ELECTROSPUN BIO-NANOCOMPOSITE WEBS BY CELLULOSE NANOCRYSTAL (CNC)-LOADED POLYLACTIDE AND ITS BLENDS

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ABSTRACT

In this study, effects of polylactide (PLA) melt flow rate, and dichloromethane (DCM)/dimethyl sulfoxide (DMSO) solvent blend ratio on cellulose nanocrystal (CNC) dispersion quality in PLA/CNC bio-nanocomposites, prepared via solution casting, were studied. Besides, the electrospinning behaviour of CNC-loaded PLAs and its blends with poly(butylene adipate-co-terephthalate) (PBAT) was explored. The rheological analysis confirmed good CNC dispersion ability in PLAs with high melt flow rate specifically in solvents comprising DMSO. Besides, it was observed that CNC loading directly affected the morphological structure of the obtained nanofibrous webs. Thermal analysis indicated that CNCs acted as a nucleation agent and promoting the crystallization process by lowering cold crystallization temperatures and increasing the degree of crystallinity. The outcomes provide a groundwork for future studies on the fabrication of bio-nanocomposite webs from PLA/PBAT blends for a variety of applications.

KEYWORDS

Polylactide; Polybutylene adipate-co-terephthalate; Cellulose nanocrystals; Bio-nanocomposite; Nanofiber.

INTRODUCTION

Cellulose nanocrystals (CNCs) are highly regarded as a leading nano-reinforcement for bio-nanocomposites (BNCs) due to their distinctive attributes, including nano-scale size, outstanding mechanical strength, ease of chemical modification, high aspect ratio, low density, renewability, biodegradability, and biocompatibility [1]. BNCs are composed of bioplastics combined with either organic or inorganic nanofillers. Although inorganic nanofillers may hinder biodegradability, organic nanofillers are more compatible with bioplastics and minimize phase separation due to improved interfacial adhesion and affinity. CNCs are produced through acid hydrolysis, which selectively targets and hydrolyzes the amorphous regions within cellulose microfibrils. Besides, sulfuric acid is commonly used in this method to generate more stable CNC suspensions [2]. On the other hand, the interacting hydroxyl groups on the surface of CNCs and the sulphate half-esters formed during the sulfuric acid hydrolysis process may cause CNCs to agglomerate in hydrophobic polymers, such as PLA. The characteristics of the matrix, including the polymer's molecular weight and crystallizability, can influence the dispersion of CNCs and the resulting properties of nanocomposites [3]. Besides, the characteristic of organic solvent, i.e., polar-nonpolar nature and dielectric constant, directly affect the dispersion of CNCs in a polymer matrix [4]. In addition, a significant breakthrough in processing CNC-reinforced BNCs is the use of electrospinning to create continuous one-dimensional fibers with diameters ranging from microscale to nanoscale. This technique enables the alignment of CNCs under strong electrostatic fields, orienting them along the fiber axis and greatly enhancing the axial strength of the electrospun nanocomposite fibers. Accordingly, in this study, polar/nonpolar binary solvent systems, and PLAs with different molecular weights were utilized to develop PLA-based nanocomposites via solution casting method, and CNC dispersion quality was investigated. Afterwards, the electrospinnability of PLA-based systems with various solvents was controlled, and key properties of BNC nanofibers were investigated.

Table 1. Properties of different PLA grades [5].

PLA Code	Melt flow rate (MFR: g/10 min, 210°C)
HPLA	6-10
MPLA	15-30
LPLA	70-85

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Table 2. Properties of the solvents [6].

Solvent	Polarity	Solubility Parameter, δ $[Cal/cm^3]^{1/2}$	Dielectric constant, ε	Boiling Point [ºC]
DCM	Non-polar	9.7	9.10	40
DMSO	Polar	12.9	48.9	189

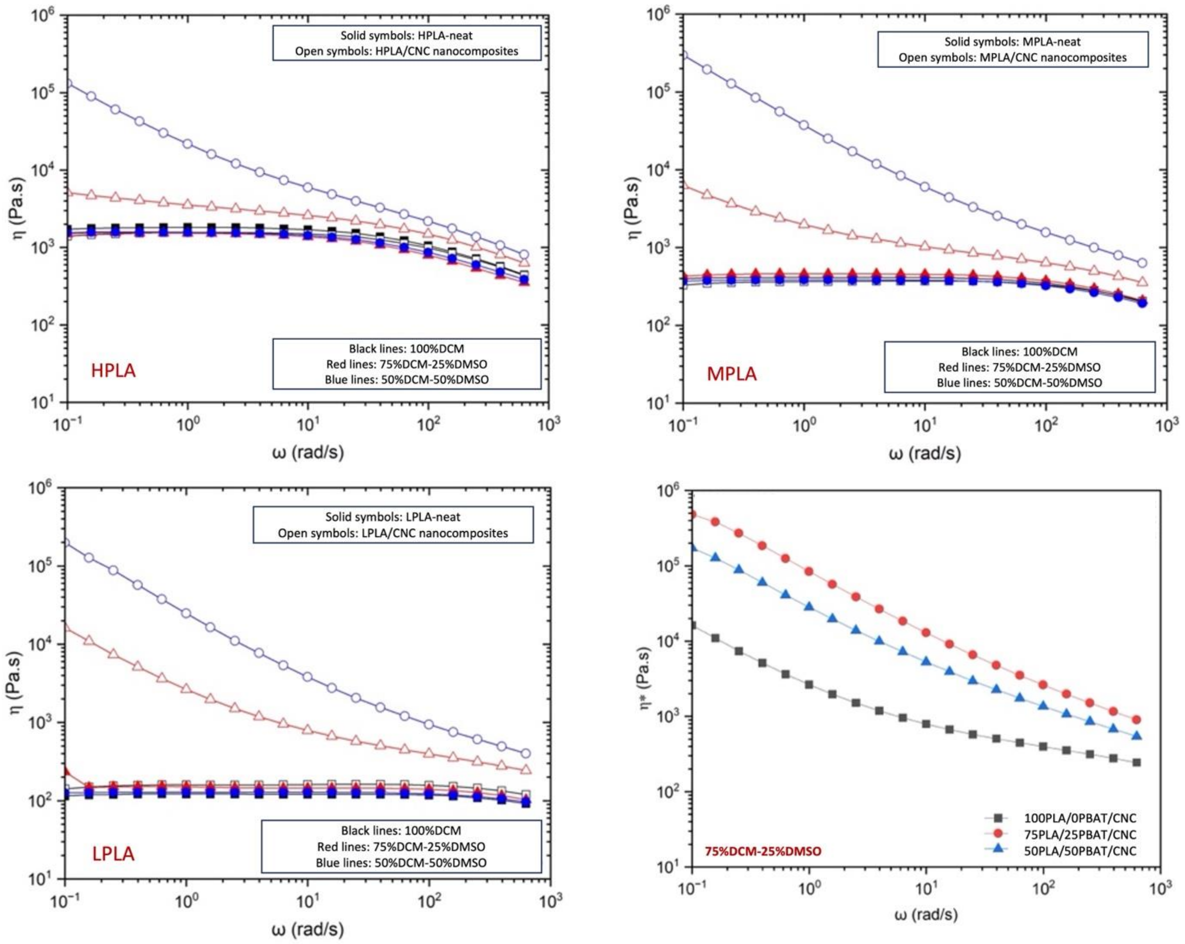

Figure 1. Complex viscosity versus angular frequency of bio-nanocomposites of (a) HPLA, (b)MPLA, and (c) LPLA (d) LPLA/PBAT blends with 3 wt.% CNC.

EXPERIMENTAL

Materials

Commercial semicrystalline PLAs with different melt flow rates (MFR) were kindly supplied by NatureWorks LLC, USA. PBAT, Ecoflex® F Blend C1200, having a polydispersity of 2.0 and an average molecular weight of 1.05×10^5 g/mol, was donated by BASF, Ludwigshafen, Germany. Spray-dried CNC in powder form was provided by CelluForce (Montreal, Canada). Organic solvents of dichloromethane (DCM) and dimethyl sulfoxide (DMSO) were purchased from Merck and Isolab Chemicals, respectively (Table 2).

Methods

CNCs were dispersed within the solvents in a water bath sonicator for 2.5 h at room temperature. Then, PLAs and PLA/PBAT granules were added to the CNC-solvent mixture and stirred on a magnetic stirrer for 3 h. Different solvent blends, i.e., 100%DCM (100DCM), 75%DCM/25% DMSO (75DCM/25DMSO), and 50%DCM/50%DMSO (50DCM/50DMSO) were employed. The CNC content in PLA based bio-nanocomposites was constant at 3 wt.%. When polymer granules were fully dissolved, polymer solutions were poured into glass petri dishes, and they were dried at 85°C in a vacuum oven.

The selected polymer solutions were individually loaded to a 1 mL syringe, with a metallic needle of 27 G, and delivered to the syringe pump in a horizontal electrospinning system. The electrospinning parameters of feed rate, voltage, and tip-to-collector distance were kept constant at 1.0 mL/h, 18-20 kV, and 15 cm, respectively. An MCR-301 rotational rheometer with a parallel plate geometry was utilized to conduct the small amplitude oscillatory shear rheological analysis. A scanning electron microscope, Tescan Vega3, was used to conduct morphological analysis at 20.00 kV. A Perkin Elmer DSC400 differential scanning calorimetry was utilized to investigate the crystallization and melting behaviors.

RESULTS AND DISCUSSION

Rheological properties of BNCs

Figure 1 shows the complex viscosity versus angular frequency of bio-nanocomposites of HPLA, MPLA, LPLA, and LPLA/PBAT samples with 3 wt.% CNC. The low frequency upturns in complex viscosity indicate CNC networking formation. Accordingly, the use of DCM solely allowed the lowest degree of CNC dispersion within all PLA matrices, while solvent blends with higher DMSO contents enabled the most homogenous dispersion of CNCs. Among three types of PLAs, LPLA bio-nanocomposites had the highest relative increase in their complex viscosity with the DCM50/DMSO50 solvent blend, and with DCM75/DMSO25 also having a significant effect. On the other hand, CNC dispersion quality was suppressed in bio-nanocomposites with PLAs having higher molecular weights. Besides, when PBAT was blended with LPLA at different weight ratios, i.e., 25 wt.% and 50 wt.%, major upturns at the low frequencies were observed, indicating CNC networking formation, as well.

Crystallization behavior of BNCs

1st heating cycles showed that neither the solution-casted films of neat PLAs nor PLA/CNC bio-nanocomposites showed cold crystallization, indicating all PLAs were almost fully crystallized during the drying step of solution casted film production. At DMSO concentrations of 25% v/v, neat PLA samples exhibited a double melting peak, which could be due to imperfect crystallinity in the PLA, attributing to the plasticizing effect of residual DMSO within the polymer matrix. During 2nd heating scans, cold crystallization temperatures of neat PLAs were always higher than those of PLA/CNC bio-nanocomposites, indicating CNC acted as a nucleation agent and promoting the crystallization process by lowering T_{cc} and increasing the degree of crystallinity.

Morphological structure of BNC-nanofibers

Based on the rheological analysis, low molecular weight PLA was chosen as the optimum PLA grade and used in electrospinning method (Figure 3). Moreover, as the obtained results showed that the blend ratio of 75DCM/25DMSO provided a good CNC dispersion for LPLA grade, this blend ratio was selected to fabricate PLA/CNC bio-nanocomposite webs as well. The average fiber diameter of neat LPLA decreased from 1510 ± 200 nm to 1218 ± 205 nm with an addition of 1 wt.% CNC; then a dramatic drop to 342 ± 97 nm was observed when the CNC ratio was 3 wt.%. The results showed that 3 wt.% CNC-loaded LPLA/PBAT bio-nanocomposite webs were successfully produced; however, bead formation was observed in 100PLA/0PBAT. The addition of PBAT, i.e., 25 w/v% and 50 w/v%, to the structure resulted in more homogenous fibers with a higher mean fiber diameter (Figure 4).

Table 3. Thermal properties of BNCs.

	1st heating			2nd heating		
Sample	**T_{cc} [°C]**	**T_m[°C]**	**X_c[%]**	**T_{cc}[°C]**	**T_m[°C]**	**X_c[%]**
HPLA	-	162-166	56	-	167	5
HPLA/CNC	-	165	48	113	167	8
MPLA	-	158-162	53	-	162	5
MPLA/CNC	-	162	51	111	164	4
LPLA	-	158-169	35	105	169	23
LPLA/CNC	-	168	60	103	169	36

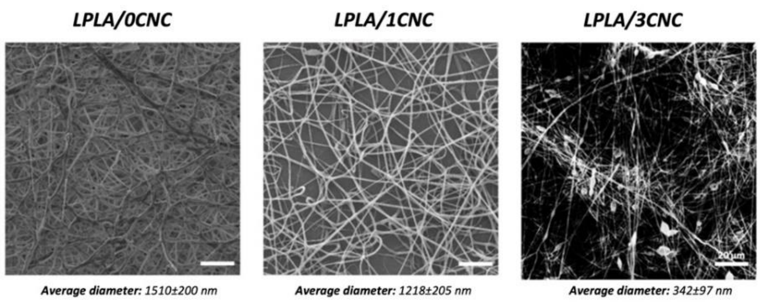

Figure 3. Electrospun bio-nanocomposite webs of LPLA having different CNC content levels.

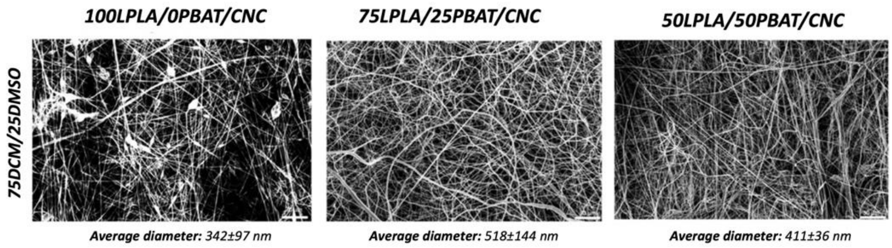

Figure 4. Electrospun bio-nanocomposite webs of LPLA/PBAT blends having 3 wt.% CNC.

CONCLUSIONS

In this study, the effects of utilizing binary solvent system of DCM/DMSO at different weight ratios, PLAs with various melt flow rates, and PLA/PBAT blends, on CNC dispersion quality through rheological analysis were revealed. The effect of CNC addition on the thermal characteristic of solution cast films were also investigated; besides, the electrospinnability of the bio-nanocomposites were studied as well. The findings provide valuable insights for optimizing the preparation of PLA/CNC bio-nanocomposites, highlighting the importance of selecting appropriate solvent blends, molecular weight of PLA and PLA/PBAT blend ratios to achieve good dispersion quality via solution solution-casting and electrospinning.

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