NOVEL METHOD OF COMPOUNDING CELLULOSE NANOCRYSTAL SUSPENSIONS INTO POLY(LACTIC ACID) AND POLY(VINYL ACETATE) BLENDS

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Abstract

Cellulose nanocrystal (CNC) suspensions were compounded into blends of poly(lactic acid) (PLA) and poly(vinyl acetate) (PVAc) using a novel wet compounding approach in which drying and compounding were carried out simultaneously. The resulting CNC/PLA composites were compared with those produced using a more traditional method of freeze-drying CNC suspensions followed by melt-blending into PLA. CNCs in wet compounded composites appeared to be well-dispersed in the PLA/PVAc blends, and films extruded from these compounds exhibited high transparency compared with melt-blended composites. Gel permeation chromatography indicated that molecular weight degradation due to wet compounding was comparable to that from melt blending. The formulation, including surfactant modified CNCs and PVAc processing aids, played a significant role in the dispersion and properties of the nanocomposites. The elimination of a stand-alone drying step for cellulose nanomaterials can potentially overcome some of the challenges associated with producing thermoplastic cellulose nanocomposites and help advance commercialization of these materials.

Introduction

Plastic waste is a growing problem nationally and globally, and although no clear remedy has emerged, many regard sustainable biobased and biodegradable polymers as a possible solution, especially for single-use plastics, and some industry has responded by committing to increasing sustainable packaging usage[1-3]. Poly(lactic acid) is one of the most commonly used bioderived and biodegradable thermoplastics[4 ,5]. However, such biopolymers currently suffer numerous drawbacks, especially in their performance and processability. For example, PLA is more brittle than polyethylene or polyethylene terephthalate and is a poor water vapor and moderate oxygen barrier. Some of these challenges can be mitigated by using additives, including plasticizers for brittleness or nanomaterials for barrier improvements. For example, the water and oxygen transmissions across PLA films were shown to be reduced by 30 and 75%, respectively, by adding as little as 1% CNCs in our previous work[6].

Although cellulose nanomaterials have been repeatedly shown to improve numerous properties of nanocomposites, including mechanical and barrier properties, challenges continue to exist for producing thermoplastic cellulose nanocomposites[6-21]. One of the most difficult problems to overcome is drying cellulose nanomaterials without losing their nanoscale structures. Spray drying and freeze drying are two popular methods being employed by researchers, but those processes often result in agglomerated fibers or particles with micrometer-scale diameters. Freeze-drying can yield plate-like structures of CNCs, and it is possible for these agglomerated CNCs to improve the mechanical and barrier properties of polymers. However, these agglomerated particles often result in reduced mechanical performance and typically have undesirable appearance due to agglomeration. Here, we describe a method in which cellulose nanomaterials can be compounded and dried in a single process using a thermokinetic mixer and which results in improved dispersion over dry compounding techniques.

Cellulose nanocomposite properties are highly dependent on the formulation, including surface modification and compatibilizers, and developing these formulations remains an intensive area of research. For example, Ansari et al. found that modifying CNCs with dodecyl trimethyl ammonium chloride (DTAC) dramatically improved the mechanical properties of poly(vinyl acetate) (PVAc) compared to both neat PVAc and unmodified CNC-PVAc nanocomposites, resulting in nanocomposites with higher transparency compared to unmodified CNCs[22]. PVAc is miscible with PLA and has been successfully used as a dispersion medium for cellulose nanocrystals in PLA[23, 24]. Because the wet compounding process involves compounding in the presence of water, materials that are compatible with water are desirable. DTAC is readily adsorbed to CNCs in aqueous suspensions, and numerous PVAc-water emulsions are available commercially. Therefore, here we evaluate the effects of surface modifying CNCs with DTAC and of including PVAc on the properties of wet compounded PLA-CNC nanocomposites.

Additionally, operating conditions of the thermokinetic mixer are expected to impact the properties of wet compounded nanocomposites. Our previous research indicated that discharging PLA-CNC compounds at lower temperature lead to improved properties compared to higher temperature[25]. Therefore, here we also examine the effect of discharge temperature and mixing speed on wet compounded nanocomposite properties.

Materials

PLA (Ingeo^{TM}, 4044D) was obtained from NatureWorks LLC® (Minnetonka, MN, USA) in pellet form. PVAc with a molecular weight of 500,000 g/mol was purchased from Sigma Aldrich® (St. Louis, MO, USA). DTAC was purchased from Fisher Scientific Co. (Pittsburgh, PA, USA). CNCs were produced at the Forest Products Laboratory (FPL) from Eucalyptus Kraft pulp by hydrolysis with 64 % sulfuric acid in a process described previously[26].

Methods

For this study, PLA-cellulose nanocomposites were produced using a wet compounding approach, and the compounds were then cast extruded into films. The effects of processing conditions and formulation on nanocomposite properties were evaluated by tensile testing, ultraviolet-visible (UV-Vis) spectroscopy, optical microscopy, and gel permeation chomotography (GPC).

CNC Modification & Nanocomposite Production

CNCs were modified with DTAC by adding the surfactant to a CNC suspension at a 1:1 molar ratio of DTAC to CNC- sulfate groups, on which positively charged DTAC is expected to ionically bond[22]. The CNC suspension was diluted to 1%, and the pH was adjusted to 10 using sodium hydroxide prior to DTAC addition.

Figure 1: Thermokinetic mixer shown with open chamber

PLA pellets were frozen with liquid nitrogen and ground using a Wiley mill into a powder passing through a 1 mm screen. A thermokinetic mixer (Synergistics Inc., St. Remi de Napierville, Quebec, Fig. 1) was used to simultaneously dry and compound aqueous CNC suspensions with PLA and/or PVAc granules/pellets. After discharge from the kinetic mixer, the compounds were cryogenically granulated again in a Wiley mill. Wet compounding controls were also created in which water with no cellulose was added to PLA in the kinetic mixer. Films were then cast using the DSM Xplore microcompounder (DSM Research, The Netherlands) with a slit die (35 mm x 0.4 mm) and drum winding accessories. Film thicknesses were about 300 – 600 µm.

Mechanical Property Testing

Films were die cut into ASTM D638 type V dogbone specimens and tested for their tensile properties according to ASTM D638-10[27]. Samples were conditioned and tested at 23 °C and 50% relative humidity using an Instron 5566 (Instron Engineering Corp., MA, USA) tensile testing machine with a 500 N load cell at a speed of 1mm/min. Extension was measured using a LX 500 laser extensometer (MTS systems Corp., MN, USA) with sampling at 10 Hz. Tensile strength was taken as the maximum stress level, and the Young's modulus was determined by fitting the data to a hyperbolic tangent and taking the initial slope of the fitted equation. Five specimens were tested for each condition.

Experimental Design

A two-level, four factor experimental design was created to evaluate the effects of formulation and operating conditions on nanocomposite properties. The independent variables were 1) presence of DTAC on the CNCs; 2) inclusion of 10% PVAc; 3) discharge temperature setpoint, T (155 or 170 °C); and 4) mixing speed, S (3700 or 6000 rpms). The response variables were tensile strength, tensile modulus, elongation at break, toughness, and normalized light transmittance at 350 nm and 500 nm. The concentration of CNCs was held constant at 1% for all 2^4 experimental conditions from the factorial design. Additionally, PLA control films were produced from both as-received pellets and samples that were wet compounded with a quantity of water comparable to samples using CNC suspensions. Experiments were analyzed using SAS® V9.4 and SAS's ADX Interface for the Design of Experiments (SAS/QC in SAS V9.4(TS1M3), Cary, NC). Additional runs, including PLA controls, were evaluated for differences from the initial experimental runs by constructing 95% prediction intervals and determining if they exceeded (higher or lower) those bounds.

Microscopy and UV-Vis spectroscopy

Films were evaluated for their appearance and light transmission using optical microscopy and UV-Vis spectroscopy, respectively. An Agilent 8453 UV-Vis spectrophotometer was used to measure light transmission through films. The absorbance measured for each film was normalized assuming a linear relationship with thickness, and this normalized absorbance was used for calculating "normalized transmission" results at both 350 nm and 500 nm. For optical microscopy, a Leitz Wetzlar optical microscope with a polarizer was used.

Gel permeation chromatography (GPC)

The number average molecular weight (M_n) of the films was measured by GPC using a Waters instrument (Waters 1515, Waters, Milford, MA) equipped with a series of HR Styragel® columns (HR4, HR3, HR2 (300*7.8 mm (I.D)) and a Refractive Index (RI) detector (Waters 2414, Waters, Milford, MA). The test was conducted at a flow rate of 1 ml/min at 35°C using the Mark-Houwink corrected constant K = 0.000174 ml/g and a = 0.736 for PLA solution in THF. Polystyrene (PS) standards ranging between $2.9*10^3$ to $3.64*10^6$ daltons were used for calibration. Approximately 20 mg of sample was dissolved in 10 ml of 99.99% pure tetrahydrofuran (THF). The samples were then filtered and transferred into 2 ml glass vials. A syringe was used to inject 100µl samples from the vial into the GPC. The detector and column were maintained at 35°C. The obtained data was analyzed using the Breeze software (version 3.30 SPA, 2002) (Waters, Milford, MA, USA). Samples were tested in triplicates.

Results and Discussion

Optical microscopy (Fig. 2) reveals that wet compounding resulted in nanocomposites with better dispersion (Figs. 2b-2f) than those melt-compounded with freeze-dried CNCs (Fig. 2a) and that surface modification of CNCs is important for good dispersion. Fig. 2c shows a microscopy image of wet compounded CNCs in PLA with no DTAC or PVAC, and significant agglomeration clearly exists, but it's considerably less than in the case of melt-blended nanocomposites using free-dried CNCs (Fig. 2a). Fig. 2e depicts samples with DTAC but no PVAc, and Fig. 2f depicts samples with both DTAC and PVAc. These samples with DTAC appear to have less agglomeration than when no DTAC was present, but samples that have PVAc but no DTAC have significant agglomeration. Therefore, DTAC clearly plays a significant role in dispersion, but PVAc does not appear to favorably impact CNC dispersion in PLA. Additionally, we notice that some contamination seems to be introduced into the compounding process (Fig. 2b), so additional work is needed to reduce such contamination.

UV-Vis measurements (Table 1) of films support the finding from optical microscopy that DTAC plays a role in dispersion and thus transparency of the films. Note that all 2^4 runs were included in the statistical analysis, but only a select few are shown in Table 1 for brevity. Statistical analysis revealed that light transmission normalized at 350 nm through wet-compounded nanocomposite films was significantly improved with the addition of DTAC with a p-value of 0.02. This trend is clearly seen when DTAC surface-modified CNCs were combined with PVAc in the composite films. For wet-compounded films, the addition of CNCs into PLA films negatively affected the transparency of the films, irrespective of the presence of DTAC and/or PVAc. Also, wet-compounded composites with DTAC and PVAc were more transparent than the melt-compounded film containing freeze-dried CNCs. The statistical analysis revealed that the effect of DTAC on transmission at 500 nm through nanocomposites was marginal with a p-value of 0.07. All nanocomposites in this case showed significantly reduced transmission, but the wet compounded nanocomposites appear mostly transparent (Fig. 3).

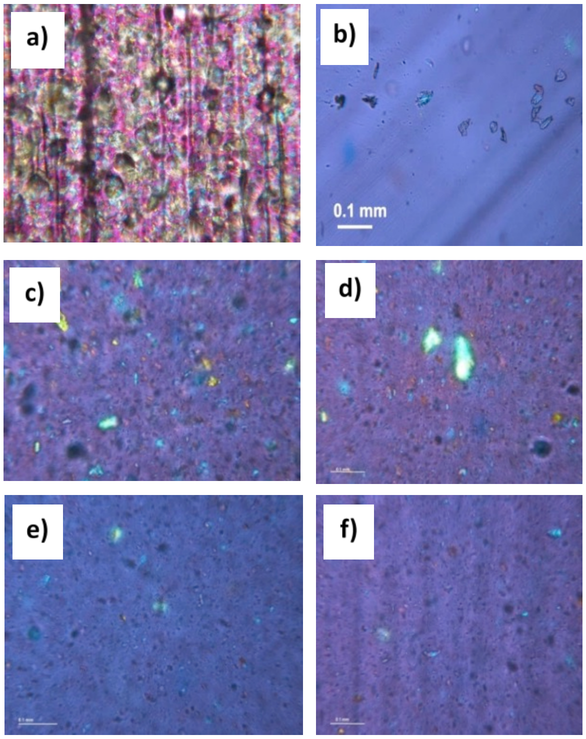

Figure 2: Optical micrograph of films (T=155°F and S=3700 rpm): a) melt-compounded PLA-CNCs (freeze-dried CNCs); b) PLA wet-blended control (No CNCs or additives); c) PLA with 1% CNCs (no DTAC or PVAc); d) PLA with 1% CNCs and 10% PVAc (no DTAC); e) PLA with 1% DTAC-CNCs (no PVAc); f) PLA with 1% DTAC-CNCs and 10% PVAc

Although quite a bit of variability was seen in the tensile data, some statistically significant factors were revealed. However, the differences in the tensile data of the nanocomposites was quite small, so these factors had limited practical effects on the tensile properties. Tensile data is shown in Table 2 for a subset of the data; since mixing speed had no significant effect on tensile properties, only the data for runs at 6,000 rpm are shown for brevity.

The effect of temperature on tensile strength was significant (p-value of 0.03) with increasing discharge temperature leading to decreased tensile strength. In addition, the presence of PVAc was found to be significant on toughness of cellulose nanocomposites (p-value of 0.05). Note, however, that control PLA samples had elongation and toughness values outside the 95% prediction interval determined for the 2^4 experimental runs. This indicates that the presence of CNCs embrittled the films so much that even with 10% PVAc, unfilled PLA samples had higher toughness than any containing CNCs. Therefore, more work is likely needed to develop formulations for these cellulose nanocomposites to improve their ductility.

Table 1: UV-Vis transmittance of select PLA films.

Sample	**Transmittance (%)**	
	350nm	**500nm**
Melt-compounded PLA-CNCs (from freeze-dried CNCs)	7.8	5.5
PLA wet-blended control (No CNCs or additives)	60.3	73.0
PLA with 1% CNCs (no DTAC or PVAc)	5.5	10.6
PLA with 1% CNCs and 10% PVAc (no DTAC)	3.6	8.8
PLA with 1% DTAC-CNCs (no PVAc)	4.6	11.2
PLA with 1% DTAC-CNCs and 10% PVAc	9.8	18.9

Figure 3: Photograph of films: a) PLA with freeze-dried CNCs; b) PLA wet-blended control (No CNCs or additives); c) wet-compounded PLA with 1% DTAC-CNCs and 10% PVAc

Table 2: Tensile mean (and standard deviation) for nanocomposite film samples at 6,000 rpm. All samples have 1% CNC except for the PLA control.

DTAC/ Temp/ PVAc	Modulus (GPa)	Max. Stress (MPa)	Elong-ation (%)	Toughness (MJ/m^3)
0/155/0%	1.58 (0.09)	57.8 (1.4)	0.13 (0.06)	0.81 (0.44)
1/155/0%	1.56 (0.05)	57.0 (1.08)	0.19 (0.06)	1.27 (0.41)
0/175/0%	1.62 (0.17)	57.2 (1.6)	0.14 (0.04)	0.89 (0.28)
1/175/0%	1.67 (0.08)	56.3 (1.3)	0.17 (0.04)	1.12 (0.26)
0/155/10%	1.63 (0.15)	59.3 (1.3)	0.22 (0.02)	1.54 (0.21)
1/155/10%	1.72 (0.10)	58.3 (0.83)	0.19 (0.04)	1.27 (0.28)
0/175/10%	1.61 (0.16)	59.3 (1.4)	0.17 (0.02)	1.19 (0.17)
1/175/10%	1.64 (0.08)	56.8 (1.7)	0.17 (0.05)	1.11 (0.32)
PLA control	1.67 (0.06)	57.9 (1.0)	0.28 (0.04)	1.93 (0.25)

Because PLA is sensitive to hydrolytic degradation[28, 29], concerns exist about the effect of compounding PLA with aqueous suspensions on its molecular weight. The number average molecular weight, as determined by GPC, is shown for several samples in Table 3. Molecular weight of as-received PLA pellets was approximately 109,000 g/mol, and the molecular weight of melt extruded film was approximately 98,000 g/mol indicating a drop of approximately 10% due to melt processing. Control samples consisting of PLA mixed with water in the thermokinetic mixer without CNCs followed by grinding and film extrusion were also tested for their molecular weight, and their molecular weight was comparable to samples that had only been melt extruded. Since neither the molecular weight nor the mechanical properties of PLA were substantially reduced, wet compounding does not appear to result in significant degradation of PLA.

Although most of the nanocomposite properties were not highly sensitive to operating conditions, molecular weight of PLA in nanocomposite samples was lower for samples processed at lower mixing speeds as shown in Fig. 4. The values shown in Fig. 4 are averaged for both discharge temperatures. An analysis of variance was performed on the molecular weight of PLA in nanocomposite samples, and mixing speed was found to be a significant factor with a p-value of 0.008, but varying temperature from 155 °C to 175 °C was not found to significantly affect molecular weight. Note that lower mixing speeds result in longer residence times with samples processed at 3,700 rpm typically taking more than 5 minutes to remove water compared to less than 2 minutes for samples processed at 6,000 rpm. Therefore, although some hydrolytic degradation was seen in wet compounding, samples processed with short residence times exhibited little degradation, similar to that of melt-processed samples.

Table 3: Molecular weight of PLA and PLA nanocomposites measured by GPC.

	Mn (g/mol)	**Standard deviation (g/mol)**
PLA pellets	109,000	14,000
PLA extruded film	97,700	4,000
PLA wet film 175° C/6,000 rpm	104,000	2,600
PLA-CNC wet film 155° C/6,000 rpm	103,000	7,400
PLA-CNC wet film 175° C/6,000 rpm	97,800	7,200
PLA-CNC wet film 155° C/3,700 rpm	92,200	1,800
PLA-CNC wet film 175° C/3,700 rpm	87,200	1,700

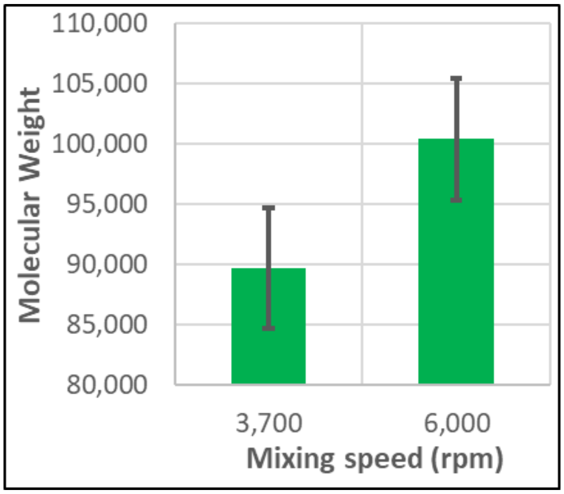

Figure 4: Molecular weight of PLA-cellulose nanocomposites as measured by GPC.

Conclusions

Wet compounding, a process in which suspensions of cellulose nanomaterials can be dried and compounded into polymers in a single step, is a promising approach for producing cellulose nanocomposites. Systematic investigation of the effects of processing conditions and of formulation on composite properties revealed that discharge temperature, mixing speed, CNC surface modification and the addition of PVAc all had modest but significant effects on composite properties. Lower discharge temperature lead to increased tensile strength, which supports our previous results[25]. Modification of CNCs with DTAC lead to improved dispersion, and the addition of 10% PVAc slightly improved the toughness of PLA-cellulose nanocomposites, although the toughness of neat PLA was higher than all nanocomposite samples. Despite the susceptibility of PLA to hydrolytically degrade, compounding PLA in the presence of water for short cycle times did not result in significant molecular weight reduction. However, compounding at lower mixing speed (3,700 rpm) resulted in cycle times exceeding 5 minutes and reduced molecular weight. Wet compounding appears to be a suitable approach to produce cellulose nanocomposites, and the properties of the nanocomposites were found to be better with appropriate formulations processed at high speeds, short cycle times and low discharge temperatures. However, additional work is needed to better understand and optimize wet compounding to produce cellulose nanocomposites.

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