Dynamic mechanical analysis of layer-by-layer cellulose nanocomposites

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ABSTRACT

Natural composites like wood are scale integrated structures from molecular to the macroscopic scale. Inspired by this design, layer-by-layer (LbL) deposition technique was used to create lignocellulosic composites from isolated wood polymers with an ordered architecture from the nano to the microscale level. The objective of this study was to investigate the effect of the LbL ordering versus a cast film composed of a blended mixture of the same polymers using dynamic mechanical analysis (DMA). The composites were made from TEMPO-oxidized nanocellulose (TONc) obtained by fibrillation of TEMPO mediated oxidized pulp fibers, organosolv lignin (OL), and a cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) used as a linking layer. DMA was performed on thin films that were saturated with ethylene glycol, utilizing a parallel-plate compression-torsion geometry. In the temperature range that was studied (0–120 °C), a single tan δ peak was observed in the 30–40 °C region for both nanocomposite films. A neat NC cast film was tested under similar conditions that displayed a similar relaxation in this region. The peak was seen to disappear in case of LbL films in the second heat, whereas it was recurring in case of cast films of the blended mixture, and neat NC films. Heating of the samples under a compressive force produced an opposite effects in the two films; the LbL films exhibited swelling, whereas the cast films showed densification Furthermore, the tan δ peak in the second heat of cast films was found to be frequency dependent, while the LbL film did not show the same behavior. The apparent activation energies calculated (65–80 kJ mol^{-1}) for these film based on the Arrhenius equation was found to be coincident to those reported for the β transition of cellulose.

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1. Introduction

The incorporation of nanoparticles into polymers is a design concept that is used in many areas of material science for the development of structural materials with improved mechanical and thermal characteristics (Capadona et al., 2007). Nanocomposites are characterized by an extremely fine dispersion of a phase of nanometer scale within a polymer matrix. The concept is attractive because it enables the creation of materials with new or improved properties by mixing multiple constituents and exploiting synergistic effects. The extremely small size of the nanometer scale phase/filler gives the composite material advantages over conventional composites (Cerruti et al., 2008). Nanoparticles include carbon nanotubes, clay particles, cellulose nanocrystals (CNCs), and metals among many others, and are characterized by very high aspect ratios and moduli. One important advantage of using nano-reinforcement or nano-fillers is that only a small amount (1–5%) of the nano-material is required for property enhancement. This result is due to the dramatic increase in surface area of the nanoparticles from conventional reinforcements or fillers, interacting with much of the bulk matrix polymers.

Biological nanoparticles such as CNCs have been shown to be very high modulus materials to use as reinforcement. Raman spectroscopic analysis of cellulose chain deformations of tunicin derived CNCs yielded a high elastic modulus value (Rusli, 2008). CNCs were first used as reinforcement in a latex matrix composed of poly(styrene-co-butyl acrylate) and the resultant composite was found to have an increase in shear modulus by two orders of magnitude (Favier et al., 1995a). Since this first report, CNCs obtained from different sources have been used to reinforce synthetic (Chazeau

et al., 1999; Favier et al., 1995b; Helbert et al., 1996; Ruiz et al., 2001) as well as natural polymer matrices (Angles and Dufresne, 2000; Dubief et al., 1999; Dufresne et al., 1999; Grunert and Winter, 2002; Noishiki et al., 2002). Another method for preparing nanoscale celluloses with length scales similar to carbon nanotubes was developed, when TEMPO mediated oxidized pulp fibers were fibrillated by mechanical agitation or ultrasonication (Johnson et al., 2009; Li and Renneckar, 2009, 2011; Saito et al., 2006). However, the use of these nanoparticles was not always associated with expected results, considering the exceptional mechanical properties of the individual nanoparticles (Šturcová et al., 2005; Treacy et al., 1996). Although there are several advantages, the negative aspects of using cellulosics are their poor miscibility with non-polar and petroleum-based thermoplastics, difficulty in processing at higher temperatures due to their degradation above 200 °C, and high moisture absorption, which leads to dimensional changes and decrease in mechanical properties (Samir et al., 2005; Fratzl et al., 2004; Lin et al., 2008; Rusli and Eichhorn, 2008). Because of these issues of poor miscibility and inadequate interfacial interaction the incorporation of these particles into composites is not always accompanied by an improvement in properties, due to poor dispersion (Rusli and Eichhorn, 2008).

One way to avoid dispersion problems is to carefully assemble nanoparticles in directed assembly processes such as layer-by-layer which have been shown to work on a variety of substrates including wood fiber (Agarwal et al., 2009; Gustafsson et al., 2012; Lin and Renneckar, 2011) and air bubbles (Winterhalter and Sonnen, 2006). In this context, the concept of layer-by-layer (LbL) adsorption offers a significant advantage in the ability to immobilize polymers/nanoparticles through electrostatic interactions in exact architectures (Decher, 1997). The technique has been used to create free-standing films composed of polymers and nanoparticles, which were aimed at several potential applications (Ashcraft et al., 2010; Becker et al., 2010; Karabulut and Wagberg, 2011; Lee et al., 2010; Podsiadlo et al., 2007). Additionally, several studies have shown the ability of using layer-by-layer methods for cellulose nanoparticles (Podsiadlo et al., 2005a; Cranston and Gray, 2006a; Renneckar et al., 2006).

Natural materials like wood, bone, and nacre have very complex structures that can be considered carefully crafted nanocomposites. Natural materials have their building blocks scale integrated and organized hierarchically over several length scales, which offers a synergistic effect compared to their individual properties, or properties of their simple mixtures (Baer and Hiltner, 1992; Munch et al., 2008). For example, the secondary cell wall of plants is primarily composed of three different types of macromolecules namely cellulose, a collection of hemicelluloses and lignin; these polymers exist as a complex, organized network that act cooperatively to external stresses (Salmén, 2004). The secondary cell wall is an elegant nanocomposite structure, wherein cellulose microfibrils acts as the reinforcement, and is embedded in a matrix of lignin and hemicelluloses. Overall, the nanoscale cell wall building blocks are carefully organized into lamellae with layers that reach a micron scale thickness and span to millimeters in length. As an initial step toward creating a scale integrated nanocomposite, cellulose and lignin were organized from the nanoscale to the microscale into planar films that were millimeters in dimension (Pillai et al., 2014). This study involved layer-by-layer assembly into second cell wall like lamellae of nanocellulose and technical lignin in combination with a positively charged polyelectrolyte PDDA. In the current study, composites were prepared using two strategies: (1) LbL assembly to create highly organized free-standing films with lamellae structure, and (2) a cast film of the blended mixture. The prepared films were analyzed using a novel dynamic mechanical analysis technique (Chowdhury and Frazier, 2013a), which enabled the analysis of thin films in an organic solvent plasticized condition. The study

was motivated to understand how the organization of polymers in a nanocomposite material impacted the dynamic mechanical properties.

2. Materials and methods

2.1. Materials

The lignin used in this study was a mixed hardwood organosolv lignin (OL); Sigma–Aldrich, Inc., Nanocellulose (NC) was produced from never dried sulfate pulp (brightness level of 88%), supplied by Weyerhaeuser Inc. The cationic polymer used in this study was PDDA (Sigma–Aldrich: $M_n = 7.2 \times 10^4$, $M_w = 2.4 \times 10^5$ g/mol).

2.2. Methods

2.2.1. Nanocellulose isolation

2,2,6,6-Tetramethylpiperidine (TEMPO) oxidation of never-dried kraft pulp of southern yellow pine (88% brightness) was carried out using the method described by Saito et al. (2006) with slight modification processing the oxidized fiber in a Warring blender followed by sonication.

2.2.2. LbL free standing film formation

Deposition of LbL films were carried out on a cellulose acetate substrate using a custom made spraying device (Krogman et al., 2007). The layers were deposited in the following sequence; (1) 0.2% (w/v) PDDA (pH 10.5), (2) DI water (10 s), (3) 0.01% (w/v) OL (pH 10.5), (4) DI water, (5) 0.5% (w/v) PDDA (pH 10.5), (6) DI water, (7) 0.1% (w/v) NC, (8) DI water. Steps 1 through 8 represents one deposition cycle with two bilayers (PDDA:OL and PDDA:NC). The spraying time was 4 s for polymer solutions and 10 s for rinse step with DI water. A dwell time of 20 s was used between each step. Therefore the total time required for one deposition cycle was 3 min 16 s. A total of 250 cycles/500 bilayers were deposited to obtain a free-standing film, which required a total spraying time of ∼13.5 h. Once the deposition was complete, the films were air-dried and extracted by dissolving the CA substrate in acetone. The extracted LbL films were soaked in acetone for 24 h and further washed 5 times in fresh acetone bath to facilitate the maximum removal of residual CA. The extracted films were then air-dried and stored until further use.

2.2.3. Cast film preparation

Batches of 0.2% (w/v) NC suspension was prepared by re-dispersing 0.5 g freeze dried NC in 250 ml Mill-Q water aided by ultra-sonication (100% power) for 15 min in a water bath (4 °C) and purification by centrifugation.

2 g of NaOH (0.2 N) was dissolved in 250 ml of NC suspension (0.2% w/v), followed by the addition of 0.35 g OL. The suspension was allowed to mix for 24 h with continuous stirring. Following this step, 0.15 g of PDDA (10 ml of 1% w/v) was added slowly and was mixed with continuous stirring for 24 h. The relative proportions of NC, OL and PDDA in the mixture was thus 5: 3.5: 1.5. It was found during the preparation of blended films that PDDA is necessary to complex the three different materials (NC, OL and PDDA). The absence of PDDA in preparation of blended films resulted in significant leaching of lignin to the solvent used for plasticizing the films. From our initial experiments, the minimum amount of PDDA required to prevent leaching of lignin from the film was found to be 15% (w/w) of the total film. The mixture was dialyzed in a 12,000–14,000 g/mol molecular weight cut off dialysis tubes (Spectrum Labs) against Milli-Q water to remove the excess NaOH. The dialysis water was replaced every 12 h until the conductivity of the Milli-Q water dropped to <2.0 μS cm⁻¹. The dialyzed mixture