
Iridescent cellulose nanocrystal/polyethylene oxide composite films with low coefficient of thermal expansion

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Abstract: Simultaneous control over optical and thermal properties is particularly challenging and highly desired in fields like organic electronics. Here we incorporated cellulose nanocrystals (CNCs) into polyethylene oxide (PEO) in an attempt to preserve the iridescent CNC optical reflection given by their chiral nematic organisation, while reducing the composite thermal expansion. The hydrophilic nature and long-range self-organisation of CNCs facilitated structural control in the PEO matrix. The coefficient of thermal expansion (CTE) was determined by using contrast-enhanced microscopy digital image correlation (CEMDIC) based on textural features revealed within CNC/PEO composites under polarised light. The attained composite films were iridescent and exhibited a significant reduction in CTE even with low CNC addition (~50% CTE reduction at ~10 wt.% CNC load). With further control over nanoparticle processing, such composites promise potentials for selective optical bandgap materials while tuning the CTE.

Keywords: cellulose nanocrystals; CNCs; iridescence; coefficient of thermal expansion; contrast enhanced microscopy digital image correlation; polymer composites.

Reference to this paper should be made as follows: Diaz, J.A., Braun, J.L., Moon, R.J. Youngblood, J.P. (2015) 'Iridescent cellulose nanocrystal/polyethylene oxide composite films with low coefficient of thermal expansion', *Int. J. Experimental and Computational Biomechanics*, Vol. 3, No. 3, pp.189–199.

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1 Introduction

The manufacture of advanced composites has been intimately connected to the realisation of new materials and the fine-tuning of their interactions to effectively control structure and enhance physical properties. Over the past two decades advances in cellulose nanocrystals (CNCs) have led to great structural versatility in the number of applications conventionally offered by cellulosic materials beyond their abundant and biorenewable nature. The long range order offered by CNC self-assembly, their rod-like nanoparticle morphology (i.e., width 5–20 nm, length 50–350 nm) (Moon et al., 2011) along with low coefficient of thermal expansion (Diaz et al., 2013) and high stiffness (Moon et al., 2011) provide unique opportunities for composite fabrication, and structural control at different length scales.

CNCs have been used as reinforcement additives to both hydrophilic and hydrophobic polymer materials, where thermomechanical properties have been significantly investigated (Mariano et al., 2014; Tatsumi et al., 2012; Xu et al., 2013). The unmodified hydrophilic surface chemistry of CNCs makes them suitable to directly interact with water-soluble polymers, in which CNC additions have enhanced the

thermomechanical properties of polymers like polyvinyl alcohol (PVA) (Zhang et al., 2013; Peresin et al., 2010), poly acrylic acid (PAA) (Lu and Hsieh, 2009), and ethylene-vinyl alcohol copolymer (EVOH) (Martínez-Sanz et al., 2010). Organic solvent-based CNC composites have been conventionally obtained by adding non-ionic surfactants (e.g., CNC/polystyrene; Rojas et al., 2009) or chemically functionalising the CNC surface (e.g., benzophenone-functionalised CNCs/ethylene oxide/epichlorohydrin – EO-EPI; Biyani et al., 2014). The range of potential applications offered by CNC composites could be greatly extended by achieving additional control of their optical properties.

One of the most attractive properties of CNCs is the angle dependent light reflection generated by their chiral nematic organisation, which has inspired research towards controlled reflection wavelength (Beck et al., 2011) and sensor (Zhang et al., 2013) applications. Both CNC helical pitch and structural uniformity (Park et al., 2014), represent main factors involved in the control of the optical properties generated by CNCs. Such factors should also prevail in the presence of other components in order to extend the optical response to designed composite materials (Cheung et al., 2013). For instance, gold nanoparticles have been incorporated in cholesteric CNC matrixes to create composites with the optical activity of CNCs and plasmonic properties of gold (Querejeta-Fernández et al., 2014). Nonetheless, all microstructural modifications performed to obtain specific optical properties are typically connected to changes in other material properties, such as thermal expansion. In fields like organic electronics, optical transparency and/or tunable reflectance are desired but the thermal stability has to be simultaneously engineered as mismatches in coefficient thermal expansion (CTE) between deposited layers and the substrate should be avoided to prevent undesired interlayer thermal stresses. Reducing the thermal expansion of polymer matrices has been conventionally achieved by introducing thermally stable fillers with low CTE (Rao and Blanton, 2008; Debelak and Lafdi, 2007), such as boron nitride (Zhi et al., 2009), carbon nanotubes (Wei et al., 2002), alumina and silica (Wong and Bollampally, 1999). However, the range of simultaneous control over both optical and thermal properties is rather limited and presents challenges as in the inclusion of fillers conventionally conveys refractive index mismatches and increased light scattering.

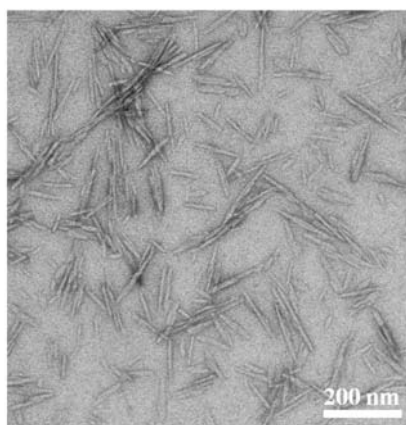
Due to the extended structural control (i.e., cholesteric organisation) and low CTE, CNCs appear as promising candidates for the fine control of the interplay between optical properties and thermal expansion in polymer composite structures. CNC films can exhibit optical iridescence and tunable wavelength for selective reflectivity while maintaining an isotropic CTE response. As CNC alignment increases in such films, so does their transparency along with a decrease and increase in their CTE in the directions parallel to and perpendicular to CNC alignment, respectively (Diaz et al., 2013). However, pure CNC films tend to be brittle with low flexibility, limiting use for many applications. Polyethylene oxide (PEO) has demonstrated to be a good polymer matrix for CNCs due to its high polar affinity, facility to achieve steric stabilisation (Kloser and Gray, 2010), capability of preserving organisation in hybrid structures (e.g., clay nanocomposites;

Chaiko, 2003) and enhanced stiffness (Changsarn et al., 2011; Zhou et al., 2011; Fujisawa et al., 2014). Here we present CNC/PEO composites that retain the optical properties typical of chiral nematic CNC films and reduced thermal expansion connected to CNC content. CNC/PEO composites revealed distinct textural features under crossed polarisers, which allowed the calculation of CTEs in a contact free fashion via contrast-enhanced microscopy digital image correlation (CEMDIC) (Diaz et al., 2014). The approach utilises the same DIC principle of image cross-correlation based on pixel intensity (Reedlunn et al., 2013) and neglects the need of physical sample modification to obtain speckled trackable features.

2 Experimental section

An aqueous suspension containing 8.7 wt.% CNCs (acid hydrolysed *eucalyptus* dry-lap cellulose fibres) with 0.81 wt.% surface-grafted sulphate content was provided by the USFS-Forest Products Laboratory (FPL), WI, USA. Figure 1 shows a transmission electron microscopy (TEM) image of CNCs produced from wood, in which the typical size range was approximately 5–20 nm in diameter and 50–350 nm in length. The TEM image was obtained using a Philips CM-100 TEM operated at 100 kV, and 92,000 $\times$ magnification over a diluted sample of re-dispersed freeze-dried CNCs. Different proportions of PEO (M_v 1,000 Sigma Aldrich) diluted as received in deionised water were mixed with the aqueous 8.7 wt.% CNC suspension to obtain ~20 mL aliquots holding approximate 6.7, 29.6 and 39 wt.% CNC/PEO in water. Composite films were prepared by solvent casting the resultant CNC/PEO suspensions in 8 cm diameter polystyrene Petri dishes under ambient conditions (23°C, 35% relative humidity). Freestanding composite films were peeled off the substrate after three days.

Figure 1 Transmission electron micrograph (TEM) showing the characteristic rod-like morphology and polydispersity present in unmodified CNCs



Thermal strains within the films were measured by the CEMDIC technique (Diaz et al., 2014). Polarised optical microscopy images (36 bit, 2,047 $\times$ 2,047 pixels, 15 ms exposure)

were obtained in a Carl Zeiss (Axio Observer A1) inverted microscope enclosed in a protective polymer film to minimise airflow thermal gradients. Images were captured at 30, 40, 60, 80 and 100°C after increasing film temperature (heating stage, Linkam PE94) at 10°C/min and 7 min stabilisation time. Composite films were thermally stable in the selected temperature range, after being thermally pretreated following the above mentioned temperature sequence before image acquisition. Images were processed in ImageJ and Adobe Photoshop and correlated for thermal expansion calculations using the HighCorr package available in MathWorks, along with the image toolbox in MatLab R2012b (Thompson and Hemker, 2007). To balance resolution and computing time, regions of interest were selected around the specimen centre (i.e., avoiding thermal warping, edge defects, etc.), and cross-correlated using 30×30 pixels as grid spacing, and 60 pixels as subset correlation size.

3 Results and discussions

The polydisperse nature of CNCs (Figure 1) is conventionally attributed to the acid hydrolysis necessary to break the hierarchical cellulosic structure present in the raw materials (Moon et al., 2011). The resultant surface chemistry of CNCs is populated with hydroxyl groups and sulphate groups that confer electrostatic stability to aqueous CNC suspensions and plays a fundamental role in the final properties of the polymer composites (Khoshkava and Kamal, 2013). The CNC interactions with water-soluble polymers such as PEO are mainly dominated by hydrogen bonds (Zhou et al., 2011). However, as a neutral polymer, PEO can coexist with CNCs in water, which interrupts hydrogen bonding without affecting the stability of the CNC dispersion. As the evaporation of the CNC/PEO suspensions proceeds the typical long-range positional and orientational order given by the chiral nematic CNC self-organisation is seemingly extended to the composite structure indicating little interaction. Alternatively, if the PEO does interact specifically with the CNC surface, it may act as an additional steric stabiliser for the CNCs as the water evaporates similar to PEO-grafted CNCs which have been used as steric stabilisers in some instances (Kloser and Gray, 2010). Regardless of the mechanism, it is known that PEO tends to preserve the organisation of some systems such as crystalline sheets of clay-polyvinylpyrrolidone (PVP) composites (Rao and Blanton, 2008). CNC/PEO composites exhibited a clear constructive interference of light, as noted by the strong iridescent coloration of the tested samples (Figure 2). The iridescence shown by the CNC/PEO composites closely approached that exhibited by bulk CNC films [Figures 2(a) and 2(b)] (Diaz et al., 2013).

The uniformly iridescent CNC/PEO composite films shown in Figure 2 revealed different textural features under linearly polarised light (Figure 3), which are mainly attributed to multiple domains exhibiting different helical pitches and angles to film normal throughout the films [Figure 2(b)]. PEO can therefore modify the in-plane thermal properties of bulk CNC films (Figure 4) without drastically affecting the iridescence of the system, an aspect that is desired for applications where CNCs typically act as a substrate (e.g., organic solar cells, organic light emitting diodes, etc.).

Figure 2 (a) Left to right: photographs of an iridescent CNC/PEO composite film coating a metallic substrate, CNC film and uncoated substrate (b) Iridescence in CNC/PEO composites as a function of concentration (see online version for colours)

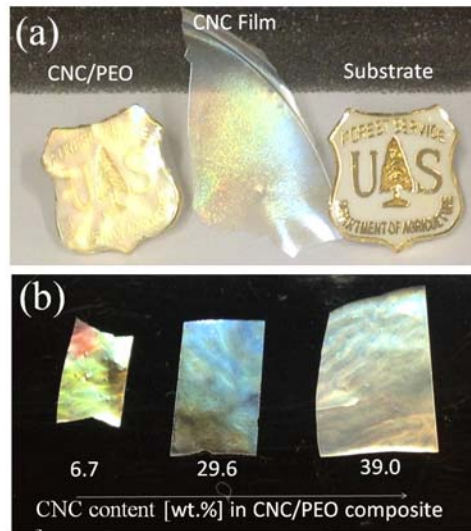
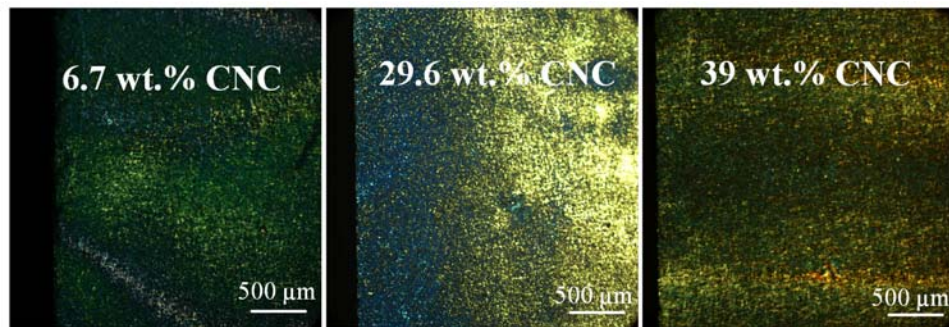


Figure 3 CNC/PEO composite films with different compositions under polarised optical microscopy (see online version for colours)



Note: Speckled texture employed in thermal strain measurements via CEMDIC shows typical variation of intensities and distribution of speckle sizes connected to the interaction of polarised light with structural film characteristics (e.g., crystalline orientation, domain size, etc.) through thickness.

Figure 4 shows representative responses of thermal strain as a function of temperature determined for CNC/PEO composites having different compositions. Thermal strains were calculated in multiple regions of interest in a contact-free way by using the textural features highlighted under polarised light (Diaz et al., 2014), where the linear CTE is calculated as the slope of the thermal strain versus temperature. Thermal strains for all composites tended to increase proportionally with temperature exhibiting linear responses, although in cases such as the 29.6 wt.% CNC composite, textural features – likely connected to regions of low structural uniformity – can render curved profiles where regions can expand faster than others as temperature increases. In such a case the

linear CTE represents an overall approximation for the whole temperature range selected. Figure 5 shows how the CTE of CNC/PEO composites decreased as CNC content increased. CTEs of all composites were calculated from room temperature up to 100°C in order to eliminate possible effects coming from humidity and the proximity to the onset of CNCs thermal degradation ($\sim 200^\circ\text{C}$) (Petersson et al., 2007). Composite films also exhibited high thermal stability at 100°C, which is around 30°C above the melting temperature of pure PEO. Such an improved thermal stability has been similarly observed in PEO/clay composites (Rao and Blanton, 2008), where heat propagation seems to be highly affected by the structural characteristics of the nanofiller. With ~ 10 wt.% CNC content the thermal expansion drops $\sim 50\%$ in the composite film as compared to the neat PEO. Such a drastic response has been achieved in other systems with nanofillers like single-walled carbon nanotubes (SWNTs) where networks are formed within the polymer matrixes rendering enhanced mechanical properties (Chatterjee and Krishnamoorti, 2007). The flexibility in composite manufacture and reinforcing capacity of CNCs can be easily comparable to that exhibited by SWCNTs [e.g., CNC vs. SWNT in poly (L-lactide) (PLLA)] (Fujisawa et al., 2014).

Figure 4 Thermal strains vs. temperature for different CNC/PEO composite films measured via CEMDIC (see online version for colours)

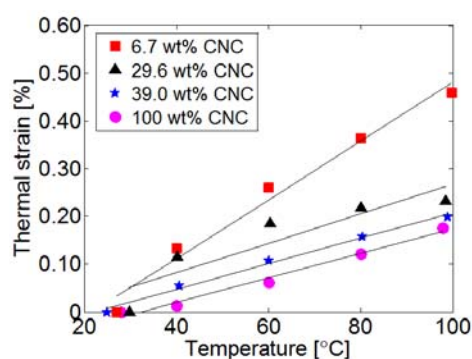
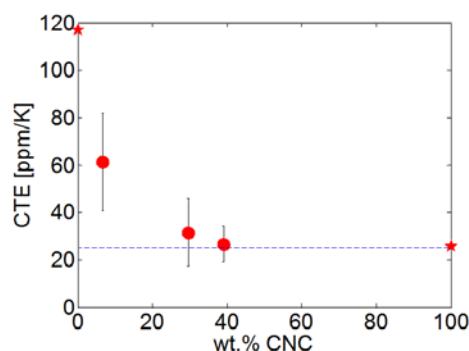


Figure 5 CTE of CNC/PEO composite films as a function of nanoparticle load (see online version for colours)



Note: CTE of neat PEO film (Rao and Blanton, 2008) and CNC film (Diaz et al., 2013) were calculated up to 60 and 100°C, respectively.

The improved thermal response observed in CNC/PEO composites is likely due to a percolating interconnection of nanocrystals guided by hydrogen bonds throughout the structure as the alignment of hydrogen bonds in shear-oriented CNC films has demonstrated to decrease the coefficient of thermal expansion (Diaz et al., 2013). The presence of possible percolation thresholds have also been suggested to model significant reinforcements in mechanical properties of different cellulosic nanomaterial composites (Moon et al., 2011; Garcia de Rodriguez et al., 2006). An additional contribution coming from PEO crystallinity could be expected (Xu et al., 2014) due to the interfacial interaction between CNCs and the PEO matrix (Fukuya et al., 2014). However, it is currently unknown if the addition of CNCs altered PEO crystallinity. Likewise, variations in the composite structural features and subsequent composite optical reflection seem to be intimately connected to nanoparticle characteristics (e.g., surface chemistry) (Roman and Gray, 2005) and thermal as well as surface gradients generated during evaporation of suspensions (Dumanli et al., 2014), nonetheless, further studies are required to obtain enhanced structural-property control. Parallel to the experimental approach, computational methodologies are starting to yield essential descriptions of the properties of single CNCs and the way they assemble (Diaz et al., 2014; Dri et al., 2013; Hector et al., 2007). As the CNC loading increased, the CTE of the composite decreased and reached a response similar to that exhibited by bulk CNC films, ~ 25 ppm/K (Diaz et al., 2013), at a CNC load of around 40%. Due to the interactions of the nanocrystals with the polymer matrix, CNC/PEO composites can attain thermal expansions similar to those found in ceramic and metallic materials, while retaining the iridescent appearance. Advances in the interplay between optical and thermal for CNC based composites can be envisioned by obtaining further understating of the interfacial interactions and their correspondent fine-tuning in multiple composite systems.

4 Conclusions

The optical iridescence given by the chiral nematic self-organisation of CNCs was successfully transferred to a PEO matrix following a simple solvent casting process. The same as in the preparation of iridescent CNC films, undisturbed conditions and homogenous dispersions were fundamental to obtain high quality composite films. Textural features highlighted by linear polarised light allowed the calculation of composite CTEs in a contact-free fashion using CEMDIC. A significant reduction of $\sim 50\%$ in the PEO CTE was achieved with ~ 10 wt.% CNC loading. Iridescence was preserved in prepared CNC/PEO composite films. Further advances on CNC processing could offer enhanced control over CNC self-assembly and optical properties of CNC-based composites. The lower CTE limit observed for the prepared CNC/PEO composites approached the CTE of bulk chiral nematic CNC films (~ 25 ppm/K) likely due to the predominant long-range structural self-organisation of the CNCs and the strong hydrophilic interfacial interaction with the PEO matrix.

Acknowledgements

The authors would like to thank the Air Force Office of Scientific Research grant #FA9550-11-1-0162 for supporting this project.

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