Fig. 1). The electrospinning parameters were selected as 0.5 mL H^{-1} for the flow rate of the polymer solution, 12.5 kV for the applied voltage and 10 cm for the tip-to-collector distance, as the most favorable results were obtained for these parameters. Electrospun nanofibers were collected on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil in an enclosed chamber at around 25 °C and 20% relative humidity. The nanofibers obtained were dried over night at 25 °C under vacuum in order to remove any residual solvent.

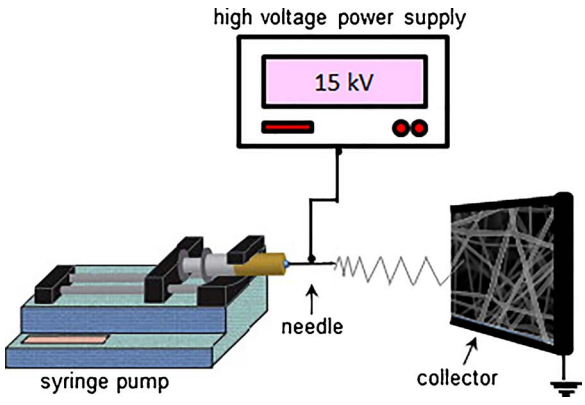

Fig. 1. Electrospinning system for generation of nanofibers.

2.3. Characterization

Rigaku X-ray diffractometer (Model, Miniflex) with CuK_α (30 kV, 15 mA, λ = 1.54051 Å) was used to obtain 2θ XRD patterns of the composites, at 25 °C in the 1° − 10° range.

Scanning electron microscope (SEM, Quanta 400 FEG, FEI) was used to investigate the morphology of nanofibers. Samples were coated with 5 nm Au/Pd (PECS-682) prior to the SEM imaging. Differential Calorimetry, (DSC) and Thermogravimetry Analyses (TGA) of about 5 mg samples were performed on a Perkin Elmer Instrument STA6000 under nitrogen atmosphere at a flow rate of 20 mL/min and a heating rate of 10° C/min. Direct pyrolysis mass spectrometry (DP-MS) analyses were performed using 5973 HP quadruple mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. 70 eV EI mass spectra, at a rate of 2 scan/s, were recorded. 0.10 mg samples in the flared glass sample vials were heated to 450 °C at a rate of 10 °C/min. Experiments were repeated at least twice to assess reproducibility.

3. Results and discussions

3.1. Morphology of PLA/PEG fibers

XRD measurements were used to determine the dispersion states of the Cloisites 30B in the PLA-PEG matrix. The diffractogram of Cloisite 30 B has a distinct maximum around 2θ = 5.0° corresponding to an inter-reticular distance of d_{001} = 1.8 nm. The characteristic peak of C30B was almost totally disappeared for 90/10 and 85/15% PLA/PEG blends involving 3 wt% C30B, whereas a weak peak was located at around 2θ = 4.5° corresponding to d_{001} = 2.0 nm in the XRD of 80/20% PLA-PEG-C30B composite

Fig. 2 The SEM images of electrospun fibers of PLA and PLA-PEG blends involving 10, 15 and 20 wt% PEG depicted in Fig. 3 revealed generations of bead-free fibers having diameters around 800–200 nm indicating slightly thicker fibers compared to neat PLA fibers in the presence of PEG [33]. However, no significant effect of amount of PEG present in the blend can be noticed.

Fig. 3 The SEM images of electrospun fibers PLA-PEG-C30B composites are shown in Fig. 4. The generation of slightly narrower fibers compared to neat PLA/PEG fibers in the presence of organically modified montmorillonite was attributed to the increase of electrical conductivity due to the presence of quaternary ammonium salt present as an organic modifier in the nanoclay. We observed a similar behavior for PLA and composites of PLA-organoclay fibers as proposed also in the literature [34–37].

3.2. Thermal properties

3.2.1. Differential scanning calorimetry analyses

DSC images of PLA/PEG fibers and composite fibers involving 3 wt % C30B are shown in Fig. 5. The corresponding curves for neat PLA, PEG and PLA/PEG blends are also included for comparison. The endothermic melting peak of PLA at around 172.3 °C was shifted to 165.7, 166.7 and 165.9 °C with the addition of 10, 15 and 20% PEG respectively, mainly due to the plasticizing effect of PEG and indicated generation of a miscible system [23]. The DSC curves of PLA/PEG fibers and composites fibers showed no noticeable shift for the melting peak of PLA compared to the corresponding blends. On the other hand, the cold crystallization temperature (T_{cc}) of PLA appeared at 86.2, 77.3 and 88.4 °C with addition of 10, 15 and 20 wt% PEG respectively. For the corresponding fibers, T_{cc} decreased to 77.0, 68.9, and 87.4 °C indicating easier crystallization. Upon addition of 3 wt% C30B, slight variations in T_{cc} were detected; T_{cc} value decreased to 75.1 °C from 86.2 °C for the sample involving 10%PEG, but increased to 71.7 and 90.0 °C for the samples involving 15 and 20% PEG respectively. The increase in T_{cc} values can be associated with the nanofiller-induced nucleation effect of the organoclay.