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FLEXIBLE CELLULOSE NANOFIBRIL COMPOSITE FILMS WITH REDUCED HYGROSCOPIC CAPACITY

Yan Qing [a, b], Ronald Sabo [b], Zhiyong Cai [b], Yiqiang Wu [a]

[a] School of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha, Hunan 410004, China
Email: qingyancsft@yahoo.com (Y. Qing); wuyiqiang@csuft.edu.cn (Y. Wu)
[b] USDA Forest Service, Forest Products Laboratory, Madison, WI 53726-2398, USA
Email: zcai@fs.fed.us (Z. Cai); rsabo@fs.fed.us (R. Sabo)

Cellulose nanofibrils (CNFs), which are generated from abundant, environmentally friendly natural plant resources, display numerous interesting properties such as outstanding mechanical strength, negligible light scattering, and low thermal expansion (Zimmermann et al., 2010). These nanofibers are usually created by mechanical fibrillation or chemical oxidation of pulp fibers. CNFs have previously been utilized in a broad range of fields, such as special printing, package, medical carriers, filtration, polymeric reinforcement, energy storage, and electronics or display substrates (Siró and Plackett, 2010).

After removing excess water in cellulose nanofibril suspensions, strong, flexible, dense, and translucence films are obtainable. These free-standing cellulose nanofibril films, produced by self-accessibly of individual nanofibrils via hydrogen bonds, are exceptional and of great potential applications. These materials are considered as potential alternatives in barrier package, optical substrates, flexible electronics substrates, and battery membranes (Siró and Plackett, 2010). However, due to abundant hydrophilic groups, these films are sensitive to humidity and water (Aulin et al., 2010). Hydrogen bonds between neighboring nanofibrils tend to deteriorate when absorbing moisture, resulting in a significant destruction of above stated properties. As a result, many attempts have recently been dedicated to modify or functionally treat cellulose nanofibril films to minimize their hygroscopic absorption.

There are essentially two different approaches that have been applied. One involves modifications which convert the hydrophilic groups on nanofibrils into hydrophobic ones, for example, by means of surface silylation (Andresen et al. 2006; Lu et al. 2008) and acetylation (Tingaut et al. 2010). Such chemical treatments significantly decrease the wettability of nanofibrils, and lead to improved water-resistance for the resultant films. However, the individual nanofibrils in films were largely combined by hydrogen bonds created between neighboring hydroxyls. Conversion of hydroxyls into hydrophobic groups is likely to reduce the generation of hydrogen bonds, depending on the substitution of hydrophilic groups. Another approach is the incorporation of resins with CNFs or coating waterproof polymers onto CNF films, which have been shown to reduce the amount of moisture absorption in the resulting composite (Herriksson and Berglund 2008; Qing et al. 2012), thus providing the potential to conserve such properties of CNF composites at high humidity. In the present study, flexible cellulose nanofibril phenol formaldehyde (CNF/PF) composites with reduced hygroscopic capacity were produced by either filtering solution of well-mixed CNFs and PF resin or impregnating the PF into wet CNF films. Swelling of CNF films prior to adding PF facilitated the impregnation of PF resin into the films. The composite films were characterized by tensile testing, transmission electron microscopy, scanning electron microscopy, and moisture/water absorption.

The cellulose nanofibrils used in this research are TEMPO-oxidized bleached eucalyptus pulp fibers, which was processed according to the work reported by Saito et al. (2009). A TEM image for these nanofibrils is shown in Figure 1a, exhibiting fiber of 4-10 nm in diameter and up to several micrometers in length. For CNF/PF mixture method, the CNF suspensions were proportionally mixed with PF resin at solid contents of 5, 10 15 and 20%. The composite films were produced by filtering CNF/PF mixture and dying the wet films consecutively (Qing, et al., 2012). When referring to impregnation of PF resin into CNF films, the dried CNF films were initially soaked in water for 2 h to facilitate resin impregnation (Qing et al., 2013). The swelled films were then soaked in PF solutions with 5, 10 15 and 20% solid concentration. Both of these type of films, including mixture and impregnation methods, were hot pressed at 130 ^{o}C for 2 min at 30 MPa between two pieces of smooth steel plates. The PF resin was successfully incorporated into CNF fibers as seen in Figure 1c and d.

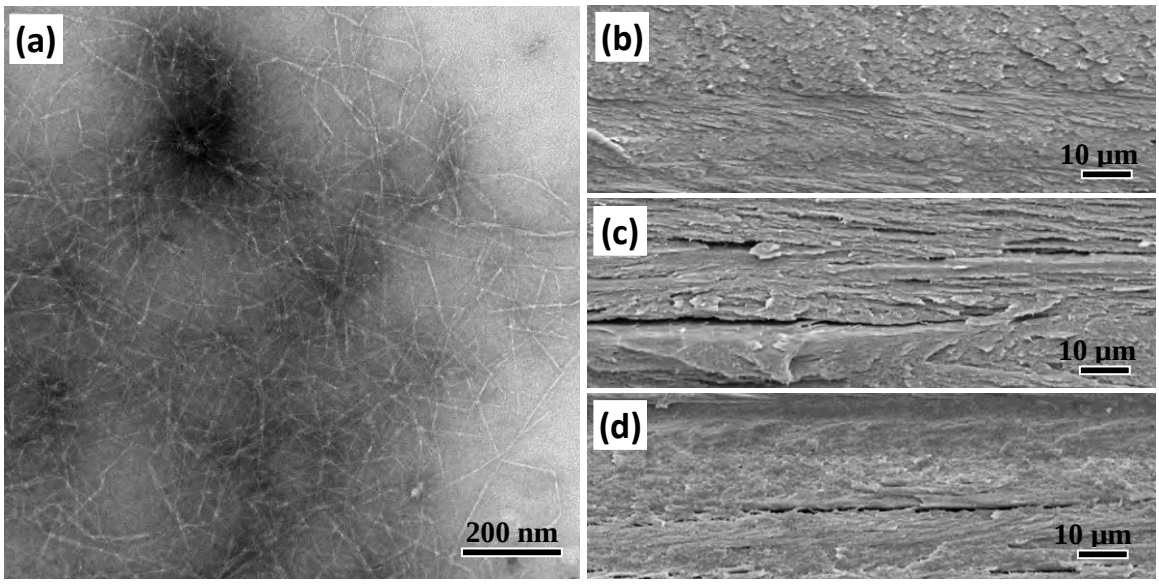

Figure 1 Typical TEM image for TEMPO-oxidized nanofibrils (a), and SEM images for CNF film (b), and CNF-PF composite films (c and d) on the cross surface.

Mechanical properties of these films were tested in tension mode on an Instron universal materials testing machine with 500N cell load according to ASTM D638-10. A typical strain-stress curve is shown in Figure 2. Interestingly, both neat and composite films with PF content less than 15% were strong and flexible. The maximum stress at break ranged in 200-250 MPa, and the corresponding strain at break were more than 10%. The work of fracture, which was calculated as area under the strain-stress curve, was found to approximately 20 MJ/m^3. The mechanical properties of neat films was similar to those with up to about 15% resin, suggesting the addition of PF resin has little effect on the enhancement of mechanical strength. On the contrary, the significant decrease of mechanical strength of composite film with high contents of PF resin indicates that the brittle nature of PF resin is likely to weaken the mechanical properties. A similar result was found in a previous study conducted by Nakagaito and Yano (2008), who proposed that the ultimate stress is extremely sensitive to such microcracks generated during sample preparation and testing, because of the brittle nature of PF modifier. It is believed the unique properties of matrix nanofibrils including uniform diameter concentrated in 7-10 nm, outstanding aspect ratio (length/diameter), and high conservation of fiber structure like molecule and crystallinity, contributed largely to the excellent mechanical properties of resulting films (Qing et al., 2012). Additionally, the comparison of different composite films at the same resin level illustrated that, the approaches adding PF modifier into CNF matrix slightly influence the mechanical performance of composite.

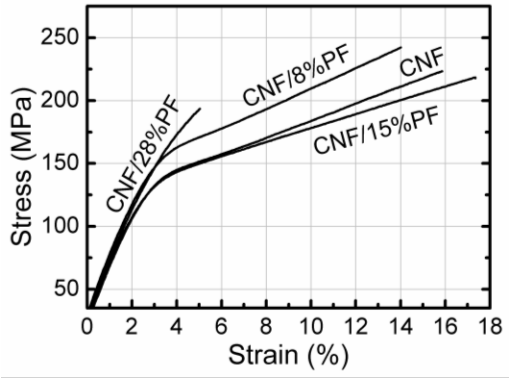

Figure 2 Representative strain-stress curve for untreated and composite films.

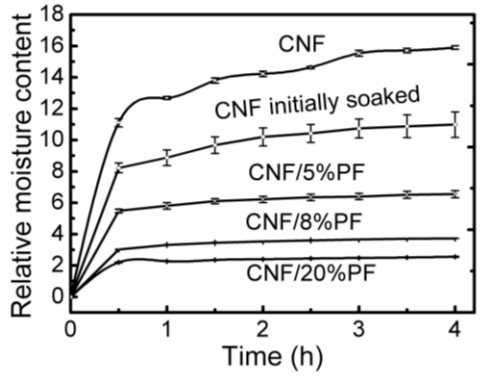

Figure 3 Evolution of relative moisture content of untreated and composite films.

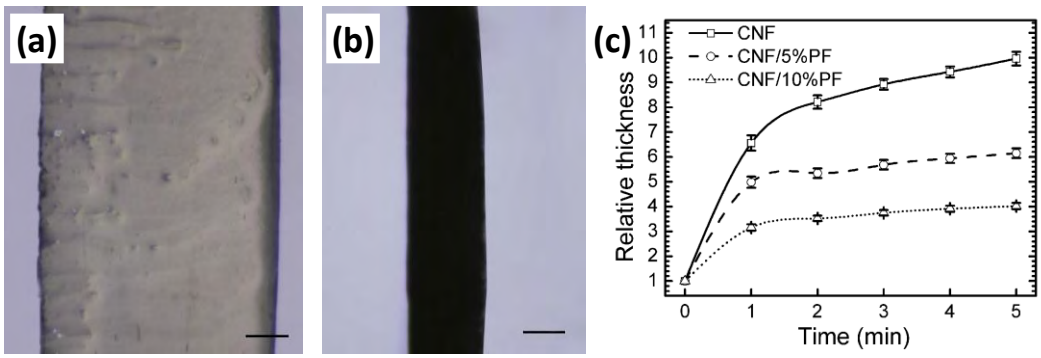

Figure 4 Photographs of untreated (a) and CNF/10%PF composite (b) films after being soaked in deionized water for 5 min. Relative thickness evolution of treated and untreated films (c) soaked in water. The scale bar is 200 μm.

Water absorption of untreated and composite films were tested by measuring the mass of rectangular specimens (20mm length by 6mm width) being soaked into deionized water in a predetermined intervals. Relative moisture content here defined as the ratio of weight gained to the initial weight. It should be noted that the CNF films initially soaked in water for 2h to be swelled sufficiently absorbed less water, compared to the films without any treatments. This phenomenon probably resulted from fiber hornification which occurred in the dewatering of wet CNF films, producing some hydrogen bonds that are water-resistant. However, the water absorption for the composite films was significantly reduced by the introduction of PF. The result also shows that composite films with higher PF content trends to adsorb less water. During testing, it was observed water appeared to form small droplets on the surface of some specimens with PF content more than 30%. These results convinced that the addition of PF resin as modifier has significant effect on the improvement of the hygroscopic capacity for CNF films. Because of reducing in water absorption, the wet strength for composite films was increased compared to the neat one (Qing et al., 2013).

In addition to water sorption, the films were characterized the moisture absorption by conditioning specimens in a stable humidity chamber at room temperature. Under low relative humidity, both the untreated and composite films absorbed little moisture. However, when the humidity increased to 60%, composite films absorbed less moisture than the neat ones. The moisture absorption discrepancy among different films is slight compared to those being soaked in water.

In order to precisely detect thickness swelling of both neat and composite films, the change of thickness of films being soaked in water was measured by recording images of cross sections via optical microscopy. Photographs for films after soaking for 5 min are shown in Figure 4a and b. It can be clearly seen from Figure 4c that incorporation of PF resin significantly decreases the thickness welling, which matches well with the result of water absorption.

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