

Progress on Cellulose Nanofiber-filled Thermoplastic Composites

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Abstract

Cellulose shows great potential for application in green materials because it is abundant, renewable, has a microfibrillar structure, can be made multifunctional, and self-assemble into well defined architectures. A current research program at the University of Maine focuses on application of cellulose nanofibrils (CNF) in thermoplastic composites. One project is examining the application of CNF in engineering thermoplastics including polyamide 6 (nylon 6) and a polyester blend (polyethylene terephthalate (PET)/poly(trimethylene terephthalate) (PTT)). Part of the emphasis in focusing on cellulose nanofibril-filled engineering thermoplastics is that the end use of these composites is especially relevant in thermally challenging areas such as the manufacture of under-the-hood automobile components as well as the higher strength and stiffness of these materials also offer potential for development of structural green thermoplastic composites in infrastructure applications. Surface treatment of CNF is another important topic being studied. The compatibility and miscibility of CNF with conventional thermoplastics is a well-known problem because of the aqueous nature of CNF. Under current polymer processing technology, significant water content in the component formulations can not be tolerated. Various treatments are being evaluated to decrease or remove moisture from CNF products with a goal of maintaining the nano scale dimensions of the fibrils. Surface modification of CNF can be achieved using appropriate chemical compounds, resulting in improvements to composite material properties. This paper will describe the overall research program including the preparation of nanocomposites via melt processing and injection molding, characterization of material properties including mechanical tests, thermal characterization via thermogravimetric analysis and differential scanning calorimetry, and dynamic mechanical thermal analysis. The material property results will be described with a discussion on the challenges and opportunities for scale-up into commercial production of this new class of green nanomaterials.

Keywords: Cellulose, nanofibrils, nanocomposites, thermoplastics, green materials

Introduction

Forest-based lignocellulose is among the most abundant renewable polymer resources on earth, and constitutes Maine's largest natural resource. Maine is the most heavily forested state in the United States, with 90% of its land base in forests, and 95% of these forests classified as commercial timberland. These forests have been and will continue to provide timber for one of the nation's largest and most diversified forest products sectors. Lignocellulose derived nanocomposite materials from Maine's forests are extremely promising materials that can provide the next generation of lightweight, renewable materials for a variety of applications including construction, automotive, defense, consumer products, biotechnology, sensors & actuators, smart papers, and coatings.

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale. Nanotechnology research and development (R&D) in the U.S. is high priority research across all segments of science and engineering since the enactment of the National Nanotechnology Initiative (NNI) in 2001. Nanomaterials derived from renewable biomaterials, especially cellulose and lignocellulose, will undoubtedly play a large role in the nanotechnology research effort.

Cellulose fibers on the nanoscale are prepared in four different ways: 1) bacterial cellulose nanofibers, 2) cellulose nanofibers by electrospinning, 3) micro- or nano-fibrillated cellulose plant cell fibers, and 4) nanorods or cellulose whiskers. Processing techniques have a significant impact on the adhesion properties of the resulting cellulose nanofibers in composite material applications. The behavior of cellulose surfaces in polymers as well as their interaction with different chemicals is of great importance in their current and future applications in nanocomposites. The mechanical performance of nanocomposites, for instance, is dependent on the degree of dispersion of the fibers in the matrix polymer and the nature and intensity of fiber-polymer adhesion interactions. Because of the hydrophilic nature of cellulose nanofibrils, many studies have focused on nanocomposites based on hydrophilic matrices (Siro and Plackett 2010). There have been fewer studies focused on the application of CNF in hydrophobic polymers and this provides challenges and opportunities for novel research approaches.

Synopsis of Research Projects

Following is a brief discussion of results from research on cellulose nanocomposites at the University of Maine.

Application of CNF in Engineering Thermoplastics

Part of the emphasis in focusing on cellulose nanofibril-filled engineering thermoplastics is that the end use of these composites is especially relevant in thermally challenging areas such as the manufacture of under-the-hood automobile components as well as higher strength and stiffness and low density of composites manufactured using engineering thermoplastics also offer potential for development of structural green thermoplastic composites in infrastructure applications. Our initial work has examined the application of microcrystalline cellulose in polyamides (nylon 6) and polyesters (polyethylene terephthalate (PET-PTT blend).

Polymer composite materials consisting of poly (ethylene terephthalate) (PET) – poly (trimethylene terephthalate) (PTT) blends and microcrystalline cellulose (MCC) were prepared by melt mixing and injection molding. Mechanical properties of the resulting composites showed improved properties to the neat PET-PTT blend (Kiziltas et al. 2010a). Thermal analysis also indicated that the MCC did not show significant initial degradation under 300°C, which implies thermal stability so that MCC-filled composites could be used for high temperature circumstances, like in “under-the-hood” applications in the automobile industry (Kiziltas 2009; Kiziltas et al. 2010b). A combination of MCC at 20 weight % loading and low levels of nanoclay show enhanced stiffness in nylon 6 (Figure 1)

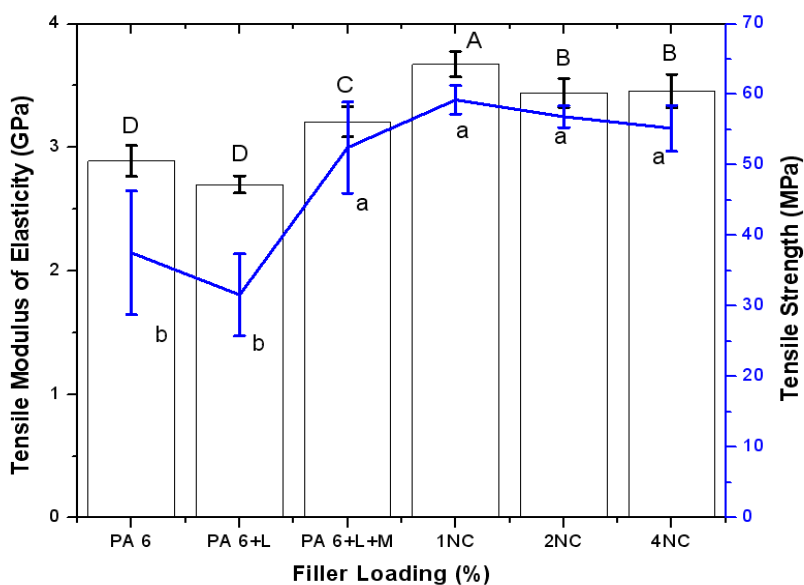


Figure 1. Tensile strength and stiffness of MCC/nano-clay-filled nylon 6.

Thermoplastic Starch (TPS) as a CNF Carrier

A homogenous dispersion of CNF in a polymeric matrix is required for obtaining well defined mechanical properties and consistent performance. CNF can not be simply added
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to a polymer melt during thermal compounding processes because of the potential for agglomeration. To prevent the cellulose from aggregating, and also to improve its dispersion in conventional thermoplastic matrices, modification of cellulose surfaces or using a carrier system for cellulose nanofibrils in polymer composites is required. A current project is examining the development of a thermoplastic starch carrier system for cellulose nanofibrils in polypropylene (PP) composites. The TPS and cellulose nanofibril-TPS filled PP composites showed comparable or lower strength and modulus compared to the control samples depending on the age of the specimens (Figure 2). During composite thermal processing, the semi-crystalline structure of starch and starch based composites is lost and the molecules are partially depolymerized. Even if stored under constant humidity and temperature conditions, the mechanical properties of thermoplastic starch can change over time due to retrogradation, which is the linear molecules, amylose, and linear parts of amylopectin molecules recrystallizing and rearranging themselves to a more crystalline structure. In addition, the absorption of moisture during the eight week conditioning period may have also contributed to the reduced strength properties.

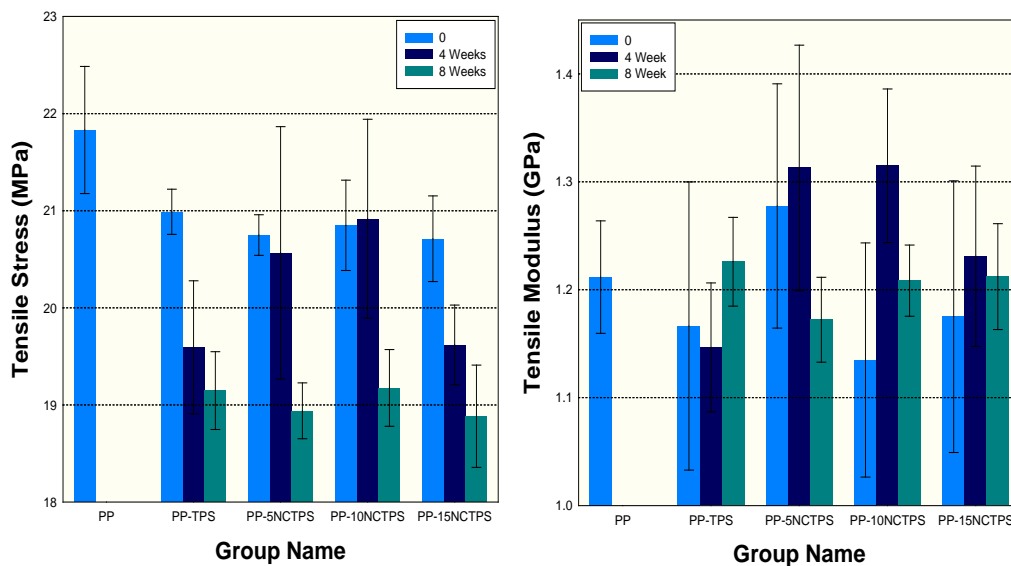


Figure 2. Tensile properties for TPS-CNF-filled polypropylene composites.

Critical Point Drying of Cellulose Nanofibrils

As mentioned previously, cellulose nanofibrils are very hydrophilic and tend to agglomerate during processing. The drying process should be selected with consideration of individual fiber separation and prevention of agglomeration. The morphology of the dried cellulose nanofibrils is directly affected by the drying method. Figure 3 shows the different morphologies of cellulose nanofibrils in dry form, which were prepared using different drying methods. We have explored critical point drying (CPD) as a means to process cellulose nanofibrils into a dry state and reduce the propensity for agglomeration. CPD requires solvent exchange from aqueous suspensions to ethanol, which is miscible with carbon dioxide followed by exchange of the ethanol with carbon dioxide under high

pressure with the subsequent removal of carbon dioxide from the CNF leaving dried nanofibrils that maintain nano scale dimensions (Figure 4). The CPD method is very efficient for drying small quantities of CNF for bench scale experiments, but may not be economically feasible for scale-up.

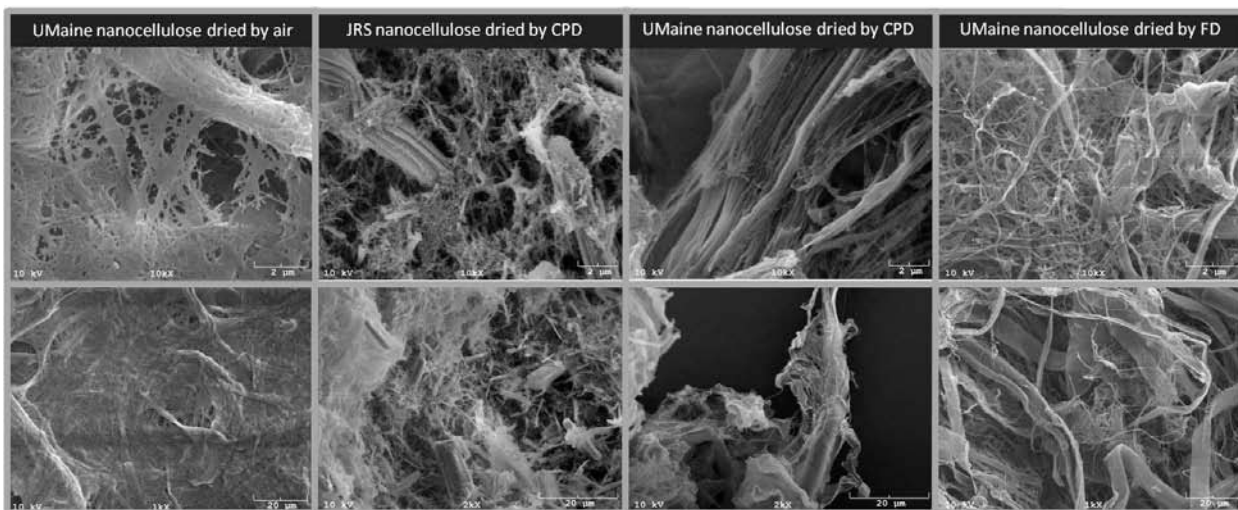


Figure 3. Different morphologies of cellulose nanofibrils using different drying processes. (CPD: critical point drying, FD: freeze drying, UMaine: products from University of Maine, JRS: products from J.Rettenmaier & Sohne, GmbH, Germany).

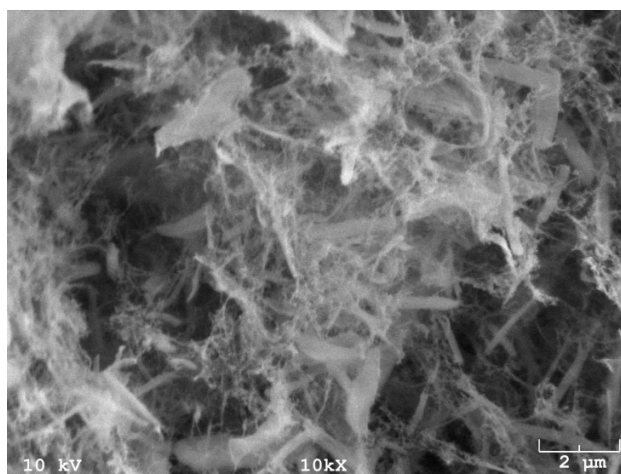


Figure 4. Critical point dried cellulose nanofibrils.

Cellulose Nanofibril Reinforced Wood-inorganic Composites

Cellulose nanofibril reinforced wood-inorganic composites are another field being studied at the University of Maine. The aqueous-based matrix of sodium silicate is helpful in dispersing cellulose nanofibrils into a composite structure (Figure 5). The addition of 2.5 weight % cellulose nanofibrils in a composite composed of sodium silicate solution and wood flour increased the flexural modulus of rupture (MOR) up to 30% compared to a control containing no CNF.

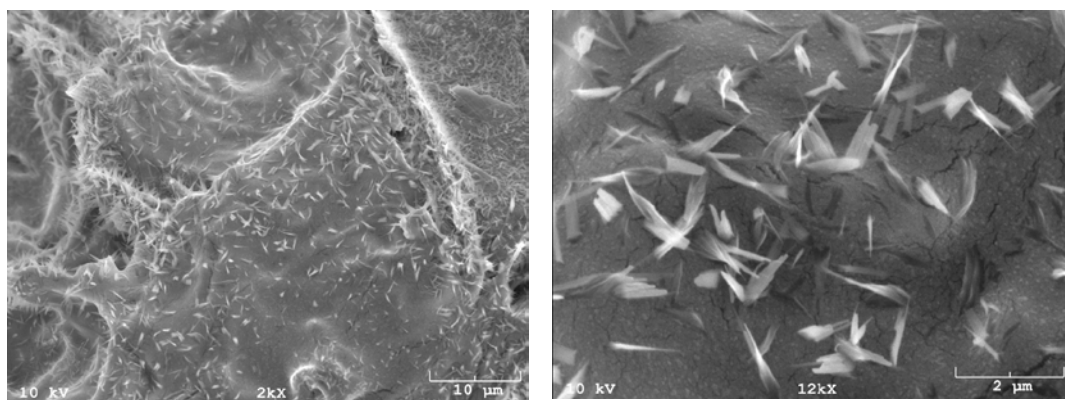


Figure 5. Fracture surfaces of CNF reinforced wood-inorganic composite.

Chemical Modification of Cellulose

The surface of cellulose can be chemically modified for further reactivity or compatibility with inert polymeric matrices. A grafted polymer, such as maleic anhydride grafted polyethylene, has been used for commercial composite products. Organic silane compounds can be used for adhesion promotion between incompatible materials by creation of a chemical linkage. The major advantage of the silane compounds is that silanes can be tailored for a specific material system since silanes can have two major domains that are designed for each component, filler and matrix, respectively. Wood fiber was coated with organic silanes (Silane1: N-[3-(trimethoxysilyl) propyl]butylamine, Silane2: (3-Chloropropyl) triethoxysilane) for creation of compatibility to polyethylene. The physical and mechanical properties were significantly improved so that adhesion between materials has been enhanced (Figure 6). The treatment can be applied to the cellulose nanofibrils with consideration of the liquid character of the cellulose suspension.

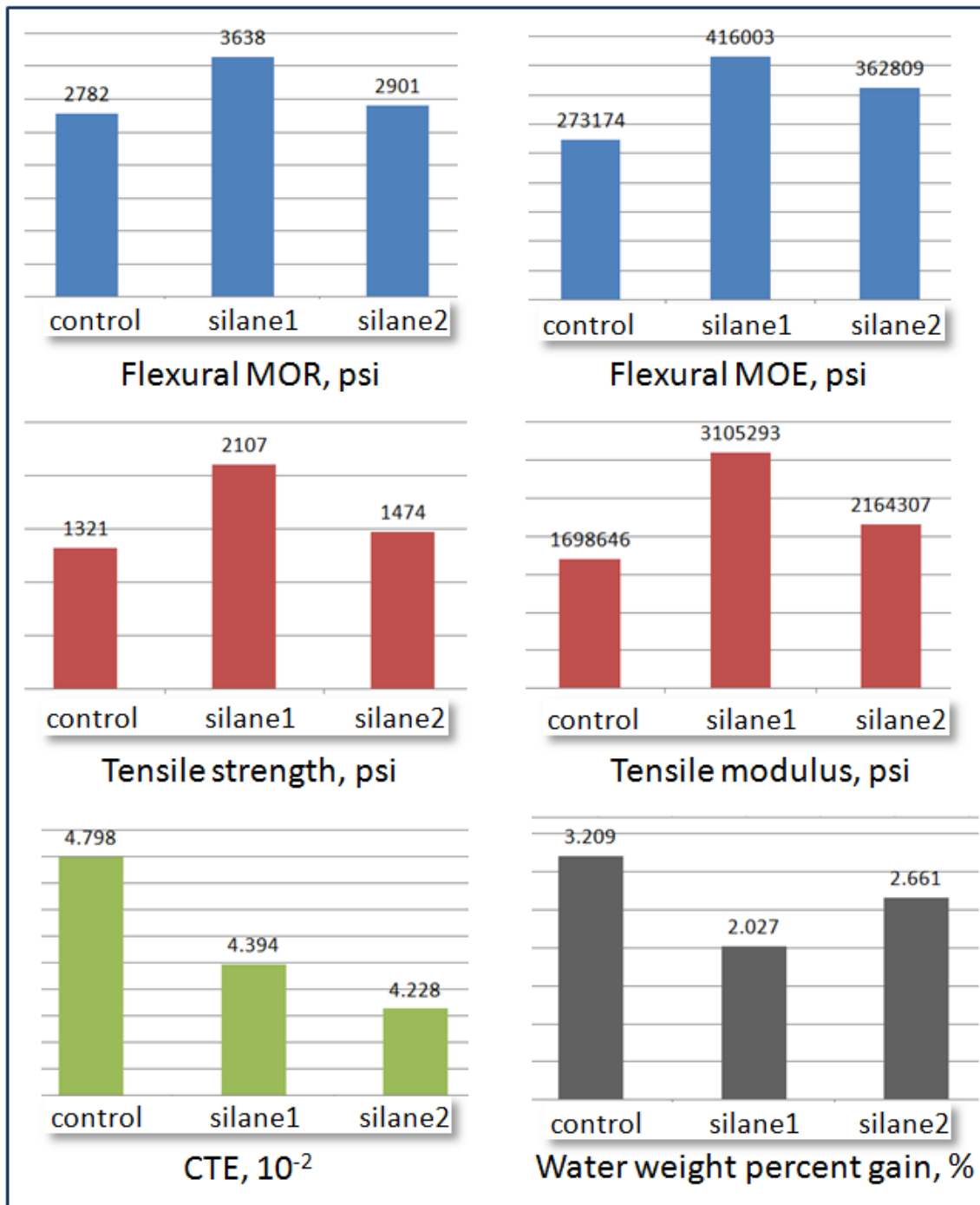


Figure 6. Physical and mechanical properties of wood plastic composites reinforced by silane treated wood fiber.

Conclusions and Future Work

Ongoing challenges for scale-up of utilizing cellulose nanofibrils in hydrophobic thermoplastics will be the need for obtaining large quantities of CNF in the dry state,
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whereas currently commercial producers typically supply CNF in aqueous suspensions. For the process of producing nano-fibrillated cellulose on the commercial scale, scale up of adequate homogenization technologies is still needed. Control of CNF agglomeration and scalable drying technologies is also a big challenge. Surface treatment of CNF via physical and/or chemical modification methods will be important to tailor CNF surfaces for application in specific polymer matrices.

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