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EFFECT OF COMPOUNDING APPROACHES ON FIBER DISPERSION AND PERFORMANCE OF POLY(LACTIC ACID)/CELLULOSE NANOCRYSTAL COMPOSITE BLOWN FILMS

Sonal S. Karkhanis and Laurent M. Matuana, Michigan State University, East Lansing, MI
Nicole M. Stark and Ronald C. Sabo, USDA-FS, Forest Products Laboratory, Madison, WI

Abstract

This study was aimed to identify the best approach for incorporating cellulose nanocrystals (CNCs) into a poly(lactic acid) (PLA) matrix by examining two different CNC addition approaches. The first approach consisted of melt blending PLA and CNCs in a three-piece internal mixer whereas the second method involved the direct dry mixing of PLA and CNCs. The prepared compounded materials were then blown into films and compared in terms of fiber dispersion, optical, thermal and barrier properties. The experimental results indicated that the extent of fiber dispersion was not influenced by the CNC addition method, i.e., good dispersion was achieved by either method. However, the melt blended PLA/CNC films thermo-mechanically degraded during the melt blending process. Consequently, the melt blended PLA/CNC films had inferior properties than their direct dry blended counterparts. Thus, the direct dry blending process appeared to be the best approach of incorporating CNCs into the PLA matrix.

Introduction

Growing concerns about sustainability, environmental awareness, government policies and increasing oil prices are driving industries and researchers to develop bio-based and biodegradable materials [1]. Poly(lactic acid) (PLA), a thermoplastic derived from renewable resources such as starch from corn and potatoes, is an eco-friendly polymer that can provide an attractive solution to mounting concerns [2-6]. PLA has several desirable properties such as high stiffness, reasonable strength, excellent flavor and aroma barrier, as well as good grease and oil resistance. It has been extensively used as implants in biomedical applications and to manufacture rigid containers for food and consumer goods packaging. However, its widespread applicability in flexible films is limited due to its poor water and oxygen barrier properties, low impact strength and brittleness [2-6].

Cellulose nanocrystal (CNC), a bio-based and biodegradable material, is often added to the PLA matrix to overcome few of its drawbacks [7,8]. For instance, well-dispersed nanocrystals can improve PLA's mechanical properties by improving stress transfer from the matrix to the CNCs [9]. Additionally, CNCs can act as nucleating agents to increase PLA's crystallinity [7-9]. Increased crystallinity is known to improve the barrier properties of materials because of the increase in packing efficiency of polymer chains, leading to a decrease in free volume [2,10]. However, the dispersion of CNCs into a polymer matrix is a challenge. CNC particles tend to agglomerate due to their high surface area to volume ratio when the aqueous medium that they are produced in is eliminated by freeze or spray drying. Moreover, CNC particles are difficult to disperse in non-polar polymers due to their high polarity and strong hydrogen forces [7,8].

Various approaches, such as solvent casting and melt compounding, have been investigated to disperse nanocelluloses into a polymer matrix. Recently, Pei and co-workers investigated the dispersion of chemically modified CNCs into a PLA matrix [11]. In this work, a predetermined amount of silylated CNC (SCNC) was dispersed in an organic solvent and mixed with a previously prepared solution of PLA. The mixture was stirred, cast on a glass petri dish and dried to form PLA/SCNC nanocomposite films. High degree of SCNCs dispersion was achieved into the PLA matrix due to fiber treatment that reduced agglomeration. The PLA/1% SCNC films had higher crystallinity compared to the PLA films, leading to a 27% increase in tensile modulus. However, the elongation at break of the PLA/1% SCNC films was significantly lower than that of PLA films due to the poor interfacial adhesion between the PLA and nanoparticles resulting in insufficient stress transfer [11]. In another study, Fortunati and co-workers reported a reduction of 34% in water vapor permeability of PLA when 1% CNC modified with an acid phosphate ester of ethoxylated nonylphenol was added to the PLA matrix using the solvent casting technique [10].

Moreover, PLA/cellulose nanofiber (CNF) composites have been prepared using a two-step process. The solvent casting technique was used to prepare a master batch, which was then crushed, diluted and dry-mixed with PLA, melt compounded in an extruder, pelletized and finally injection molding. The PLA/5% CNF samples prepared by the described technique had a 24% and 21% increase in tensile modulus and tensile strength, respectively. Nonetheless, large standard deviation in the modulus values reported indicated a non-homogenous dispersion of CNFs in the PLA matrix [8].

Herrera and co-workers [12] described another approach to disperse CNFs into a PLA matrix. They prepared aqueous suspensions of CNF in a slurry of plasticizer, acetone and water. The prepared suspension was melt compounded with PLA pellets in a twin-screw extruder equipped with a liquid feeder and vents for removal of acetone and water. The obtained extrudate was then compression molded into films for testing of mechanical properties. The results indicated that addition of only 1% CNF increased the elongation at break of the plasticized PLA by 27% due to the slippery effect of CNFs coated with plasticizer and the crazing phenomenon attributed to the presence of CNFs [12].

Although good nanoparticle dispersion into PLA matrix was reported by different solvent casting techniques, these have various drawbacks [8,10,11,12]. The solvent casting technique requires drying of films, which add more energy consumption in film manufacture. Solvent disposal could also be an issue for this process because some solvents may be harmful to workers and the environment. Moreover, trace amounts of solvents can remain in the produced films, which could pose regulatory compliance issues. The residual solvent can also act as a plasticizer, thereby reducing the strength, stiffness and barrier properties of the produced films [13].

Due to the drawbacks of solvent-based mixing techniques, alternative approaches to manufacture PLA/CNC composite films should be considered. This study examined two different approaches of adding CNCs into PLA matrix. The first approach was to melt blend CNCs with PLA in a three-piece internal batch mixer to maximize homogenous dispersion of CNCs into the matrix while minimizing the loss of CNCs that may occur in high volume mixers [14]. Although this technique eliminates the use of solvents, it is a time-consuming batch process that subjects heat-sensitive PLA to additional thermal history. Therefore, a second approach employing conventional direct dry blending was also examined. In this method, CNCs were directly added to the PLA matrix during conventional dry compounding. This solvent-free and less time-consuming approach minimizes exposure of PLA to high temperature.

To the best of our knowledge, these investigated blending approaches have not been previously used to manufacture PLA/CNC composite blown films. Consequently, the goal of this study was to compare the performance of PLA/CNC blown films prepared by the melt blending and direct dry blending techniques in terms of fiber dispersion, optical, thermal and barrier properties to identify the most effective blending approach.

Materials

Poly(lactic) acid (PLA 4044D) with a melt flow rate of 3.95 g/10 min (190°C, 2.16 kg) and density of 1.24 g/cm^3, obtained from NatureWorks® LLC (Minnetonka, MN) was used as the resin in this study. CNCs (2012-FPL-CNC-043) were prepared by sulfuric acid hydrolysis at Forest Products Laboratory (FPL), in Madison, Wisconsin, USA.

Preparation of PLA/CNC composites

PLA pellets and CNCs were oven-dried at 50°C for at least 24 hours to remove moisture before compounding through the following two different approaches of incorporating CNCs into the PLA matrix:

Melt blending process (MB)

Mixing temperature, speed and time affect the dispersion of additives into polymer matrices [15]. Blending of CNCs with PLA took place in an electrically heated 60 ml three-piece internal mixer/measuring head (3:2 gear ratio) with counter-rotating roller style mixing blades (C.W. Brabender Instruments, South Hackensack, NJ) at 160°C for 3 minutes with the rotor speed set at 30 rpm. A 5.6 kW (7.5 hp) Intelli-Torque Plasti-Corder Torque Rheometer (C.W. Brabender Instruments, South Hackensack, NJ) powered the mixer. These processing conditions were optimized in our preliminary study. The CNC loading was fixed at 1 wt%, which was determined as the ideal concentration from our previous study [2]. The compounded materials were pulverized using a Thomas-Wiley Laboratory Mill-Model 4 (A.H. Thomas Co., Philadelphia, PA) and then blown into a film as described in the following sections.

Direct dry blending (DB)

The direct dry blending of 1 wt% CNCs into PLA was carried out in a kitchen mixer (Blender MX1050XTS from Waring Commercial Xtreme) at 22,000 rpm for approximately 1 min. The compounded materials were then used to manufacture blown film as described below.

Film manufacturing

PLA pellets and the compounded materials described above were blown into films using a 19 mm single screw extruder (C.W. Brabender Instruments, South Hackensack, NJ), powered by a 3.73 kilowatt (5 hp) Prep Center® D52 (C.W. Brabender Instruments, South Hackensack, NJ). The extruder had a length-to-diameter ratio of 30:1 and was fitted with an annular die of diameter 25.4 mm and die opening of 0.889 mm. Starting from the hopper to the die, the temperature profile of the extruder was set at 180-180-180-180°C. The rotational screw speed of the extruder was set at 35 rpm whereas the speed of take-up rollers for drawing the film upward was set at 40 rpm. An internal air pressure of 0.517 kPa (0.075 psi) was used to inflate the film. The blow-up ratio of the film, defined as the ratio of the diameter of the final tubular film to the diameter of the annular die, was calculated as 5. The average thickness was measured as ~0.027 mm at 10 random locations around the film using a digital micrometer (model 49-70 from TMI, Ronkonkoma, NY, USA) with a resolution of 0.001 mm [2].

Property evaluation

Differential scanning calorimetry (DSC)

DSC was performed on the prepared films using a Q100 instrument (TA Instruments, New Castle, DE) in accordance with ASTM D3418. The DSC cell was purged with liquid nitrogen flowing at 70 ml/min. Each test employed 6-10 mg of sample tested with a set of heating and cooling cycles. The samples were heated from 25°C to 200°C at a ramp rate of 10°C/min and held at 200°C for 5 mins to erase their thermal history. Subsequently, the samples were cooled to 25°C and reheated to 200°C at the same ramp rate. The glass transition temperature (T_g), cold crystallization temperature (T_c), melt peak temperature (T_m), enthalpy of the cold crystallization process (ΔH_c) and melting peaks (ΔH_m) were determined using the software Universal Analysis 2000, V4.5 (TA Instruments, Delaware). The percentage crystallinity (% χ_c) was calculated from the second heat curve using the following equation [16]:

$$\%\chi_c = \frac{\Delta H_c - \Delta H_m}{\Delta H_m^{\infty} \times \left[1 - \left(\%\text{wt CNC}/100\right)\right]} \times 100 \qquad (1)$$

where % wt CNC is the total weight percentage of CNC (1 wt %). The melt enthalpy of a spherulite of infinite size (ΔH_m^{∞}) used for PLA was 93 J g^{-1} [6,16]. The test was performed in duplicates.

Thermogravimetric analysis (TGA)

TGA measurements of the PLA and PLA/CNC composite films were performed in triplicates using a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE) on samples weighing between 6-10 mg. The samples were heated from 25°C to 700°C at a ramp rate of 10°C/min under nitrogen atmosphere (40 ml/min).

Gel permeation chromatography (GPC)

The number average (M_n) and weight average molecular weight (M_w) of the films were 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 $\alpha = 0.736$ 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.

Ultraviolet-visible (UV-Vis) spectroscopy

A UV-Visible spectrophotometer Perkin-Elmer Lambda 25 (Perkin-Elmer Instruments, Beaconsfield, UK) was used to record the transmittance of PLA and PLA/CNC composite films. The UV-Visible spectra were obtained over a wavelength range of 200 to 900 nm at a scan rate of 240 nm/min. Samples were tested in triplicates.

Light microscopy

PLA and PLA/CNC composite films were observed using an Olympus BX41 optical microscope (Olympus, Center Valley, PA) equipped with a camera (Olympus Qcolor3).

Water vapor transmission rate (WVTR)

The WVTR of PLA and PLA/CNC composite films was measured in accordance with the desiccant method in ASTM E 96, as described previously [2]. At least four replicates of films manually cut and sealed onto 3/4" depth vapometer cup assemblies (Thwing-Albert Instrument Co., West Berlin, NJ) cups were placed in a controlled humidity chamber (Model LH 1.5 from Associated Environmental Systems, Ayer, MA) set at 38°C and 85% RH. The inside of the cups was maintained at ~0% RH by using a desiccant (anhydrous calcium sulfate). The cups were periodically weighed to the nearest 0.0001g for determining the weight gain as a function of time. The slope of the linear portion of weight gain versus time plots was used to calculate the WVTR, using the following equation:

$$\text{WVTR} = \frac{(W/t)}{A} \qquad (2)$$

where W is the weight gain at time t, A is the effective area of exposed film (31.67×10^{-4} m^2), and W/t is the slope of the straight line.

Statistics

Means were compared by the ANOVA (analysis of variance) and Tukey's HSD (honestly significant differences) tests at 5% level of significance using IBM SPSS Statistics 22 (Armonk, NY).

Results and Discussion

Effects of blending process on fiber dispersion and PLA's optical properties

CNC dispersion in the PLA matrix was examined using light microscope (Figure 1). As seen in Figure 1, homogenous distribution of CNCs in the PLA matrix was achieved, irrespective of the blending technique. However, some agglomerates were still visible. The difference in CNC dispersion in the direct dry blended and melt blended films was not apparent from the obtained images. Therefore, UV-Vis spectroscopy was performed to further investigate the dispersion of CNCs into the PLA matrix (Figure 2).

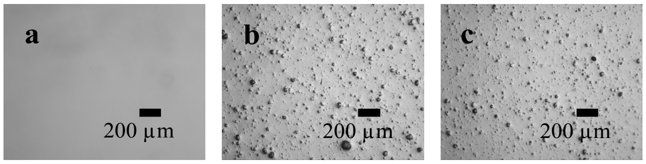

Figure 1. Light microscope of (a) PLA, (b) PLA/1% CNC (DB) and (c) PLA/1% CNC (MB) films.

Transparency can be used as an indicator of the dispersion of nanoparticles in a matrix, if the size of individual nanoparticles is smaller than the wavelength of visible light (380-700 nm) [12]. In other terms, if nanosize distribution of CNC in PLA matrix is obtained, the addition of CNCs will not affect the transparency of resulting films, because pure CNC films are highly transparent [17]. The UV-Vis spectroscopy result (Figure 2) shows that the light transmission of neat PLA decreased slightly by adding 1% CNCs, irrespective of the blending technique. Reduced transparency of PLA due to the addition of CNCs, irrespective of blending method, implied that nanoscale dispersion did not fully occur and some agglomerations could still be present. Moreover, the light microscope images showing agglomerations of CNCs (Figure 1) corroborate the UV-vis results (Figure 2). Generally, fiber agglomeration sizes larger than the incident wavelength tend to scatter light and reduce light transmission [12].

Although there is still need for improvement to completely eliminate agglomerations, a transparency in the range of 75-78% was achieved in this study, clearly indicating that good dispersion of CNCs occurred in PLA matrix, irrespective of the blending approach. It is worth mentioning that the PLA/CNC melt blended films had slightly lower transparency (~75% transmission) than their direct dry blended counterparts (~78% transmission) (Figure 2). This reduced transparency could be attributed to color changes occurring in the films prepared by melt blending because of the thermo-mechanical degradation occurring during the blending process. Reduced light transmission by PLA films due to degradation has been reported by other researchers [18]. The hypothesized thermal degradation of PLA/CNC composite films prepared by the melt blending process was further investigated using TGA, DSC and GPC, as described in the following sections.

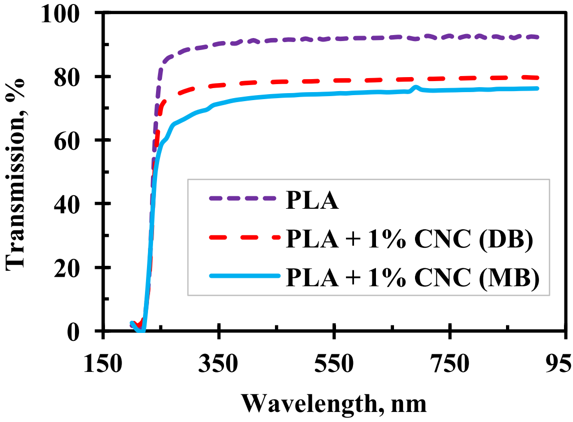

Figure 2. Effect of CNC addition and blending process on the transparency of PLA and PLA/CNC composite films.

Effects of CNC addition and blending process on PLA's thermal properties

The UV-Vis results (Figure 2) indicated that PLA/CNC composite films prepared by the melt blending approach were degrading during the blending process. Thus, TGA and DSC were performed to investigate this hypothesized degradation. Table 1 lists the degradation onset temperature (T_{onset}) and temperature at which maximum degradation ($T_{maximum}$) occurred for the PLA and PLA/CNC composite films.

Table 1. TGA for PLA as well as direct dry and melt blended PLA/1% CNC films.

Materials	T_{onset}, $^{o}C^{a}$	$T_{maximum}$, $^{o}C^{a}$
PLA	312.9 ± 0.8^{a}	364.1 ± 3.5^{a}
PLA + 1% CNC (DB)	316.5 ± 5.4^{a}	364.7 ± 1.1^{a}
PLA + 1% CNC (MB)	314.7 ± 1.8^{a}	364.1 ± 2.2^{a}

[a] Same superscript letters within the same column are not significantly different based on the ANOVA results at 5% significance level.

The melt blending process subjected the PLA/CNC films to additional heat as compared to their direct dry blended counterparts during the blending process. Consequently, these films were expected to start degrading at a lower temperature. However, irrespective of the blending process used, there was no noticeable difference in the degradation temperatures measured on addition of 1% CNCs. Similar results have been reported by Lizundia and co-workers for PLA-grafted CNCs at 1wt% [19]. This lack of observed differences in thermal stability could be attributed to the TGA measurements that are not representative to the real degradation during processing conditions of temperature, shear and residence time [20]. Nevertheless, other researchers have reported improved thermal stability of PLA films filled with 2% CNCs [9]. Thus, GPC, described in the next section, was used as a complimentary technique to study the degradation of PLA during compounding.

It was evident that all the films were thermally stable up to a temperature of ~310°C and showed maximum degradation at ~364°C. This degradation of PLA above 200°C has been reported by various researchers and can been attributed to hydrolysis of ester bonds in the main chain, unzipping depolymerization reactions catalyzed by residual polymerization catalysts, and transesterification reactions leading to the formation of low molecular weight monomers and oligomeric esters [21].

Table 2 lists the thermal transition temperatures (T_g, T_c and T_m) and degree of crystallinity (%χ_c) measured for PLA as well as PLA/CNC composite films manufactured by the direct dry and melt blending techniques. No notable changes were observed in the T_g of the PLA films on addition of CNC, irrespective of the blending technique. Intermolecular interaction and chain flexibility can cause a change in a material's T_g [22]. As expected, the low concentration of added CNCs did not significantly change the PLA's chain flexibility nor intermolecular interaction and consequently had no noteworthy effect on its T_g.

Table 2. DSC analysis for PLA as well as direct dry and melt blended PLA/1% CNC films.

Materials	T_g, °C^a	T_c, °C^a	T_m, °C^a	χ_c, %^{a}
PLA	60.8 ± 0.1^a	125.2 ± 0.01^a	150.7 ± 0.4^a	1.4 ± 0.5^a
PLA + 1% CNC (DB)	60.6 ± 0.3^a	122.3 ± 0.9^b	150.3 ± 0.2^a	4.3 ± 0.3^b
PLA + 1% CNC (MB)	60.8 ± 0.1^a	113.2 ± 0.1^c	147.9 ± 0.01^b	4.4 ± 0.3^b

[a] Same superscript letters within the same column are not significantly different based on the ANOVA results at 5% significance level.

The T_c values of direct dry blended and melt blended PLA/CNC films were significantly lower than that of neat PLA (control films). This decrease in T_c can be an indication of faster crystallization due to the nucleation effect of CNCs. Increased crystallinity of the PLA/CNC composite films as compared to the neat PLA films confirmed the hypothesized role of CNCs as nucleating agents. Other researchers have reported similar results for PLA/CNC films [9]. It is also worth mentioning that by comparison of the two blending techniques, a significantly lower T_c was observed for the melt blended PLA/CNC films. This decreased T_c could be attributed to the nucleating effect of its degradation products. However, this decrease in T_c was not accompanied by a further increase in crystallinity. GPC (described in the next section) was performed to confirm the degradation of melt blended PLA/CNC films.

The T_m of direct dry blended PLA/CNC films remained unchanged as compared to neat PLA. In contrast, the melt blended PLA/CNC films had a significantly lower T_m, which was attributed to the degradation of these films. Generally, degradation of films is accompanied by a reduction in molecular weight leading to reduced chain length and chain entanglement. Shorter and less entangled chains require less energy to slide past each other and melt.

Effect of CNC addition and blending process on the degradation of PLA

The UV-VIS (Figure 2) and DSC (Table 2) results indicated that the extra heat and mechanical shear experienced in the melt blending process were degrading the PLA/CNC melt blended films. GPC was performed to validate these results (Table 3).

The addition of CNCs decreased in the M_n and M_w of PLA films, irrespective of the blending technique. The mechanical shear generated at 22,000 rpm during the direct dry blending process could be contributing to this observed molecular weight reduction of direct dry blended PLA/CNC compounds. However, the M_n and M_w of PLA/CNC films produced by the melt blending process were even lower than their direct dry blended counterparts, which can be attributed to the additional thermo-mechanical degradation of these compounds during the melt blending process. The mechanism of degradation for the PLA/CNC compounds could be random main chain cleavage resulting from hydrolysis or chain scission. However, the average molecular weight (M_n) reduction was not very pronounced, as is common with hydrolytic degradation. Thus, the dominating mechanism of degradation was more likely to be chain scission and not hydrolysis [20].

Table 3. Molecular weights of PLA as well as direct dry and melt blended PLA/1% CNC films obtained by GPC.

Materials	M_n, g/mol	M_w, g/mol
PLA	51,394 ± 6130	85,114 ± 6811
PLA + 1% CNC (DB)	47,624 ± 1417	77,478 ± 812
PLA + 1% CNC (MB)	44,188 ± 335	76,787 ± 826

Effect of CNC addition and blending process on the WVTR of PLA

The incorporation of 1% CNCs by the direct dry blending and melt blending techniques improved the water barrier performance of PLA films by 33% and 24%, respectively (Table 4), due to the increased crystallinity of the composite films (Table 2). Increased crystallinity due to increased packing of polymer chains reduces the free volume of a polymer available for permeant penetration. Moreover, the impermeable crystals create a tortuous diffusion path for the permeant (water vapor). Consequently, the permeant diffuses slowly and leads to a lower transmission rate [2]. Nonetheless, it should be mentioned that the WVTR of PLA/CNC melt blended films was higher than direct dry blended films because of their thermo-mechanical degradation as demonstrated by the UV-Vis (Figure 2), DSC (Table 2) and GPC (Table 3) results. From obtained WVTR results, direct dry blending appeared to be the best approach for incorporating CNCs into the PLA matrix to enhance its water barrier properties.

Table 4. WVTR of PLA as well as direct dry and melt blended PLA/1% CNC films.

Materials	**WVTR at 38°C and 85% RH, 10^{-7} kg/m·s^{2} [a]**
PLA	55.6 ± 1.9^{a}
PLA + 1% CNC (DB)	37.1 ± 2.0^{b}
PLA + 1% CNC (MB)	42.0 ± 11.1^{a,b}

[a] Same superscript letters are not significantly different based on the ANOVA results at 5% significance level.

Conclusions

Two different approaches of incorporating CNCs into a PLA matrix were examined. The first method involved the melt blending of PLA and CNCs in a three-piece internal mixer for homogenous dispersion of CNCs into the matrix. The second method, direct dry blending, consisted of direct dry mixing of PLA and CNCs. The experimental results indicated that the melt blended PLA/CNC films were thermo-mechanically degrading during the blending process. Therefore, their optical, thermal and barrier properties were inferior to their direct dry blended PLA/CNC counterparts. In conclusion, the direct dry blending technique appeared to be the best approach for incorporating CNCs into the PLA matrix because it exposed the samples to less heat and thus minimized thermal degradation.

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