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Published in:
Journal of Colloid and Interface Science

DOI:
10.1016/j.jcis.2021.04.032

Published: 15/09/2021

Document Version
Peer reviewed version

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Please cite the original version:
Cellulose Nanofibers and the Film-Formation Dilemma: Drying Temperature and Tunable Optical, Mechanical and Wetting Properties of Nanocomposite Films Composed of Waterborne Sulfopolyesters

Soo-Ah Jin,1 Emily G. Facchine,1 Orlando J. Rojas,1,2,3 Saad A. Khan1* and Richard J. Spontak1,4*

1Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA
2Department of Bioproducts and Biosystems, Aalto University, Espoo 02150, Finland
3Departments of Chemical & Biological Engineering, Chemistry and Wood Science, University of British Columbia, Vancouver, Canada V6T 1Z3
4Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA

ABSTRACT

Hypothesis
Waterborne sulfopolyesters have gained considerable interest as coating materials due to their excellent film-forming and optical properties. Their commercial use has been limited, however, due to their fragile nature. Incorporating cellulose nanofiber (CNF), a sustainable biopolymer, into the polymer matrix is expected to enhance the mechanical integrity of the nanocomposite as these two components synergistically interact.

Experiments
In this study, we have investigated the suspension and film characteristics of three sulfopolyesters varying in charge density, glass transition temperature and molecular weight, as well as their mixtures with CNF. We have performed steady-shear rheology on mixtures with different CNF loading levels, and resulting films have been subjected to quasistatic uniaxial tensile and water contact-angle tests to elucidate the effects of CNF on mechanical and surface properties.

Findings
Addition of CNF to waterborne polyester promotes shear-thinning behavior that remains unaffected by the CNF content. Solid films cast from these suspensions possess enhanced mechanical properties, as well as tailorable surface hydrophilicity, depending on composition and film-drying temperature. Tensile tests reveal that films containing 10 wt% CNF display the greatest mechanical improvements, suggesting the existence of a previously unidentified Goldilocks composition window.

* To whom correspondence should be addressed (e-mail: khan@eos.ncsu.edu or rich_spontak@ncsu.edu).
INTRODUCTION

Environmental issues associated with new materials development continue to remain a worldwide concern. Many stringent regulations focus on the mitigation of toxic air pollutants, such as volatile organic compounds (VOCs), which directly derive from a wide range of industrial activities. A major source of VOC emission can be traced to industrial paints and coatings that rely on organic solvents. As a consequence, the many regulations imposed on these market sectors have spurred the growth of low-VOC technologies, generating a paradigm shift in coating industries from solvent-borne polymer systems to waterborne polymer systems [1–4]. Although water-based polymer systems continue to gain tremendous attention, the replacement of established solvent-based polymer systems with waterborne ones has made gradual progress [4–6]. Many efforts have been devoted to develop and synthesize latex polymer dispersions for use in a broad spectrum of coating industries, ranging from aesthetic coatings (e.g., paints) [6–9] to functional (e.g., protective, anti-microbial and fire-retardant) coatings [7,8,10,11]. Due to the intrinsically low polarity of most polymers, their homogeneous dispersion in an aqueous medium has remained a technological challenge, since dispersibility dictates the overall quality and function of as-cast films and coatings. Furthermore, the presence of residual water in the resultant film can adversely affect properties [12,13] by compromising mechanical performance or optical transparency.

While numerous studies have been conducted [4,14–16] to elucidate film formation from polymer dispersions, fundamental studies addressing the evolution of waterborne polymer dispersions to solid film are still somewhat limited. The widely recognized mechanism of this transformation can be summarized in terms of three principal stages: (1) packing of latex particles due to water removal via evaporation, (2) filling interparticle voids as latex particles
deform and interfacial tension decreases, and (3) coalescing particle boundaries by polymer interdiffusion, resulting in a contiguous and, ultimately, defect-free film [8,12,16–21]. These process-regulating steps do not, however, occur sequentially [12,22], but rather simultaneously, especially during the particle deformation and polymer interdiffusion stages. Although numerous factors influence the last two stages of film formation, one of the most important parameters that must be controlled is the drying temperature. In particular, the minimum film formation temperature (MFFT) must be judiciously selected [14,19] since it tends to lie near the glass transition temperature \( T_g \) [19,23,24] and is thus sensitive to polymer composition, molecular weight, chemical structure, and morphology. When a latex dispersion is cast at a temperature above its \( T_g \) (> MFFT), the particles undergo deformation and interdiffusion to yield contiguous films. Conversely, latex dispersions dried at temperatures below \( T_g \) (< MFFT) can form cracked or opaque films, as well as compacted powder [19,25]. Therefore, the choice of drying temperature is critical to obtain contiguous films that exhibit the expected thermomechanical properties and appearance needed for targeted applications. The sulfopolyesters examined here are of considerable interest due to their ability to form high-quality films at ambient temperature [5].

Casting films and coatings at ambient temperature requires that the latex polymer possesses a relatively low \( T_g \) to undergo sufficient deformation and interdiffusion. A major compromise typically associated with films and coatings cast from a low-\( T_g \) polymer dispersion yields a combination of poor mechanical properties. Some coatings, especially those designed for protective purposes, require substantial hardness, which cannot be achieved with low-\( T_g \) polymers [8,26]. This deficiency can be overcome by adding a coalescing aid to plasticize a high-\( T_g \) polymer and thereby reduce its \( T_g \) and the MFFT [27–29]. Addition of a coalescent, however, raises important environmental concerns, since coalescent, as well as potentially other
VOCs, are emitted from the system upon evaporation. This trade-off is referred [12,26,30] to as the “film-formation dilemma.” Among the various waterborne polymers that are commercially available, sulfonated polyester dispersions enjoy considerable advantages: they do not require additional coalescing agents to form high-quality films at ambient temperature, and their cast films display superior optical (transparent and glossy) properties [4,31]. As alluded to above, a common problem linked to sulfopolyester films is that they possess poor mechanical properties relative to other waterborne polymers. Films cast from sulfopolyester dispersions tend to be highly brittle and fragile, and are susceptible to crack formation even under small deformation. This drawback restricts the use of sulfopolyesters in a variety of applications especially in the coating industry, wherein durability constitutes a nontrivial criterion of success.

One simple, yet effective, strategy to enhance the mechanical properties of most polymers is to incorporate a reinforcing agent to the polymer matrix. In this spirit, nanocellulose has been regarded as an excellent reinforcement species on the basis of its availability, sustainability, biocompatibility, and superior mechanical properties [32–34]. Due to its nanoscale size (which yields a high aspect ratio), it can be easily introduced into different polar polymeric matrices without further surface modification. Alternatively, nanocellulose can be used as a highly versatile biomaterial since its surface properties can be tuned via physical [35–40] (by intermolecular interaction) or chemical [41–44] (by chemical reaction with the host matrix) means due to its abundant hydroxyl moieties. The amphiphilicity of nanocellulose not only facilitates its use in polar/hydrophilic environments but also promotes good dispersion in nonpolar/hydrophobic matrices, which account for most polymer classes of commercial relevance. Obtaining a homogeneous distribution of nanocellulose in a polymer matrix is crucial to the mechanical performance of the nanocomposite system. Prior efforts have demonstrated the
synergy between nanocellulose and a diverse range of polymers, including polyurethane [45–49], poly(lactic acid) [50,51] and poly(vinyl alcohol) [52–54]. In all these cases, bulk mechanical, thermal and barrier properties are significantly enhanced. Here, we investigate the suspension and film behavior of three series of sulfopolyesters varying in charge density, $T_g$ and molecular weight, and modified with cellulose nanofiber (CNF) at different loading levels. Results obtained here reveal that the flow properties of these polyester/CNF suspensions are modestly altered, while the optical transparency of the subsequent nanocomposite films remains unaffected upon CNF incorporation. Conversely, the mechanical and surface properties of these films are sensitive to both CNF loading level and drying temperature.

**EXPERIMENTAL**

**Materials**

Three Eastman AQ™ polymers (aqueous sulfonated polyesters) were provided in solid pellet form by the Eastman Chemical Company (Kingsport, TN). These water-dispersible polyesters consisted of alternating diacid and glycol moieties at varying ratios of isophthalic acid (IPA), 5-sodiosulfoisophthalic acid (SSIPA), diethylene glycol (DEG), and 1,4-cyclohexanediethanol (CHDM), ethylene glycol (EG) or polyethylene glycol (PEG). The general chemical structure and relevant property information of these polyesters are displayed in Figure 1 and listed in Table 1, respectively. The fundamental properties of these polyesters in aqueous suspension were recently described by Islam *et al.* [5]. The never-dried sodium form of TEMPO- (2,2,6,6-tetramethylpiperidine-1-oxyl radical) oxidized CNF used here was manufactured and purchased from the Cellulose Nanomaterials Pilot Plant (U.S. Forest Service) at the Forest Products Laboratory (FPL) in 1.1% w/w aqueous gel form. Our reason for selecting TEMPO-oxidized
CNF here reflects its ability to remain stable in aqueous suspensions due to the presence of negative surface charges that promote electrostatic repulsion.

Table 1. Properties of the three sulfopolyesters examined here, as reported elsewhere [5].

<table>
<thead>
<tr>
<th>Commercial designation</th>
<th>Polymer designation</th>
<th>Tg (°C)</th>
<th>Charge density (meq/g polymer)</th>
<th>Zeta potential (mV)</th>
<th>Average particle diameter in water (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastman AQ 38S</td>
<td>PolyA</td>
<td>38</td>
<td>0.43</td>
<td>−55</td>
<td>50</td>
</tr>
<tr>
<td>Eastman AQ 48 Ultra</td>
<td>PolyB</td>
<td>48</td>
<td>0.89</td>
<td>−52</td>
<td>13</td>
</tr>
<tr>
<td>Eastman AQ 55S</td>
<td>PolyC</td>
<td>55</td>
<td>0.66</td>
<td>−52</td>
<td>35</td>
</tr>
</tbody>
</table>

*In all cases the acids comprising these sulfopolyesters consist of IPA/SSIPA, while the glycols consist of CHDM/DEG.

Methods

Stock dispersions (30 wt%) of polyesters A, B and C in Table 1, denoted here as PolyA, PolyB and PolyC, respectively, for convenience, were prepared by gradually adding the solid pellets to deionized (DI) water, followed by mixing on a magnetic stir plate operated at ~70-80 °C (above Tg) overnight. These dispersions were then cooled to ambient temperature before diluting to desired concentration. Each polyester/CNF mixture was subsequently prepared by combining predetermined masses of CNF, polyester and DI water, and mixing for at least 1 h. The concentration of polyester in the mixture was varied so that the overall CNF concentration was fixed at 0.2 wt%. The concentration ratios reported here are based on the solid masses of polyester and CNF. These suspensions were subjected to low-temperature probe sonication with a Cole-Parmer 750-Watt Ultrasonic Processor, operated at 0 °C to prevent overheating and CNF charge destabilization. The energy input was chosen on the basis of the mass of CNF (2000 J/g CNF) at 60% amplitude with a pulse cycle of 2 s on, followed by 3 s off. All suspensions were degassed to remove excess dissolved oxygen before casting into either square polystyrene (10
cm x 10 cm) or round polypropylene (5 cm diameter) Petri dishes. For water contact-angle (WCA) measurements and atomic force microscopy (AFM) analysis, suspensions were cast onto pre-cleaned glass slides. All the samples were dried at either low (35 °C) or high (60 °C) temperature for at least 1 week, and the resultant films were stored in a desiccator prior to further characterization. Planar AFM height images were acquired on an Asylum MFP-3D instrument.

Steady-shear viscosity measurements of polyester/CNF suspensions were performed at shear rates from 0.5 to 200 s⁻¹ on a TA Instruments Discovery Hybrid Rheometer-3 rotational rheometer. To minimize wall slip, roughened parallel plates measuring 40 mm in diameter were used at a gap distance of 1 mm. Precautions such as the use of lightweight aluminum plates were taken to ensure there were no inertial effects in the experiments. Measurements were repeated in triplicate at ambient temperature with a standard error of less than 10%. Quasistatic uniaxial tensile tests of solid nanocomposite films were conducted on an Instron Universal Machine 5943 load frame at ambient temperature. As-cast sample films were cut into rectangular strips measuring 6.0 cm x 0.6 cm with a CO₂ laser mounted on a Universal Laser VL3.50 system, and each strip was strained at a constant crosshead speed of 1 mm/min in at least triplicate. Film thicknesses were recorded by taking the average of at least 5 measurements from each sample with a digital thickness gauge. For cross-sectional imaging, field-emission scanning electron microscopy (SEM) was performed on an ultrahigh-resolution FEI Verios 460L instrument with a Schottkey emitter operated at an accelerating voltage of 2 kV without stage bias. Nanocomposite films were cryofractured in liquid nitrogen and the exposed cross-section was quickly sputter-coated with 5 nm Au/Pd prior to imaging. Surface WCA properties were measured on a First Ten Angstroms 1000B Goniometer, and values reported here are the average of at least 10 tested areas examined at ambient temperature.
RESULTS AND DISCUSSION

All three sulfonated polyesters investigated here are copolymers with alternating hydrophobic and hydrophilic moieties along the polymer backbone. A previous study [5] focusing on the colloidal properties of these sulfonated polyester in aqueous suspension has reported that, according to dynamic light scattering and cryo-SEM analyses, multiple polyester chains undergo self-assembly into discrete nanospheres when they are dispersed in water. In similar fashion as micelles, each nanosphere is composed of a hydrophobic core and a hydrophilic shell, and the overall hydrophobicity of the polymer is highly dependent on the ratio of the two acid and glycol sequences. On the basis of the properties listed in Table 1, PolyA exhibits the most hydrophobic behavior with the lowest SSIPA content, followed by PolyC, whereas PolyB possesses the highest charge density indicative of hydrophilic behavior. The hydrophilic shell of each polyester nanosphere is decorated with negatively charged SSIPA moieties, which allow the nanospheres to be electrostatically stabilized in water over long periods of time. (The surface of CNF is also covered with negative charges from the carboxylic groups introduced during TEMPO-mediated oxidation and likewise remain colloidally stable in aqueous suspension.) The average diameter of these charged nanospheres ranges from ca. 10 to 50 nm as discerned by Islam et al. [5], in which case it follows that the more hydrophilic polyesters form smaller nanospheres than those with a higher hydrophobic content. In the case of PolyC, however, aggregates of the nanospheres can develop at neutral pH levels and measure more than 80 nm in diameter. According to the AFM images acquired here and presented in Figure S1 (with the corresponding surface roughness values provided for completeness in Figure S2), we estimate that the nanospheres and their aggregates measure ca. 40-100 nm in diameter after drying below $T_g$ at 35 °C (the features become less distinct and larger after drying above $T_g$ at 60 °C). In this
work, we have elected to study the performance of 5 systems: pure polyester films, pure CNF films and 3 polyester/CNF nanocomposite films at 3 different polyester/CNF mass ratios (90/10 for polyester matrix continuity, 50/50 for co-continuity and 10/90 for CNF matrix continuity). All of these formulations are included in the AFM images provided in Figure S1. In addition to their apparent pH and temperature sensitivity, the sulfopolyester nanospheres can also be significantly enlarged through the introduction of electrolytes above a critical concentration [5].

**Rheological properties of CNF and sulfopolyester/CNF suspensions**

To address the rheological properties of the neat CNF suspension and mixed polyester/CNF suspensions, we have performed steady-shear measurements with different polyester/CNF ratios, and representative viscosity results are presented as a function of shear rate for comparison in Figure 2. Unlike most thermoplastic polymers that exhibit shear-thinning viscosity profiles, all three sulfopolyesters display Newtonian behavior up to 30 wt% solids content in water over the shear rate range examined in Figure 2. On the other hand, aqueous suspensions with as little as 0.2 wt% CNF (designated as 0/100 polyester/CNF) reveals non-Newtonian (shear-thinning) behavior. Such behavior is consistent with our previous studies on various types of nanocellulose: CNF [55] and MFNC (micro/nanofibrillated cellulose) [56]. Adding 10 wt% CNF to polyester dispersions consistently transforms the viscosity profile from Newtonian to shear-thinning. That is, the polyester/CNF suspensions at polyester/CNF composition ratios of 90/10, 50/50 and 10/90 collectively confirm the existence of shear-thinning behavior (Figure 2a for PolyA/CNF, Figure 2b for PolyB/CNF and Figure 2c for PolyC/CNF), indicating that the viscosity of these suspensions is dominated by CNF. In all cases, the data can be described by a scaling relationship of the form \((\text{viscosity}) \sim (\text{shear rate})^a\), where \(a\) ranges from -0.45 to -0.22.
For the PolyA/CNF and PolyB/CNF systems in **Figures 2a and 2b**, respectively, the viscosities of the polyester-dominant (90/10 polyester/CNF) and CNF-dominant (10/90 polyester/CNF) suspensions overlap, suggesting that the most hydrophobic PolyA and the most hydrophilic PolyB nanospheres contribute little to the viscosity compared to the entangled CNF.

In the case of PolyB, the viscosity appears nearly independent of CNF content, suggesting that this water-dispersible polyester has little impact on flow properties. This is a huge advantage in preparing reproducible suspensions for film casting, as well as generating films that possess precise properties for target applications. PolyA, on the other hand, exhibits a minimum in viscosity at an equimass CNF loading level, confirming that the viscosity in this suspension is slightly composition-dependent. In marked contrast, however, interactions between the intermediate hydrophilic/phobic PolyC and CNF are responsible for a much more pronounced composition-dependent viscosity profile. In **Figure 2d**, we observe a slight viscosity reduction at low PolyC levels and an increase in viscosity at higher ones. Similar phenomena are often evident for charged colloids and are attributed [57] to charge screening of the electrostatic double layer (EDL). For the polyester-dominant suspension (90/10 polyester/CNF), PolyC nanospheres behave as electrolytes that interact with the surface charges of the nanofibrils. If the EDL of the nanofibrils is compressed due to this electroviscous effect, neighboring CNF particles are drawn closer together due to van der Waals attraction, which, in turn, increases nanofibrillar entanglements and network formation. This yields an increase in viscosity, as reflected in **Figures 2c and 2d**. Reductions in PolyC concentration to 50/50 and 10/90 polyester/CNF are accompanied by viscosity decreases due to a less pronounced electroviscous effect. Interestingly, both PolyA/CNF and PolyC/CNF suspensions exhibit the lowest viscosities at 50/50 polyester/CNF, which might be indicative of interpolymer complex formation [58].
**Film formation and properties of sulfopolyester/CNF nanocomposites**

Water-dispersible polyesters are well-known for their excellent film-forming properties [5]. When sulfopolyester nanospheres are dispersed in water, they behave in similar fashion as traditional hard colloids wherein colloidal interactions and stabilizations are governed by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [59,60]. These nanoscale aggregates form optically transparent and contiguous films at ambient temperature, and their film-forming mechanism is similar to that of latex-type polymers. **Figure 3** displays the films generated from all three sulfopolyester series with different levels of incorporated CNF. Images in the left column correspond to pure polyester films cast from a 2 wt% dispersion, whereas those in the right column have been acquired from neat CNF films cast from a 0.2 wt% suspension. All of the films produced here, regardless of composition, are optically transparent, which confirms that (i) these polyesters and CNF do not macrophase-separate and (ii) both constituents are uniformly distributed (at least at macroscale dimensions) throughout each film. In the absence of CNF, each polyester film possesses different degrees of stiffness and flexibility due to differences in polymer chemistry, as well as variations in copolymer composition and molecular weight. PolyA exhibits the most flexible properties, whereas PolyC is brittle, shattering into pieces even under small applied forces. Films generated from pure CNF suspension are paper-like with relatively high flexibility. **According to the methodology employed elsewhere [61] to quantify the optical properties of transparent nanocomposites, we calculate the turbidity at a wavelength of 600 nm to be 9.26 x 10^{-4} \text{\mu m}^{-1}.** When both materials are combined, we obtain films with intermediate properties that depend on composition. A film containing 10 wt% CNF in a polyester matrix, for instance, still maintain its stiffness, but an increase in CNF loading level to 50 wt% causes the film to gain flexibility. Moreover, increasing the CNF content to 90 wt% changes the role of
CNF from reinforcing agent to matrix material, in which case the polyester imparts stiffness.

To quantify the composition-induced change in mechanical properties of polyester/CNF nanocomposite films, we have conducted quasistatic uniaxial tensile tests on PolyC/CNF films, since their parent suspensions revealed the greatest composition-dependent viscosity (cf. Figure 2c). In addition to examining the effect of CNF content on the mechanical properties of these films, we also desire to elucidate the influence of drying temperature on film properties. To produce contiguous films with satisfactory mechanical performance, the suspensions should be dried at a temperature higher than the MFFT in keeping with previous reports [14,19,23,24] of waterborne latex systems. Since the MFFT is close to the $T_g$ for most amorphous glassy polymers [19], we have selected two drying temperatures – 35 and 60 °C – so that one is below while the other is above the $T_g$ of PolyC (55 °C, see Table 1). Tensile stress-strain results acquired from PolyC/CNF films dried at these two temperatures are provided in Figure 4. At each drying temperature, similar trends are apparent in the mechanical properties as the loading level of CNF is varied. As mentioned earlier, neat PolyC films are very fragile and readily undergo catastrophic failure at small deformations, an empirical observation supported by the tensile data at both drying temperatures in this figure. By incorporating at least 10 wt% CNF in PolyC, the tensile strength and, in most cases, the elongation at break are substantially improved, increasing the tensile strength by at least 3x upon addition of only 10 wt% CNF after drying at 35 °C in Figure 4a.

Four mechanical properties – Young’s modulus, tensile strength, elongation at break, and fracture energy – extracted from the stress-strain data displayed for PolyC/CNF films dried at 35 and 60 °C in Figure 4 are summarized in Figure 5. In all property categories (especially fracture energy, measured as the area under the nominal stress-strain curve), the neat polyester films
dried at 60 °C consistently exhibit comparable or improved performance relative to those dried at 35 °C. This outcome is expected and in agreement with latex-type polymer films [19,26,22], since tightly packed latex particles can only undergo sufficient polymer deformation and interdiffusion (to ensure the formation of a contiguous film) when the drying temperature is above the polymer T_g. When the drying temperature is lower than T_g, particle packing, deformation and interdiffusion are hindered, thereby resulting in defective films and poor film performance [19,26]. For the PolyC/CNF nanocomposite films tested, we find more complex trends. For example, the Young’s modulus in Figure 5a increases with increasing content to a maximum at 50 wt% CNF and then decreases at higher CNF loading levels. Moreover, the dependence of the modulus on drying temperature also appears to be pronounced at 50 wt% CNF. At 90 wt% CNF, the modulus is most likely representative of the continuous CNF matrix, and drying below the T_g of PolyC yields a higher modulus since defects in PolyC as the minor nanocomposite constituent contribute less to property development. Interestingly, this unexpected comparative observation extends to all the other property metrics except the elongation at break, for which no statistical difference exists between values measured from films dried at both temperatures.

Recognizing that mechanical properties can be sensitive to specimen preparation, the Young’s modulus previously reported [57] for neat CNF films prepared by casting/drying aqueous CNF suspensions is 4.79 GPa, which is considerably higher than the moduli measured here for PolyC/CNF nanocomposites. Similarly, the tensile strength, elongation at break and fracture energy for neat CNF films are found to be 232 MPa, 12.6% and 20.5 MJ/m^3, respectively. Caution must be exercised, however, in quantitatively comparing these data to our present findings. For instance, the tensile strength values provided in Figure 5b are also much
lower than that expected for neat CNF, but reveal that the drying temperature has no discernible influence on property development at 10 and 50 wt% CNF. In comparison, however, both nanocomposites possess a significantly higher tensile strength than the neat PolyC films. While drying temperature has little impact on the elongation at break or fracture toughness in the nanocomposites with 10 and 50 wt% CNF, it is particularly noteworthy that the PolyC/CNF nanocomposites with 10 wt% CNF in Figures 5b-d consistently exhibit the most improved tensile strength, elongation at break and fracture energy of all the compositions tested. Such simultaneous improvement of all these properties evinces strong interaction between the polyester molecules and the cellulose nanofibrillar network, therefore requiring extra force to break the network and fracture the film. The nanofibrils, expected to be uniformly distributed throughout the film, serve as reinforcing agents by delaying crack propagation at energy absorption points. This is demonstrated by the dramatic increase in fracture energy by ~500% and ~200% relative to the neat polyester film dried at 35 and 60 °C, respectively, in Figure 5d.

At the higher drying temperature, water is removed faster from the system, thereby increasing the solids level at an escalated rate compared to that induced at the lower drying temperature. An increase in solids level concurrently increases the viscosity and promotes kinetic arrest, which subsequently hinders the ability of CNF to spread uniformly throughout the hydrated polyester medium. As a consequence, rather than interacting with polyester molecules, CNF is presumed to interact with itself to form aggregated flocs. This series of events also reduces the population of energy absorption points required to slow crack propagation, which explains why the films with 10 wt% CNF are mechanically tougher when dried at 35 °C, instead of 60 °C. Similar behavior is observed in the film with 90 wt% CNF, but this film possesses a CNF matrix, in which case the contribution of the polyester is less important. Expedited film
formation due to rapid water removal generally affects the mechanical properties of CNF films significantly, resulting in densified CNF layers [52]. Since these films are sensitive to drying temperature, it is not surprising that comparable behavior is likewise apparent in Figures 5a-b,d for PolyC/CNF films containing 90 wt% CNF. While the incorporation of such a high loading of CNF enhances all the property metrics relative to the neat polyester in Figure 5, the addition of PolyC appears to compromise all the mechanical properties of neat CNF. At this CNF loading level, we posit that the PolyC serves as a plasticizing, rather than reinforcing, agent for CNF. This scenario is qualitatively consistent with the rheological behavior of the same suspension portrayed in Figure 2c, in which the viscosity is lowered as the polyester plasticizes the strong nanofibrillar network of the CNF suspension.

Unlike the previous cases discussed above, however, the mechanical properties of PolyC/CNF nanocomposites with 50 wt% CNF are, with notable exception of the Young’s modulus, independent of drying temperature. Moreover, these nanocomposites generally exhibit tensile strength, elongation-at-break and fracture energy measurements that lie between those determined from nanocomposites with lower (10 wt%) and higher (90 wt%) CNF loading levels. Although the precise reason for this observation is not known at present, we speculate that it is due to unsuccessful competition between the constituent network-forming species. While numerous material factors influence the mechanical properties of polymer/CNF hybrid nanocomposites (e.g., the degree of dispersion, porosity and moisture content), the most important underlying consideration is the adhesive interaction between the polymer and CNF. In the case of the PolyC/CNF nanocomposites containing either 10 or 90 wt% CNF, the role of each component is distinct: PolyC is the matrix and CNF is the filler at 10 wt% CNF or vice-versa at 90 wt% CNF. In contrast, the roles of PolyC and CNF in the nanocomposite with 50 wt% CNF
are unclear. This does not imply that the PolyC and CNF are macrophase-separated, since the films included in Figure 3 are optically transparent. In fact, the formation of nanoscale aggregates of polyester and/or CNF would not necessarily compromise optical properties, but the formation of such discrete aggregates could have a largely deleterious influence on ultimate mechanical properties (i.e., those properties evaluated at failure) by facilitating crack propagation. If this is the case, the morphological characteristics of the films must be scrutinized to establish a meaningful correlation between film structure and mechanical properties.

As depicted in Figures 6 and 7, the cross-sectional views of the hybrid PolyC/CNF films vary significantly depending on composition and, to a lesser extent, drying temperature. Two distinctive matrices are apparent: one attributed to PolyC at low CNF loading levels and the other representative of CNF at high CNF levels. The fracture surfaces of neat PolyC films dried at 35 and 60 °C appear relatively smooth in Figure 6. Upon addition of 10 wt% CNF, the cross-section becomes noticeably rougher, and sharp fracture features reminiscent of brittle materials develop. In the films with 50 wt% CNF, CNF-induced stratification becomes apparent, but the film morphology consists of coexisting regions that are both smooth and layered in Figure 7. Discrete nanoscale polyester aggregates are also evident at both drying temperatures. These images suggest that PolyC coats or adheres to the CNF layers without completely impairing the stratified CNF layers. In other words, the nanocomposite with 50 wt% CNF possesses a polyester-coated laminated morphology and ensures that the CNF comprises the matrix to template the PolyC as it coalesces into a coating. Micrometer-scale roughness, along with discrete protrusions and holes, are clearly observed. The presence of multiple dense layers and PolyC aggregates interferes with interfibrillar interactions and thereby weakens the binding strength of neat CNF. Such nonuniform film morphology is expected to be responsible for the
reduced mechanical properties of PolyC/ CNF films containing 50 wt% CNF. At 90 wt% CNF, however, a dominant stratified structure is prevalent in Figure 7 and resembles that of neat CNF (included in the figure). Unlike the uniformly dense layers apparent for neat CNF, nanofibrils, nanofibrillar bundles and possibly PolyC aggregates are pulled out from the film surface during cryofracture, with the result appearing as holes measuring ca. 110 ± 30 nm (irrespective of drying temperature) at 90 wt% CNF. The population of nanofibrils and nanofibrillar bundles that bridge adjacent layers is ultimately responsible for mechanical integrity, whereas those species susceptible to pull-out during cryofracture provide evidence of weakened interfibrillar interactions [63], which contribute to a reduction in mechanical properties relative to neat CNF.

Both PolyC and CNF are known [4,52] for their excellent film-forming properties. This waterborne polyester not only forms contiguous and defect-free films over a wide temperature range (even at temperatures below its T_g), but also synergistically interacts with CNF to improve the mechanical properties of PolyC/CNF nanocomposite films (cf. Figure 5). In addition to such significant enhancement of mechanical properties, these nanocomposites exhibit tunable surface properties. By controlling the composition and selecting a suitable drying temperature, we can control the surface hydrophobicity of the resulting nanocomposite films. In Figure 8, the WCA is displayed as a function of film composition at 3 different drying temperatures: (1) 35 °C (below T_g), (2) 60 °C (above T_g), and (3) 35 °C and post-dried at 80 °C. For the neat PolyC and CNF films, surface hydrophilicity is nearly independent of drying temperature. The surface of neat PolyC films is slightly hydrophilic with a WCA of ~75°, which is reasonable considering that PolyC consists of both hydrophobic and hydrophilic moieties along its backbone. On the other hand, the surface of neat CNF films is highly hydrophilic with a WCA of ~30°. As both materials are combined to form nanocomposite films, the WCA expectedly decreases with
increasing CNF content, but the change does not follow a simple rule of mixtures. Rather, films at intermediate composition remain more highly hydrophobic than anticipated, whereas those that are CNF-rich behave more hydrophilic (like CNF). For films dried at 35 °C, the nanocomposite with 10 wt% CNF possesses a WCA of ~69°, which reflects the fact that the PolyC comprises the film matrix and resides at the surface (since the polar hydroxyl groups on CNF prefer to remain subsurface). This scenario is corroborated by the observation that an increase in drying temperature (and, hence, PolyC molecular mobility) drives the WCA up to ~73° at 60° C and ~77° at 35/80 °C. While the WCA for films containing 50 wt% CNF and dried at 35 °C drops to a predictable intermediate value (based on a linear rule of mixtures), the effect of drying temperature on WCA remains evident. For films with 90 wt% CNF, the PolyC has insufficient mobility to migrate to the film surface at 35 °C (below its T_g), in which case the CNF is able to endow the surface with enhanced hydrophilicity (the WCA is ~36°, which lies near that of neat CNF). As the drying temperature is increased, PolyC molecules are able to diffuse to the film surface and render it more hydrophobic.

**CONCLUSIONS**

In this study, we have investigated the interaction between different grades of commercially available sulfopolyesters and CNF in both aqueous suspensions and solid films. Aqueous polyester dispersions and polyester/CNF suspensions display excellent colloidal stability due to their negative charges. Rheological studies reveal that, upon CNF addition, the suspension viscosity profiles display a nontrivial change from Newtonian to shear-thinning behavior, which is advantageous in processing and coating formulation. Furthermore, the viscosities of the mixed suspensions are, for the most part, insensitive to CNF content, which facilitates reproducible
preparation of polyester/CNF suspensions for films and coatings without complicated flow properties. In two of the sulfopolyester/CNF suspension series, incorporation of 50 wt% CNF promotes the lowest viscosity, suggestive of interpolymer complexation. Solid films cast from these mixtures display distinctive differences in mechanical, as well as surface, properties that depend sensitively on both composition and drying temperature. Of particular interest, films composed of PolyC with 10 wt% CNF reinforcement yields the greatest improvements in most of the mechanical properties considered here, especially the fracture energy. We attribute this observation to the presence of cellulose nanofibrils that are uniformly distributed throughout the polyester-rich film, inducing energy dissipation and dampening crack propagation. Changes in mechanical properties are qualitatively related to internal film morphologies, as discerned by electron microscopy of cryofractured cross-sections. Moreover, we have achieved tunable surface hydrophilicity, as expressed in terms of the WCA, by simultaneously modulating the composition and drying temperature of polyester/CNF nanocomposite films.

This work demonstrates that the combination of waterborne sulfopolyesters with CNF yields hybrid nanocomposites with highly tunable and, in several cases, synergistic properties that are especially beneficial for coating applications. Our findings reported in this study corroborate the potential of CNF as a green reinforcing agent [64], especially for a commercially promising waterborne polymer. While numerous studies have addressed the effectiveness of cellulose nanocrystal (CNC) in this role (due primarily to its facile and predictable dispersability) [45,46,49,54], CNF remains a much less attractive choice due to its propensity to entangle and form aggregates. Chemical modification of CNF is frequently necessary to reduce the extent to which entanglement and aggregation occur and thus enhance dispersion uniformity [47]. The system examined here is advantageous in that no pre-processing functionalization is required to
achieve an optimum CNF dispersion state within the waterborne sulfopolyester matrix.

AUTHOR CONTRIBUTIONS

All analytical tests were conducted by Dr. S.-A. Jin and Dr. E.G. Facchine. The experimental plan was conceived, and the manuscript was written, through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENTS

This work was supported by the Eastman Chemical Company and was performed, in part, at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI).
FIGURES

**Figure 1.** The general chemical structure of the waterborne sulfopolyesters investigated in the present study, wherein w and y represent the mole fractions of diacid (IPA and SSIPA, respectively) and x and z represent the mole fractions of glycol (DEG and CHDM, respectively). The mole fractions w + y and x + z add to unity.
Figure 2. Viscosity profiles of CNF (0.2 wt%, square) and polyester/CNF dispersions: (a) PolyA/CNF (circles), (b) PolyB/CNC (triangles), and (c) PolyC/CNF (diamonds) at different polyester/CNF mass ratios (w/w, color- and symbol-coded): 90/10, 50/50, and 10/90. Solid lines are power-law regressions to the data. Error bars representing the standard error are smaller than the symbols.
Figure 3. Photographs of polyester/CNF films cast at 35 °C. The polyester used (left) and the loading level of CNF in the film (top) are labeled.
Figure 4. Nominal stress presented as a function of tensile strain during quasistatic uniaxial deformation of PolyC/CNF films dried at (a) 35 °C and (b) 60 °C at different compositions (w/w, color-coded): 100/0, 90/10, 50/50, and 10/90.
Figure 5. Mechanical properties of polyC/CNF films dried at 35 °C (blue) and 60 °C (red) extracted from tensile stress-strain measurements: (a) Young's modulus, (b) tensile strength, (c) elongation at break, and (d) fracture toughness. Error bars represent the standard error.
Figure 6. SEM images acquired from cryo-fractured cross-sections of PolyC and PolyC-rich PolyC/CNF films prepared at different compositions and dried at 35 and 60 °C (labeled).

Figure 7. SEM images acquired from cryo-fractured cross-sections of CNF and CNF-rich PolyC/CNF films prepared at different compositions and dried at 35 and 60 °C (labeled).
Figure 8. (a) Dependence of the WCA on CNF loading level in PolyC/CNF films dried at different temperatures (color-coded), and (b) representative water droplets used to measure the WCA. The colored dashed boxes in (b) identify the temperature at which the films were dried in (a).
REFERENCES


Here, we provide AFM images and surface roughness values measured from PolyC/CNF nanocomposite films dried on glass at 35 and 60 °C and varying in CNF content.

**Figure S1.** Series of AFM height images acquired from PolyC/CNF films dried on glass slides at two temperatures (left labels) and varying in CNF content (top labels). Bright features indicate an increase in relative height on the specimen surface. Images displayed at low CNF loading levels focus primarily on nanoscale features that are representative of the sulfopolyester whenever possible.

**Figure S2.** Values of the rms surface roughness measured from AFM images presented as a function of CNF content for PolyC/CNF nanocomposites dried at different temperatures (in °C): 35 (blue), 60 (green) and 35-80 (red). The solid lines serve to connect the data.