Research Article

Mechanical and Optical Properties of Polylactic Acid Films Containing Surfactant-Modified Cellulose Nanocrystals

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The addition of surface-modified cellulose nanocrystals (CNCs) to polymeric matrices can lead to an enhancement of the mechanical and optical properties of host polymers. The use of surfactants can provide an easy and effective way to change the CNC functionality and to evaluate the effects of surface chemistry in the reinforcement mechanisms. In this work, CNCs were solution blended with polylactic acid (PLA) and melt extruded into films. The PLA toughness increased from 1.70 MJ/m³ to 2.74 MJ/m³, a 61% increase, with the addition of 1% of decylamine-modified CNCs without a decrease of the tensile strength or modulus. In this work, we investigated the use of two surfactants, decylamine and cetyltrimethylammonium bromide, to enhance CNC compatibility with the hydrophobic PLA matrix. Decylamine at 1.0 wt.% with respect to CNC loading was found to significantly enhance CNC compatibility and property enhancement. The low concentration of surfactant is notable, as other works typically use significantly higher loadings for CNC incorporation and property enhancement. At high CNC concentrations, mechanical properties decreased but the aligned assembly of the CNCs provided intricate colors to the films when observed between crossed polars. The alignment and nanoscale structure of CNCs within the films play an important role in the properties obtained.

1. Introduction

Polylactic acid (PLA) is a well-known biodegradable polymer that has potential to serve as a sustainable alternative to petroleum-derived plastics and is one of the most widely used biopolymers on the market [1]. PLA accounts for nearly 40% of the bioplastic total market, with nearly \$700 million in revenue in 2017 and a projected growth to over \$2 billion and 830,000 metric tons by 2023 [2]. PLA is synthesized from lactic acid made from corn starch or sugar cane [3], and the production requires 25–55% less energy than petroleum-based polymers due to its relatively lower melting point (T_m) [4, 5], thus reducing the net CO₂ emission to the environment [6, 7]. Moreover, PLA has received much research attention in the last two decades due to its high tensile properties, transparency, and low toxicity. The result is an improved material at a competitive cost with emergence in a highly competitive polymer market [8–12]. On the other hand, the brittleness and low vapor and gas barrier properties

of PLA are potential limitations in extending its applications, thus representing areas of current development [1].

One avenue to address these limitations is the reinforcement of PLA with cellulose nanocrystals (CNCs). This nanofiller has attracted much attention as a polymer reinforcement material due to its exceptional mechanical properties, ability for surface functionalization, abundance, and renewability [13–16]. Similar to other nanofillers, CNCs exploit properties not found in macrosized materials, specifically their high surface areas, aspect ratios, and multifunctionalities. These nanocrystals can be isolated from a variety of sources such as cotton, wood pulp, tunicate, or bacteria usually by acid hydrolysis [17]. Through this process, noncrystalline regions of the cellulose are hydrolyzed while the highly crystalline ones resist acid attack, resulting in a crystalline, high-performance material. Crystalline cellulose has been estimated to possess a higher elastic modulus than Kevlar and higher tensile strength than steel wire with 80% less weight than the

latter one [18, 19]. However, to incorporate all of the benefits of CNCs into polymer nanocomposites, the CNC surface needs to be modified to enhance compatibility with the desired polymer matrix.

Surface modifications such as acetylation, silylation, oxidation, polymer grafting, and absorption of surfactants, among others, have been reported in the literature [17]. For example, a single-step method for the acetylation of CNCs, proposed by Braun and Dorgan [20], is one method for successful dispersion of CNCs in organic solvents. Moreover, it is believed that CNC acetylation enhances the absorption of surfactants, promoting a better dispersion of CNCs in an organic matrix without compromising the cellulose degradation temperature. Recent research suggests that the absorption of surfactants and long-chain molecules have shown to be effective in the compatibilization of CNCs with hydrophobic polymers, increasing the toughness of the composites [17]. However, it is usually observed that a high amount of surfactant addition ranging from 0.5:1 to 4:1 molar ratio of surfactant to the CNC hydroxyl group (50 to 200 wt.% surfactant to CNC) is required for compatibilization, thus restricting the nanocomposite properties or performance [21]. For this reason, it is important to explore surfactants having similar effects but at lower proportions. In this study, we explore decylamine (DA) and cetyltrimethylammonium bromide (CTAB) for solution compatibilization within PLA-CNC film nanocomposites.

The reinforcement of polymers varies as a function of the nanocrystal morphology, functionality, polydispersity, and the processing conditions [17]. Therefore, the results reported in literature differ considerably, suggesting that future research is needed to identify the variables and the mechanisms of reinforcement. Past research indicates that good dispersibility of CNCs within the matrix, with minimal aggregation, is important for composite reinforcement [22]. Interestingly, some hydrophobic matrices have been reinforced using hydrophilic CNCs [23], while in other cases, surface-modified CNCs have not exhibited the enhancement in the mechanical properties that would be expected from improved compatibility with rigid fillers [24]. These behaviors can be attributed to different stress transfer mechanisms. A percolating network can be formed at a critical filler concentration, in which stress transfer is facilitated by filler-filler interactions, usually increasing the tensile strength and modulus of the composites [25]. On the other hand, at low filler concentrations, the stress transfer is mainly through filler-matrix interactions, for which good compatibility usually results in increased toughness [17]. Additionally, fillers with larger aspect ratios tend to increase the tensile modulus, while smaller sizes, such as that of the nanocrystals, have been observed to enhance toughness [26].

The aim of this work is to enhance the toughness of PLA by the addition of acetylated CNCs plus the absorption of surfactants. We have previously shown that surfactant introduction improves CNC stability and self-assembly in organic solvents. For this work, PLA-CNC nanocomposite films (0, 1, 3, 5, and 10 wt.% CNCs) were extruded and mechanically tested using an Instron testing machine. An increase in toughness was observed at low CNC concentrations when

using DA surfactant, while the tensile strength and modulus remained constant compared to neat PLA. The CNC orientation and self-assembly were studied using polarized light microscopy, demonstrating significant organization for the toughened composites. Moreover, these organized structures within the composites provided colored properties to the films when observed between crossed polars and which have the potential for advanced applications such as biodegradable security papers and defense applications.

2. Experimental Section

2.1. Materials. PLA was purchased from NatureWorks 2003D (95% L-PLA and 5% D-PLA) and used as received for the polymer matrix. Clippings of ashless filter aid from Whatman™ were used as the CNC starting material. Other reactants for the synthesis (glacial acetic acid and hydrochloric acid 37% w/v) were ACS grade obtained from VWR. Chloroform and decylamine were ACS grade reagents obtained from Sigma-Aldrich. High-purity grade cetyltrimethylammonium bromide (CTAB) was obtained from AMRESCO.

2.2. Synthesis and Characterization of CNCs. CNCs were synthesized according to the method developed by Braun and Dorgan [20] as briefly described here. Cotton cellulose filter aid (10 g) was soaked overnight in 225 mL of acetic acid. Concentrated hydrochloric acid (0.8 mL, 37%) and 24.5 mL of deionized water were added, and the 10 hr reaction time began when a reaction temperature of 105°C was reached. After the reaction, the mixture was cooled in an ice bath and centrifuged to remove the solvent in the supernatant. DI water was added to the precipitated cellulose to the original volume and mixed for 2 minutes with a vortex mixer using a Vortex-Genie 2 (Scientific Industries Inc.). The centrifugation and redispersion were repeated for two additional cycles. The cellulose dispersion was then sonicated using a Fisher Scientific 550 Sonic Dismembrator for 5 cycles of 7 min in an ice bath. The suspension was again centrifuged and redispersed for additional cycles until a cloudy supernatant was observed. The aqueous supernatant of isolated acetylated CNCs was obtained by combining the following 2-3 dispersion supernatants. The nanocrystals were transferred to an organic solvent by dispersion in acetone with two centrifugation and redispersion cycles, with final dispersion in THF. Vigorous mixing was performed with a final 40 min of vortex mixing until minimal agglomeration was visible in the resulting suspension. The desired surfactant (decylamine or CTAB) was subsequently added to the suspension and mixed for 5–10 min.

The CNC dimensions were measured by transmission electron microscopy (TEM) using a Hitachi 7600 TEM with an accelerating voltage of 120 kV. CNC samples were prepared by nebulizing a diluted CNC suspension (~0.01% w/v) onto a formvar carbon-coated copper grid (Ted Pella). Thermal gravimetric analysis (TGA) (TA instruments SDT Q600) was performed to determine the CNC degradation temperature. A sample of CNC organic suspension was dried, and the remaining powder was placed in the TGA

TABLE 1: Nomenclature and composition of PLA-CNC nanocomposites prepared in this work.

Sample name	CNC (%)	PLA (%)	Surfactant (1 wt.% w.r.t. CNC)
PLA	0	100	—
PLA-CNC(1%)-UM	1	99	—
PLA-CNC(5%)-UM	5	95	—
PLA-CNC(1%)-DA	1	99	Decylamine
PLA-CNC(5%)-DA	5	95	Decylamine
PLA-CNC(1%)-CTAB	1	99	CTAB
PLA-CNC(5%)-CTAB	5	95	CTAB

alumina pans. The sample was heated to 110°C for 25 min to remove residual solvent, cooled to 80°C, and then heated at 10°C/min to 650°C. The TGA was carried out under a nitrogen atmosphere (100 mL/min) and then switched to oxygen from 650°C to 800°C.

2.3. Preparation of PLA-CNC Nanocomposites. PLA nanocomposites were made by blending a 5% (w/v) solution of PLA in chloroform with a 1% (w/v) CNC suspension using an overhead stirrer. These PLA-CNC solutions, with CNC contents of 1, 3, 5, and 10 wt.%, were allowed to dry overnight at room conditions in a glass dish. The films were placed under vacuum at 70°C for 12 h and then to 120°C for 1 h to remove any residual solvent. Approximately 15 g of nanocomposite films was cut and compounded in a DSM Xplore corotating twin-screw microcompounding extruder for 10 min at 195°C. The extruder was set to a constant force at the die of 500 N, allowing variable screw rotation to obtain a constant melt flow. The polymer melt was extruded through a rectangular cross-sectional-shaped die, cooled with ambient nitrogen gas, and collected on a chill roll with a take-up speed of 120 rpm. The films were cut into 95 mm × 12.5 mm strips using a hydraulic press and a custom-made metal die for tensile testing. A minimum of 10 samples was prepared for each CNC composite loading and type of surfactant. The thicknesses of the films were taken at 4 different sections of the films, and an average of 0.18 ± 0.02 mm was obtained. Table 1 lists some of the nanocomposites prepared and their respective names in this work.

2.4. Nanocomposite Characterization. Tensile testing of the nanocomposites was performed using an Instron 1125 tensile testing instrument. The initial grip separation was 45 mm and set to a strain rate of 4 mm/min. Information on displacement and force exerted in the stretching of the films was obtained in stress-strain curves shown in supplemental information Figure S1 and used to determine tensile strength, tensile modulus, and toughness (energy at break) of each film.

PerkinElmer Pyris 1 differential scanning calorimetry (DSC) was used to determine the crystallinity of the nanocomposites. Between 5 and 6 mg of the sample was carefully sealed inside an aluminum pan. The samples were heated to 210°C at 20°C/min under nitrogen atmosphere and maintained at a constant temperature for 2 min prior

to cooling at a rate of 20°C/min. The crystallinity of PLA-CNC films was calculated by measuring the area under the melting and crystallization curves and using

$$X_c[\%] = \frac{\Delta H_m - \Delta H_{cc}}{(\Delta H_m^{\infty}) * X_{PLA}} * 100\%, \quad (1)$$

where ΔH_m and ΔH_{cc} are the enthalpies of melting and crystallization, respectively, measured by DSC. X_{PLA} is the fraction of PLA in the composites as described in Table 1 [23]. The theoretical enthalpy of fusion of 100% crystalline PLA, ΔH_m^{∞} , was taken to be 93.0 J/g [27].

The optical properties of the films and orientation of the CNCs in the nanocomposite were investigated by optical polarized light microscopy (Olympus BX60) in transmission mode with the polarizer below the sample and the analyzer rotated 90° above. The films were placed directly on glass slides and analyzed at 10x magnification with the stage being rotated from 0 to 135°. Adobe Photoshop was used to increase the contrast for display purposes and to measure the percentage of colors.

In order to elucidate CNC orientation direction or the sign of birefringence, a first-order red plate was added between the polarizer and analyzer (see orientation of filters in Figure S2). The direction of the slow red axis of the filter is oriented at 135°, and therefore, orientation at 135° appears blue. CNCs oriented in the 45° direction appear yellow due to the lower-interference colors resulting from the slow axes being perpendicular. CNCs oriented at 0° and 90°, as well as nonoriented crystals, will appear magenta. The first-order red plate is designed for low-retardation structures, which appear as a gray scale between crossed polars, which eliminates the ability to properly analyze the 5% and 10% CNC composites since their brightness is too strong.

In order to fully characterize the extent of orientation and directionality, the sample is rotated to discern between non-oriented and parallel or perpendicular orientation. The total extent of orientation is calculated theoretically by adding the colors blue and yellow from the 0° and 45° angle images. Image analysis was performed with Photoshop software to quantify the percentage of colors magenta, blue, and yellow from the entire area of the images.

3. Results and Discussion

3.1. Characterization of Cellulose Nanocrystals. The nanoscale dimension and high aspect ratio of the CNCs are important for polymer property enhancement with particle orientation. The high surface area to volume ratio enables good molecular level interactions with different matrices [20], and a high aspect ratio ensures enhanced stress transfer to the nanocrystals [22]. Figure 1 shows a representative TEM micrograph of CNCs dried from a THF suspension, confirming the successful isolation of the nanocrystals. These nanocrystals are observed to have the tendency to aggregate after drying which is due to the lack of surface charge for the acetylated CNCs [22]. It is expected that the introduction of compatibilized CNCs into an organic media will reduce

FIGURE 1: TEM image of cellulose nanocrystals synthesized using acetic acid and stabilized with decylamine surfactant. Bar: 2 μm .

the tendency to agglomerate due to enhanced filler-matrix interactions. The CNCs were measured to be 250 nm long and 35 nm wide, which is in agreement with reported literature values [20].

The thermal stability of nanofillers is important for nanocomposite melt processing due to the relatively high melting point and temperatures required for melt compounding. Figure 2 shows the degradation temperatures of CNCs without surfactant and with decylamine (DA), demonstrating the excellent thermal stability of the CNCs. The onset degradation temperature was 331°C for acetylated CNC with and without surfactant, which is well above the processing temperature of the PLA (190°C). This CNC modification, as shown by Braun and Dorgan [20], has the advantage of maintaining the thermal stability of native cellulose, contrary to other common modifications which significantly reduce the degradation temperature of cellulose [28–30].

3.2. Mechanical Properties of the Nanocomposite Films. The mechanical properties of the nanocomposite films from the stress-strain curves are presented in Figure 3. The energy at break or toughness of PLA-CNC nanocomposites exhibited a maximum enhancement at 1% CNC content before decreasing with increasing loading. This maximum enhancement occurred for the nanocomposites with DA surfactant and represented a 61% increase from 1.70 MJ/m³ for neat PLA to 2.74 MJ/m³. For the 3% DA-modified CNC composites, a slight enhancement of 8% was exhibited, while for the 5 and 10% composites, the toughness was decreased with respect to neat PLA. The unmodified (UM) and CTAB-modified nanocomposites exhibited a decreased toughness compared to PLA and PLA-CNC-DA at each CNC concentration. The composites at 10% CNC load were more brittle, demonstrating a reduced toughness of up to 95% less than that for PLA. The decrease in toughness in nanocomposites has been attributed to large agglomerations of nanofillers [22, 31]. These agglomerations can act as stress concentrators, which facilitate the spreading of defects generated at the interface. These defects can grow larger than the critical crack size, resulting in film failure.

In comparison with other literature focused on melt extrusion of CNC reinforcement of PLA with added

FIGURE 2: TGA weight loss as a function of temperature for the acetylated CNC without surfactant (solid line) and with decylamine surfactant (dotted line).

surfactants, our results show enhancement at lower values of loading. Bondeson and Oksman investigated NaOH-neutralized sulfuric acid-hydrolyzed CNC with the addition of phosphate anionic surfactant with loadings of 5% CNC and surfactant loadings of 5 to 20% [14]. They observed optimal results with an increase in tensile modulus from 2.65 to 3.10 GPa with 5% CNC and 5% surfactant; however, a 16.5% decrease in strength was observed. In all cases, the tensile strength was reduced. These results are not that different from our results with higher CNC loading. Fortunati et al. also investigated NaOH-neutralized sulfuric acid-hydrolyzed CNC with a phosphate ester surfactant and added silver nanoparticles for antimicrobial properties [15]. Their work also observed optimal performance at 5% CNC with surfactant where the modulus was increased from 2.4 to 4.4 GPa and the strength was maintained at 54 MPa. As a result, the percent elongation was decreased. While the strength was maintained for this result, the composite became more brittle, and again, CNC loadings below 5% were not investigated. Muiruri et al. took a different approach where homo- and copolymers of caprolactone and lactic acid were grafted onto the surface of CNC by ring-opening polymerization [16]. The CNC with PDLA grafts at 2.5 and 5.0% loading, the tensile strength, and modulus decreased nominally, and the elongation at break nominally increased. Incorporation of the caprolactone rubber graft also exhibited decreased strength and modulus, but the elongation at break was drastically increased from 8% for neat PLLA to 247% for 10% loading. Along this same line, Dhar et al. covalently grafted PLA onto the CNC surface and observed a 40% increase in tensile strength and 490% increase in modulus but with significantly decreased elongation at break, which is indicative of a brittle material [32]. While surface grafting is a viable alternative, the simplicity of using noncovalent surfactants is an attractive alternative; however, special attention must be paid to the composite toughness for many applications.

In other related works, Hossain et al. observed a 31% increase in modulus and a 34% increase in the strength of solvent cast thin films of PLA with 1% CNC but these

FIGURE 3: Mechanical properties of PLA-CNC composites using different surfactants. ■: UM; ●: DA; ▲: CTAB.

were not extruded into films [31]. Kamal and Khoshkava did not perform tensile tests of their PLA-CNC composites but did determine that the network structure of agglomerates contributes significantly to good dispersion in the PLA matrix [33].

A maximum in the reinforcement of toughness is frequently observed when good dispersions occur at low filler concentrations [34, 35] as observed for the PLA-CNC(1%)-DA composites. This improvement can therefore be the result of favorable dispersions and better interfacial compatibility of CNC-DA with PLA compared to UM- and CTAB-modified CNCs [36, 37]. There are a few toughening mechanisms with rigid fillers discussed in the literature; however, this discussion is inconclusive for CNC nanocomposites. Toughening mechanisms include the formation of microvoids [38], crack bifurcation and crack path alteration [39], interfacial debonding [26], assembly into spiral orientation [40], and shear yielding resulting from the difference on the Young's moduli of the filler and the matrix [41]. In our previous work, the addition of DA improved the CNC

compatibility with aprotic solvents compared to plain CNCs, which agrees with the enhanced mechanical properties obtained when using this surfactant in the present work.

The tensile strength and modulus of the composites followed similar trends as it can be observed in Figures 3(b) and 3(c), remaining fairly constant up to a 3% CNC load but decreasing drastically after 5%. At a 10% load, the mechanical properties were deteriorated obtaining at best a 45% and 32% reduction for the strength and modulus, respectively. This behavior follows the same trend as the energy at break for the 10% films, and it may be indicative of CNC agglomeration.

It has been demonstrated that one mechanism occurring in the reinforcement of the tensile properties of CNC nanocomposites is the formation of a percolating network which transfers the stresses effectively throughout the nanocomposite when high concentrations of filler are added [17, 25]. This mechanism has been often observed with hydrophilic- or surface-charged CNCs when the filler-filler interactions are stronger than the filler-matrix ones and they do not tend to easily aggregate [42, 43].

FIGURE 4: Polarized light microscopy images demonstrating the agglomerations on the 3% CNC nanocomposites. (a) UM; (b) DA; (c) CTAB. Length of the longest side of each image: 1.5 mm.

In non-surface-charged nanocrystals, such as the acetylated CNCs in this work, a percolating network is more difficult to form without the formation of agglomerates, introducing defects and thus reducing polymer reinforcement [22]. Therefore, the reinforcement exhibited at low filler concentrations can be attributed to the stress transfer through filler-matrix interactions. However, the relatively low aspect ratios of the CNCs, which are estimated to be approximately 6 to 12, may not enable a perfect transfer of the stresses, possibly reducing the effect of the good compatibility provided by the surfactant [25]. According to the Halpin-Tsai model for short-fiber composites, only nanofillers with aspect ratios larger than 50 can guarantee an efficient reinforcement of the elastic modulus [44].

The addition of surfactants does not seem to significantly affect the tensile strength and modulus of the films as observed in Figures 3(b) and 3(c). However, DA-modified composites possessed overall slightly higher values compared to the other two modified composites, which may also confirm the enhancement of the filler-matrix interactions. Even though these tensile properties were not significantly increased, they were not reduced for the toughened composites (PLA-CNC(1%)-DA), which is frequently a disadvantage in the toughening of polymers. The tensile properties of pure PLA are already comparable to other petroleum-based polymers; therefore, enhancing toughness without compromising other properties becomes an integral step in the reinforcement of PLA.

3.3. Alignment of CNCs and Agglomerations. The CNC agglomeration in all of the 3% CNC nanocomposites was

observed by polarized light microscopy (Figure 4). All composites have relatively large agglomerations; however, the agglomerates in PLA-CNC(3%)-UM (Figure 4(a)) are considerably more than those for DA (Figure 4(b)) and less than those for CTAB composites (Figure 4(c)). This confirms that DA enhances the interfacial interaction and increases CNC compatibility in the composite. Moreover, this also endorses the proposed idea that the detriment of the mechanical properties occurs due to agglomerations forming at high concentrations as a result of insufficient compatibility. PLA-CNC(3%)-DA also displayed white bands under polarized light that can be attributed to ordered assembly resulting from local CNC self-assembly within the composite.

The ordering and self-assembly of the nanocomposite films was studied using polarized light microscopy. Figure 5 shows strong birefringence and anisotropy in the PLA composites at different CNC loads and rotation angles. An ordered anisotropic phase is formed when molecules or particles assemble into a semiorganized structure, changing the refraction of the incident light and allowing the transmission of light between crossed polarized films. The brightness or birefringence observed on the composites in Figure 5, especially at 45° and 135° , increases with CNC concentration, indicating a higher level of crystal organization in the films. In this case, the polarizer and analyzer are fixed at 0° and 90° , respectively. Nonoriented crystals and crystals aligned in the 0° or 90° direction will not diffract light since they possess the same angle of the polarized light. As a result, a bright phase will appear when crystals are oriented at 45° or 135° from the polarizer. For example, at 45° rotation angles in

FIGURE 5: Polarized light microscopy images of PLA-CNC-DA composites at different CNC loads: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 10% CNC. At different rotating angles 0°, 45°, 90°, and 135°. Images demonstrate the increasing formation of birefringence in the composites. Length of the longest side of each image: 1.5 mm.

FIGURE 6: Polarized light microscopy images of the 3% CNC-loaded nanocomposites using a first-order red filter: (a) neat PLA; (b) UM; (c) DA; (d) CTAB. At 0°, 45°, 90°, and 135° rotation angles. Length of the longest side of each image: 1.5 mm.

Figure 5, the bright phase indicates that the crystals are oriented either at 45° and 135°, indicating that the crystals are oriented parallel or perpendicular to the film extrusion.

Figure 6 shows the polarized light microscopy images with the red plate for neat PLA and the composites at 3% CNC loading. As discussed above, the levels of agglomeration

TABLE 2: Approximate percentage of colors of PLA-CNC composites observed under polarized light microscopy with a first-order red plate.

	Magenta	0° Yellow	Blue	Magenta	45° Yellow	Blue	Estimated oriented area
PLA	100%	0%	0%	100%	0%	0%	0%
PLA-CNC(1%)-UM	53%	42%	5%	77%	22%	1%	70%
PLA-CNC(3%)-UM	92%	3%	5%	0%	89%	11%	108%
PLA-CNC(1%)-DA	43%	23%	34%	59%	26%	14%	97%
PLA-CNC(3%)-DA	40%	38%	21%	60%	26%	14%	100%
PLA-CNC(1%)-CTAB	100%	0%	0%	100%	0%	0%	0%
PLA-CNC(3%)-CTAB	97%	1%	2%	95%	2%	3%	8%

FIGURE 7: Crystallinity of PLA-CNC composites estimated by DSC. ■: UM; ●: DA; ▲: CTAB.

for the UM- and CTAB-modified composites are evident, correlating also with the low degree of CNC orientation in the films. On the other hand, CNC films with DA clearly display a change of color between the angles of rotation, indicating that the crystals are oriented. The total areas occupied by the oriented crystals were quantified by adding the percentage of colors magenta, blue, and yellow from the entire area of the images. The 1 and 3% CNC-loaded composites were analyzed at 0° and 45° angles as observed in Table 2. For neat PLA, the orientation is negligible, resulting in a 0% oriented area. As the CNC load increases, the total calculated oriented area increases in different proportions for each of the composites. The orientation in the CNC-DA composites increases from ~97% to ~100%; while for the UM, it increases from ~70% to ~100% (108% was measured) with an increasing CNC content. Such results indicate a better organization for DA composites at low concentrations as discussed above. The assembly of CNC for the CTAB composites is the lowest among all (0% and 8% for PLA-CNC(1%)-CTAB and PLA-CNC(3%)-CTAB, respectively), correlating with the poor mechanical properties obtained for those composites.

The high level of assembly for the DA composites does not necessarily mean having well-oriented fillers in the direction of the extrusion. Indeed, the DA composites only have ~26% of their organized crystals oriented parallel to the

extrusion of the flow, ~14% is perpendicular, and around 60% is distributed between 45° and 135° with respect to the extrusion direction. In the case of UM composites, an unexpected high orientation of the crystals was observed in the direction of extrusion (~89% for PLA-CNC(3%)-UM). Poorly oriented crystals cannot necessarily be translated to poor mechanical properties. It has been suggested in the literature that a lower degree of CNC orientation may enhance the nanocomposite toughness, although a reduced tensile modulus is accompanied [40]. Therefore, it can be thought that this distribution of crystal orientation may change the path of the crack sufficiently enough to dissipate energy and increase toughness. The ability for acetylated CNCs to self-assemble in organic media in stationary and shear states was studied in our previous work, agreeing with the self-assembly observed in the nanocomposites in the present study.

3.4. Crystallinity of Nanocomposite Films. PLA-CNC nanocomposite crystallinity was determined by DSC, and the results are shown in Figure 7. Neat PLA exhibited low crystallinity, which is likely due to the enantiomer composition, L (95%) and D (5%). It is observed that the addition of CNCs did not significantly affect PLA crystallinity, which is advantageous to the enhancement of toughness and elongation at break. However, a slight increase in crystallinity occurs for the DA composites, which were observed to be the least agglomerated and most oriented out of the 3 modifications studied in this work. DSC analysis also revealed a double melting peak for PLA which occurs at specific conditions of cooling and heating rates [45]. The double peaks have been attributed to a melting-recrystallization mechanism of PLA in which small and imperfect crystallites change into more stable crystals during the melting of the polymer [46].

3.5. Optical Properties. The study of the optical properties of the films is important for advanced and commercial applications. The transparency of the PLA-CNC-DA films, which also exhibited improved toughness, can be observed in Figure 8, showing significant optical transparency for the low concentration of CNCs.

Besides a good transparency, the nanocomposites with high CNC concentration also exhibited interesting optical properties when observed between crossed polars. Colored phases appeared as the thickness was increased by stacking

FIGURE 8: Example of the transparency of PLA-CNC-DA composites with CNC loads of (a) 1%, (b) 3%, (c) 5%, and (d) 10%.

FIGURE 9: Photographs of four PLA-CNC(10%)-DA films that are stacked on top of one another with an offset such that the edges are one film thick and the center is four films thick. The stacked films are viewed (a) in unpolarized light, (b) between crossed polars at a 0° angle, and (c) between crossed polars at a 45° angle.

layers of the composite films (Figure 9). This behavior is believed to be the result of the self-assembly of CNCs within the films despite the agglomerations observed at high CNC concentrations. The colors are the result of high retardations that are dependent on both the thickness of the films (t) and the difference of the refractive index of the two crystallographic axes of the liquid crystal material ($n_2 - n_1$) or birefringence. The DA-modified films showed the most intense colors, visually demonstrating a higher birefringence and confirming once more the ability of DA to aid the formation of semiorganized structures. The birefringence can also be quantified using the Michel-Levy chart [47], which includes the colors obtained at a wide range of retardations (R). This chart can also be expressed by the following equation [48].

$$R = t \times |n_2 - n_1|. \quad (2)$$

Assuming that $(n_2 - n_1)$ remains constant for a specific CNC concentration, it is possible to predict the retardations when the thickness is varied and, therefore, also predict the colors of the films. The nanocomposites with 5 and 10% CNCs were the only ones that showed colorful arrangements between crossed polars when the thickness was varied. These colors were matched with the colors in the Michel-Levy chart, and the retardations were read from the chart. Using (2), the birefringence ($n_2 - n_1$) was then determined to be 0.0017 ± 0.0001 for the PLA-CNC(10%)-DA films and 0.0008 ± 0.0001 for the PLA-CNC(5%)-DA films. For the PLA-CNC(10%)-UM and the PLA-CNC(10%)-CTAB composites, the birefringence values were 0.0015 ± 0.0002 and 0.0011 ± 0.0003 , respectively. These results have the same trend as the resulting mechanical properties and dispersibility of CNCs within the matrix as discussed earlier in the work, demonstrating that self-assembly occurs in spite of the agglomerations obtained at higher

concentrations. The birefringence values can be used for the prediction or targeting of certain colors by changing the thickness of the composites or the CNC concentration. These optical properties can have potential applications in areas such as decorative coating, security papers, and liquid crystal displays among others.

4. Conclusions

Surface-modified CNCs were added into PLA as reinforcement, resulting in enhanced mechanical and optical properties of extruded films. The toughness of the PLA composites was enhanced by 61% compared to that of neat PLA when using 1% of DA-modified CNCs without detriment to the tensile strength or modulus. As the concentration increased, toughness gradually decreased to very low values for the 10% loading. For unmodified and CTAB-modified CNCs, toughness decreased with concentration worsening the properties of PLA. The increase in toughness was attributed to a relatively good dispersion and good interfacial adhesion between the CNCs and the matrix. Tensile strength and modulus remained fairly similar compared to neat PLA, but as CNC concentration increased, these properties decreased more than 45% for the 10% CNC composites. The lack of surface charge on the surface of the CNCs may induce the formation of agglomerations at high concentrations preventing the development of a percolating network which has been previously shown to increase the tensile properties. Polarized light microscopy images of the CNC nanocomposites revealed the formation of oriented CNC, which provided interesting colors to the composites at high CNC loadings. It was shown that a better dispersion of CNCs results in a better organization in the composites, especially in the ones modified with DA. However, the degree of alignment was found to be relatively low with CNC orientation pointing at multiple directions around the extrusion line for the toughened composites, which has been attributed to the inherent spiral assembly of cellulose as reported in the literature [40]. The crystallinity of the nanocomposites was not increased by the addition of the CNCs, which also facilitated the toughening of the composites by the addition of the filler. Overall, this work demonstrated the ability to increase the toughness and optical properties under polarize light of PLA films without sacrificing good tensile properties by the addition of low percentage of acetylated CNCs functionalized with surfactants.

Data Availability

The experimental data used to support the findings of this study are included within the article and supporting information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Figure S1: representative stress-strain curves for 10 samples of (a) pure PLA, (b) PLA with 1 wt.% CNC without added surfactant, (c) PLA with 1.0 wt.% CNC and decylamine surfactant, and (d) PLA with 1.0 wt.% CNC and CTAB surfactant. Values for the tensile strength, tensile modulus, and toughness (energy at break) were determined for each curve and averaged to yield values in Figure 3. Figure S2: orientation of the polarizer, analyzer, and the first-order red filter (red slow direction) and colors observed when liquid crystals are oriented in the corresponding angles of rotation. Figure S3: polarized microscopy of PLA-CNC-UM films at different CNC loadings using a first-order red plate (5% and 10% lack of meaning when analyzed with the red plate due to the high retardations). Figure S4: polarized microscopy of PLA-CNC-DA films at different CNC loadings using a first-order red plate (5% and 10% lack of meaning when analyzed with the red plate due to the high retardations). Figure S5: polarized microscopy of PLA-CNC-DA films at different CNC loadings using a first-order red plate (5% and 10% lack of meaning when analyzed with the red plate due to the high retardations). Figure S6: PLA-CNC (5% and 10%) composite films with (a) unmodified CNCs; (b) DA-modified CNCs; and (c) CTAB-modified CNCs. Figure S7: low magnification polarized light microscopy of PLA-CNC(10%)-DA nanocomposites showing colored optical properties. (Supplementary Materials)

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