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Advanced Cellulosic Nanocomposite Materials

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1. Introduction

Biomass, especially woody biomass, represents the most important sustainable resource which can be used as feedstock for producing biofuels and bioproducts. In the past decade, overdependence on petroleum products has consistently increased. Biodegradable products from renewable materials are becoming increasingly more attractive due to escalating prices and shortages of crude oil. Cellulose, synthesized mainly in biomass by photosynthesis, is the most abundant natural biopolymer in the world. Natural cellulosic fibers, particles, fibrils (micro and nano scale), and crystals/whiskers are attractive replacements for man-made fibers (e.g., glass and aramid fibers) used as reinforcement and fillers when making environmentally friendly products. These cellulosic materials have many advantages including: renewable, low cost, low density, low energy consumption, high specific strength and modulus, high sound attenuation, nonabrasive, and a relatively reactive surface.

Recent research has focused on determining how to use biomass effectively as low cost, environmentaly friendly raw materials in many products while reducing the dependence on petroleum based resources. In the past two decades, research and manufacturing efforts have focused on using natural fibers to replace artificial fibers such as glass fibers for reinforcement material and fillers and to make environmentally safe products (George et al., 2001). Fibrils (in micro and nano scale) isolated from natural fibers have much higher mechanical properties as compared to original fibers. Given this, important research is being conducted on generating fibrils and combining them with polymers to form nanocomposites with the expectation of improving strength and stiffness as compared to composites reinforced with artificial fibers (Berglund, 2005; Cheng et al., 2007a; Cheng et al., 2007b; Cheng et al., 2009b; Herrick et al., 1983; Turbak et al., 1983;). Microfibres are defined as cellulose fibers 0.1-1 μm in diameter, with a corresponding minimum length of 5-50 μm (Chakraborty et al., 2006). Franks (1987) defined nanotechnology as "the technology where dimensions or tolerances in the range 0.1 to 100 nm (from the size of an atom to the wavelength of light) play a critical role". The definition of nano-size material has broadened significantly to include a large variety of systems that have at least one-dimension at the nanometer scale (1-100 nm) (Jordan et al., 2005). As one of the next generation of environmentally friendly materials, bio-based nanocomposites have grown rapidly and include composites that are completely biodegradable (both the fibril and polymer matrix are biodegradable) and partly biodegradable (at least the fibril is biodegradable).

It is still a challenge to isolate fibrils (in both micro and nano scales) at a reasonable cost with low degradation, and to effectively disperse them evenly in polymer matrixes. However, many methods have been developed to generate fibrils (e.g., chemical and mechanical) and to produce bio-nanocomposites (e.g., film casting and freeze dry followed by compressive molding and/or extrusion). Problems and challenges in nanocomposites reinforced with cellulose fibrils (micro and nano scales) include: 1) disintegration of cellulose to fibrils without severe degradation; 2) producing low cost, environmentally friendly nanocomposites; 3) characterizing the mechanical properties of single fibrils (to evaluate the effects of the isolation process) used in producing nanocomposites; 4) dispersing cellulose fibrils in polymer matrixes; 5) adhesion between the fibrils and polymer matrixes; 6) applications of bio-based nanocomposites in the ecological system; 7) biodegradability of nanocomposites partly or completely in the ecological system.

This chapter will review cellulosic nanocomposites development at the Division of Forestry and Natural Resources, West Virginia University and the Center for Renewable Carbon, University of Tennessee, as well as several other institutes. Cellulosic nanofibers/nanocrystals were isolated directly from hardwood residues and hybrid poplars, and used to reinforce poly(vinyl alchole) (PVA) when making nanocomposites at West Virginia University. At the Center for Renewable Carbon, cellulose fibrils were isolated from Lyocell fiber, a regenerated cellulose fiber, pure cellulose fiber, and pulp fiber through a high intensity ultrasonic treatment. The resulting fibrils were characterized for physical and mechanical properties and used as reinforcements for several polymers, such as poly(lactic acid) (PLA), PVA, and polypropylene when making cellulosic nanocomposites. These research efforts provided alternative methods to isolate cellulosic fibrils and nanofibers and to reinforce polymers when fabricating cellulosic composites in a manner that produces higher yields in an more environmentally friendly and energy efficient way, as compared to current techniques..

2. Cellulose

Cellulose is the world's most abundant natural, renewable, biodegradable polymer, and a classical extracellular high-performance skeletal biocomposite consisting of a matrix reinforced by fibrous biopolymer. The whisker like microfibrils, which are near defect free crystals with axial physical properties approaching those of perfect crystals, are biosynthesized and deposited in a continuous fashion by plants or animals. Wood, one of the most important plants for society , is not only a good building material, but also an abundant cellulose source.

Although the first investigations on cellulose were performed by Braconnot in 1819 and Payen in 1839, the structure of cellulose was clearly established by Staudinger in 1926, (Lima and Borsali, 2004). Cellulose is a high-molecular-weight linear homopolymer, consisting of repeating β-D-glucopyranosyl units joined by (1-4) glycosidic linkages in a variety of arrangements. Cellulose is a (1-4)-link β-D-glucoglycan, β-D-glupynanose unit, which is joined to form a linear-molecular chain (Fig. 1) (Chaplin, 2010). The hydrogen bonds formed between the ring oxygen atom of one glycosyl unit and the hydrogen atom of the C-3 hydroxyl group of the preceding ring hinder the free rotation of the rings on their linking glycosidic bonds resulting in chain stiffening. The adjacent cellulose chains fit closely together in an ordered crystalline region, so that high strength and insolubility (in common solvents) can be observed in plants, and in some cellulose-constituted

animals. In nature, cellulose chains have a DP of approximately 10,000 glucopyranose units in wood cellulose and 15,000 in native cellulose cotton (Chaplin, 2010; Sjostrom, 1993).

Microfibrils are constituted by amorphous and crystalline domains, are biosynthesized, and are self-assembled from cellulose chains. The degree of crystallinity (ratio of the mass of crystalline domains to the total mass of the cellulose) and typical dimensions are dependent on their origin (Sarko and Muggli, 1974; Woodcock and Sarko, 1980). Cellulose exists basically in four different forms, cellulose I (I_α and I_β), II, III, IV, which can be interconverted by chemical and thermal processes (Lima and Borsali, 2004; Woodcock and Sarko, 1980). Cellulose was described displaying six different polymorphs, namely I, II, IIII, IIII$_I$, IVI , and IVI$_I$ with the possibility of conversion from one form to another (O'Sullivan, 1997; Samir et al., 2005).
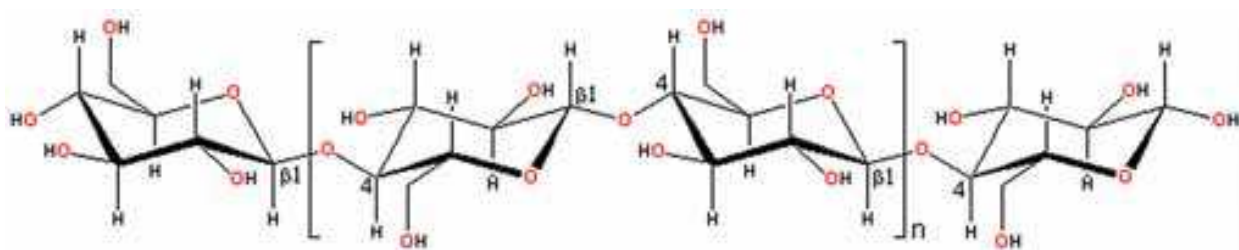

Fig. 1. Bassic chemical structure of cellulose (Reprinted from Chaplin, 2010 with permission)

3. Isolation and characterization of cellulosic nanocrystals/microfibrils

3.1 Cellulosic nanofibers/nanocrystals isolation

Two common methods, chemical and mechanical, have been developed to obtain fibrils. Stron acid hydrolysis, which removes the amorphous regions of cellulose fiber, is the main chemical method. This method can be used to generate cellulose crystals or nanofibers, commonly called cellulose whiskers or nanocrystals. The most common mechanical method utilizes strong shear forces, such as those obtained using a homogenizer, to separate cellulose fiber to fibrils. This method can be used to generate cellulose microfibril or bundles, commonly called microfibrillated cellulose (MFC).

Cellulose nanocrystals can be generated by chemical treatment, especially acid hydrolysis, from various biomass resources. A typical procedure to prepare cellulose nanocrystals has five steps: hydrolysis by acid, centrifugation and neutralization, rinsing with deionized water by centrifuge, dispersion by ultrasonic irradiation, and ultrafiltration to remove any remaining ions (Choi and Simonsen, 2006). Cellulose whiskers or nanocrystals have been obtained from many cellulosic materials, such as wood fibers, cotton, ramie, tunicate mantles, sugar beet pulp, and bacterial cellulose (Beck-Candanedo et al., 2005; Chakraborty et al., 2005; Dufresne et al., 1997b; Edgar and Gray, 2002; Kvien et al., 2005; Lu et al., 2005; Pu et al., 2007; Zimmermann et al., 2004). In terms of mechanical methods, a process using high-intensity ultrasonication (HIUS) was developed at the Center for Renewable Carbon to isolate fibrils from several cellulose resources, which is discussed in Section 3.3.

3.2 Cellulosic nanocrystals/microfibers characterization

Many methods have been used for fibril characterization, including morphological characterizations, degree of fibrillation, and crystalline characterizations. Several tools can

be used for morphological observation, such as a scanning electron microscope (SEM), an atomic force microscope (AFM), and a transmission electron microscopy (TEM) (Bhatnagar and Sain, 2005; Bondeson et al., 2006; Chakraborty et al., 2005; Choi and Simonsen, 2006; Wang and Sain, 2007; Zimmermann et al., 2004). The degree of fibrillation of the fibers used to isolate MFC/microfibrils/aggregates by mechanical methods may be evaluated by water retention value (WRV) (Cheng et al., 2007a; Cheng et al., 2010a, b; Herrick et al., 1983; Turbak et al., 1983; Wang and Cheng, 2009; Yano and Nakahara, 2004). Wide angle X-ray diffraction (WAXD) is used to study the crystallinity of the fibrils (Bhatnagar and Sain, 2005; Chakraborty et al., 2006; Cheng et al., 2007a; Gindl and Keckes, 2005).

Mechanical properties of a single cellulose fibril are very important, especially when the ultimate use of the fibrils is for reinforcing composite materials. The elastic modulus of the crystalline region of cellulose has been determined either experimentally or theoretically, such as experimental deformation micromechanics of natural cellulose fibers using Raman spectroscopy and X-ray diffraction (Matsuo, 1990; Sakurada et al., 1962; Wiley and Atalla, 1987). Mechanical properties of a single polymeric nanofiber and bacterial cellulose nanofibers have been measured by an atomic force microscope (AFM) (Cheng and Wang, 2008; Cheng et al., 2009a; Tan and Lim, 2004; Wan et al., 2006).

3.3 Isolation of cellulosic fibril aggregates by ultrasonication

A novel process using high-intensity ultrasonication (HIUS) to isolate fibrils from several cellulose resources (Fig. 2), such as regenerated cellulose fiber (Lyocell fiber), pure cellulose fiber (TC40, 180, and 2500), microcrystalline cellulose (MCC), and pulp fiber, was developed (Wang and Cheng, 2009; Cheng et al, 2010a). HIUS produces very strong mechanical oscillating power (Abramov, 1998), which forms hydrodynamic forces of ultrasound to separate cellulosic fibrils in micro/nano scales.
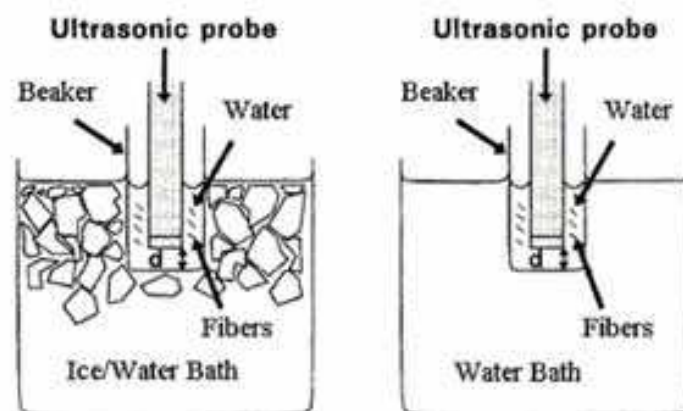

Fig. 2. A scheme for HIUS treatment of fibers using ice/water bath or water-only bath (Reprinted from Wang and Cheng, 2009 with permission from Wiley)

During the HIUS process, cellulose materials were soaked in distilled water until saturated, then a HIUS was directly applied to cellulose fibers suspended in water. Six factors, including ultrasonic power (P, %), treatment time (t, min), treatment temperature (T), fiber concentration (C, %), fiber size (FS, μm), and ultrasonic probe to container bottom distance (d, mm), were considered and three or four levels for each factor were used to check the effects of cellulose fibrillation. Water retention value (WRV) measured by a centrifuge

system (Cheng et al., 2007a; Cheng et al., 2010b) was used to evaluate and compare the effects of different factors. The treated and separated fibrils in micro and nano scales by HIUS were investigated using polarized light microscopy, SEM, and AFM. The crystallinities of treated and untreated cellulose fibers were studied by Wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectroscopy (FTIR) (Cheng et al., 2010a).

The temperature of water suspension during HIUS treatment changes with different powers and cooling methods. Generally a higher temperature can be reached, and a higher speed of temperature increase can be obtained, by using more power. Fig. 3 shows the WRV of the untreated and treated Lyocell fibers for different treatment time and temperature. The degree of microfibrillation of the treated fibers increased as the treatment time increased. It indicates that the fibers became smaller and more surface area on the fibrils as treatment time and temperature increased because WRV is related to fibril and microfibril surface and volumetric phenomena. The longer the treatment time, the smaller the fibrils can be obtained in the suspension mixture. Higher temperature of the suspension was very helpful for cellulose microfibrillation. Measured by Kajaani FiberLab 3, the continuous fiber length distributions of Lyocell fiber and TC180 including before and after treatment, and separated fibrils indicate that there were more short fibers in the treated materials and separated fibrils (Wang and Cheng, 2009).
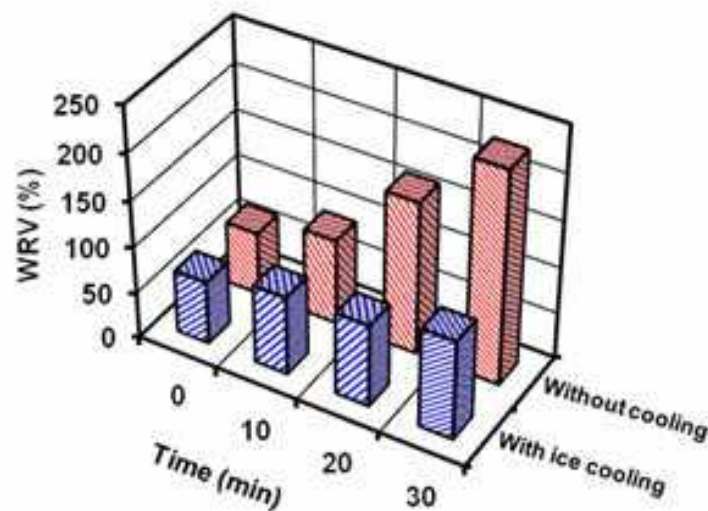

Fig. 3. WRVs of Lyocell fibers treated by HIUS for different durations and at different temperatures (Reprinted from Wang and Cheng, 2009 with permission from Wiley)

After HIUS treatment, a mixture suspension of fiber and fibril with a diameter ranging from microns to tens of nanometers was obtained. Many small fibrils with a diameter less than 1μm were peeled from Lyocell fibers. Some fibrils were still on the surfaces of the big ones that dominate the treated fibers, while some were already isolated from the big fibers. The structure and appearance of the Lyocell fibrils on silicon wafers observed by SEM and AFM are shown in Figs. 4 and 5. The diameters or widths of the fibrils isolated from Lyocell fibers were in a wide range of tens to hundreds nm, and have a wide range of aspect ratio (length/diameter).
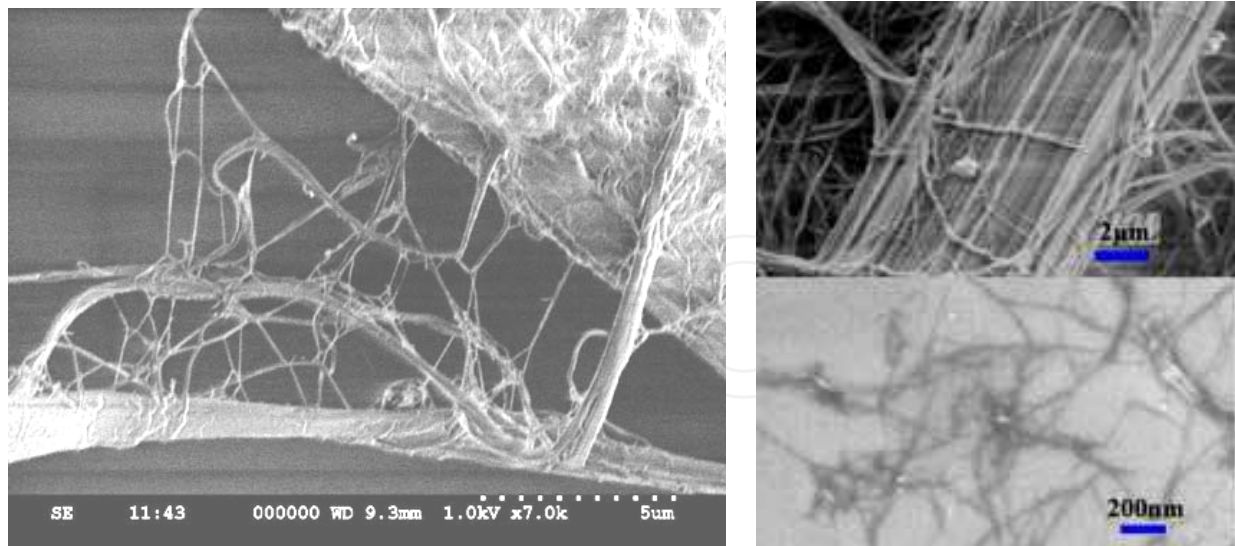
Fig. 4. SEM images of Lyocell fibers and fibrils treated 30 min by HIUS (Reprinted from Cheng et al., 2010a with permission from Wiley)
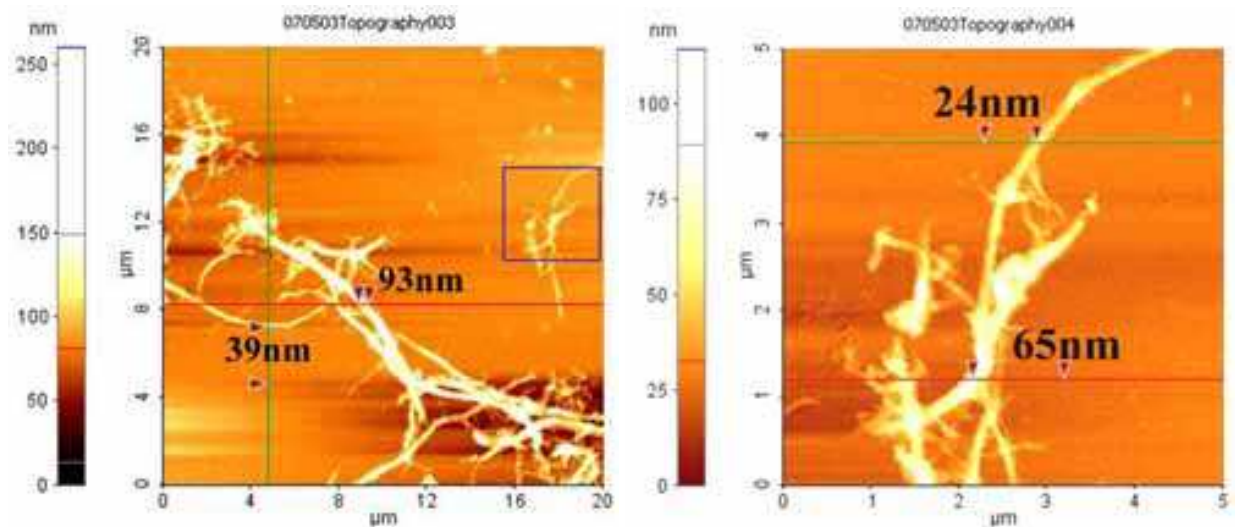

Fig. 5. AFM images of Lyocell fibrils treated 30 min by HIUS (Reprinted from Cheng et al., 2010a with permission from Wiley)

4. Cellulosic nanocomposites

4.1 Fabrication and characterization of cellulosic nanocomposites

The fabrication of nanocomposites with cellulose fibrils of a high aspect ratio for load-bearing applications is relatively new. A wide range of nanocomposites has been studied to investigate the reinforcements of the fibrils/crystals, but there are still some problems, such as the dispersion of cellulosic materials in polymer matrices, especially when they are hydrophobic. The most frequently used method is solvent evaporation casting, including water soluble and other solvent soluble. Nanocomposite materisls can be made by solvent casting method in Teflon or propylene dishes (Favier et al., 1995; Taniguchi and Okamura, 1998). Hot-pressing method after freeze-drying of fibrils can also be used

(Dufresne et al., 1997a). A mat formation followed by resin imersion and curing by UV light was used to make optically transparent composites reinforced with plant fiber-based cellulose microfibrils (Iwamoto et al., 2005). Another mat method was used to make PF resin composite using hot press with high pressures (Nakagaito and Yano, 2005). A method of filtration mats followed by compression molding was also used (Cheng et al., 2007b).

Various analysis instruments can be used to investigate the characterization of the obtained composites, including mechanical properties, morphological characteristics, and thermal properties. Tensile and bending tests are normally used to measure the mechanical properties (Bhatnagar and Sain, 2005; Cheng et al., 2007a, 2009b; Choi and Simonsen, 2006; Taniguchi and Okamura, 1998; Zimmermann et al., 2005; Nakagaito and Yano, 2005). Additionally, dynamic mechnical analysis (DMA) tests can also be used used to evaluate composite performance under various conditions of temperature and relative humidity (Choi and Simonsen, 2006; Favier et al., 1995). For morphological characterizations of nanocomposite, AFM, SEM, and TEM are common tools (Cheng et al. 2009a; Kvien et al., 2005; Pu et al., 2007; Taniguchi and Okamura, 1998; Zimmermann et al., 2004; Zimmermann et al., 2005). These techniques are helpful to investigate the homogeneity of the composite, presence of voids, dispersion level of the fibrils within the continuous matrix, presence of aggregates, sedimentation, the interface between the fibril and the polymer matrix, and possible orientation of the fibrils. Thermal properties are very important for nanocomposites. Differential scanning calorimetry (DSC), Thermogravimetric analyzer (TGA), and DMA have been used to evaluate thermal properties (Ljungberg et al., 2006; Orts et al., 2005; Samir et al., 2006; Wang et al., 2010).

4.2 PVA Cellulosic nanocomposites reinforced with cellulosic nanofibers

Pure cellulose and pulp fiber are the common raw materials for the isolation of nanocrystals and nanofibers in current research. Wood particles, such as hardwood residues and fast plantation poplar, were directly used to isolate cellulose nanifibers/nanocrystals by acid hydrolysis following lignin removal (Cheng et al., 2009c). In this section, we introduce cellulosic nanofibers isolated from juvenile poplar wood samples, and the mechanical and thermal properties of polyvinyl alcohol (PVA) nanocomposites reinforced by these nanofibers (Wang et al., 2010).

Two poplar samples, black cottonwood (*Populus trichocarpa*) (PT) and a hybrid poplar (HP), were used as raw materials. Microcrystalline cellulose (MCC) was used as reference material. Wood stems were debarked, dried, and milled to particles passing a 60-mesh screen. An acidified sodium chlorite solution was used to remove the lignin in wood particles (*Wise, 1946*). After lignin removal, wood particles were then placed in a 60% H_2SO_4 (v/v) solution for 2 h at 45°C with medium stirring. The obtained mixture was centrifuged and decanted after hydrolysis. Then the solid cellulosic particles were washed and then subjected to ultrasonic irradiation in deionized water to disperse the nanofibers. All the obtained samples were turbid suspension, however, after ultrasonic treatment, the suspensions were transparent. The diameters of most cellulose nanofibers were about 20-30 nm and lengths were in the hundreds nm range as illustrated in AFM height image (Fig. 6), indicating that the nanofibers were still bundles of single nanocrystals since a single wood cellulose crystal is about 3-5 nm in diameter.
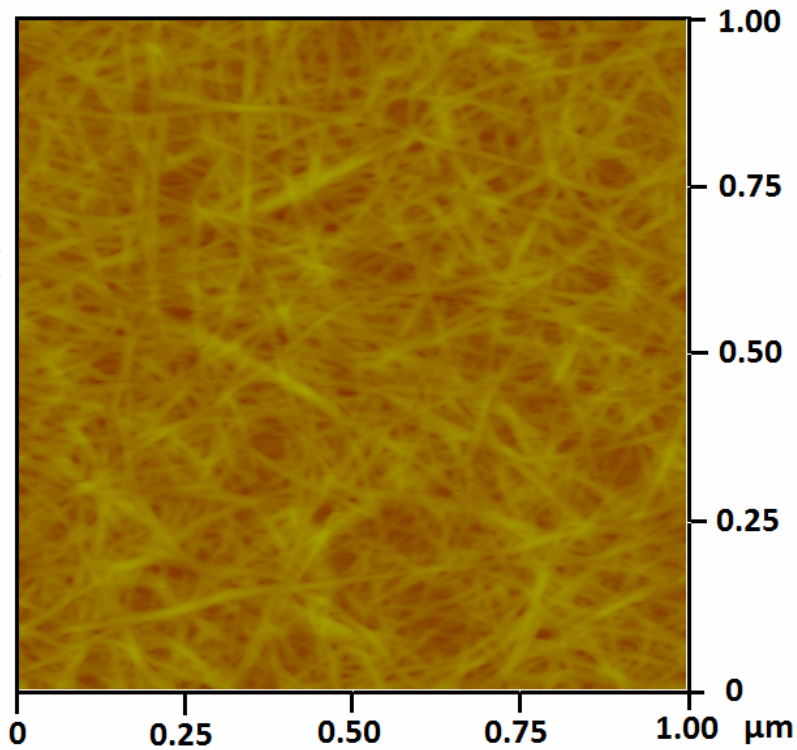
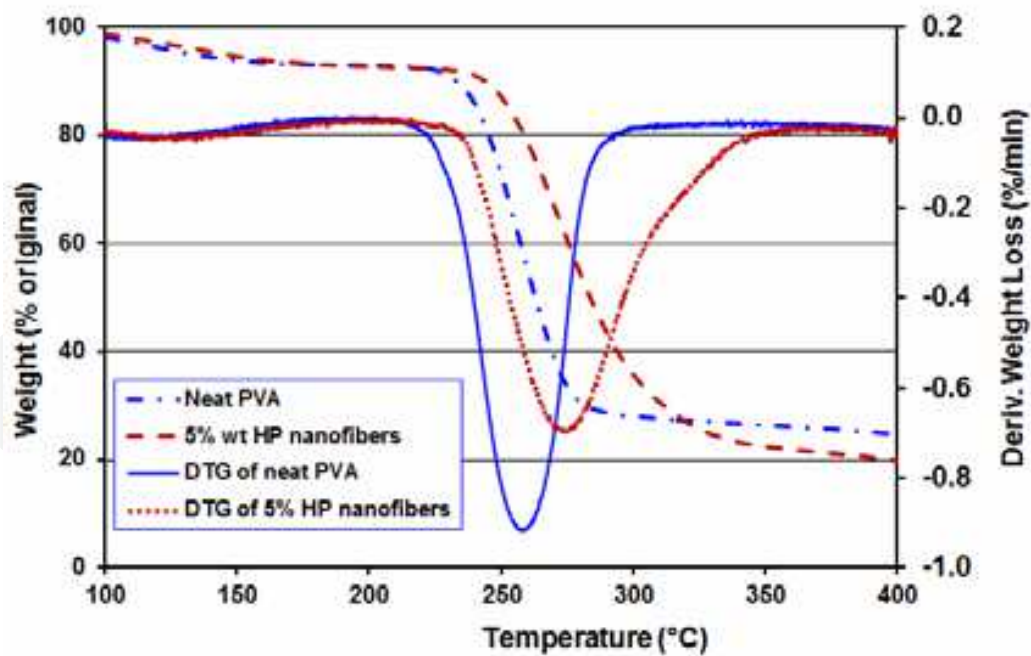Fig. 6. AFM image of nanofibers from hybrid poplar

Fig. 7. TGA and DTG thermograms of neat PVA and its nanocomposites with 5% HP nanofibers

Adding cellulosic nanofibers and MCC particles decreased PVA's elongation to break, which indicated that the toughness of PVA increased by these cellulosic materials because

the elongation is related to the toughness of a material. The nanofiber reinforced PVA nanocomposites had much higher mechanical properties (tensile modulus and strength) than those of neat PVA and MCC reinforced composites. PVA strength was not decreased by cellulosic nanofibers, but PVA tensile strength was significantly decreased by MCC particles. Presumably, the small nanofibers had higher mechanical properties and higher aspect ratios (length/diameter) than those of MCC. The modulus of PVA was significantly increased by only 2% cellulosic nanofibers (Wang et al., 2010).

Thermogravimetric analyzer (TGA) results indicated that the thermal degradation behavior of PVA was influenced by adding cellulosic nanofibers (Fig. 7). The weight loss of PVA started at its melting point with a very narrow temperature range of degradation, while pure nanofibers started to degrade at a lower temperature and showed a very broad degradation temperature range. Cellulosic nanofibers increased the degradation temperature of PVA. The decomposition peak temperature of the nanocomposites was clearly increased by cellulosic nanofibers. The derivative thermogravimetric (DTG) curves of PVA and 5% HP nanofiber reinforced composites are shown in Fig. 7. The nanocomposite showed thermal events with a shift toward higher temperature compared to the neat PVA, which indicated that the reinforced nanocomposites should be more thermal stable.

4.3 PVA cellulosic nanocomposites reinforced with cellulosic fibrils

Cellulose fibrils, in micro and nano scales, were generated from several cellulose sources, including regenerated cellulose fiber (RCF), pure cellulose fiber (PCF, TC180), and microcrystalline cellulose (MCC), by ultrasonic treatment to reinforce PVA to make biodegradable nanocomposites by film casting. A mixture of fiber and fibril in micro and nano scales was obtained from RCF, PCF, and MCC after HIUS treatment. The tensile properties of PVA were improved significantly by most cellulosic small fibrils, and seperated small fibrils provided better reinforcement than that of untreated big fibers (Cheng et al., 2009b).

Fig. 8 shows the tensile modulus and strength of neat PVA and its composites reinforced by untreated and treated MCC, and small MCC fibril with 2%, 6%, and 10% by weight. The PVA tensile modulus was decreased significantly by 2% of untreated MCC particles, but was increased by treated MCC and seperated small MCC fibrils. The PVA tensile strength was decreased by untreated and treated MCC particles, however, it was increased by small MCC fibrils. All the results indicated that untreated MCC was not suitable for PVA reinforcement because it has a low aspect ratio, while the treated MCC and seperated small fibrils had a high aspect ratio that could reinforce PVA mechanical properties.

The tensile modulus and strength of PVA and its composites reinforced with 2% untreated and treated PCF, and small and big fibrils from PCF are shown in Fig. 9. The composites with small fibrils had much higher modulus and strength properties than those of neat PVA, untreated and treated PCF reinforced composites. However, the mechnical properties of the composites with big fibrils did not significantly change. Both PVA modulus and strength were decreased significantly by untreated PCF. Seperated small PCF fibril reinforced composites had higher improvement for both modulus and strength than those of big fibrils, presumerly because small PCF fibrils had higher mechanical properties than those of big fibrils (Cheng and Wang, 2008; Cheng et al., 2009a).
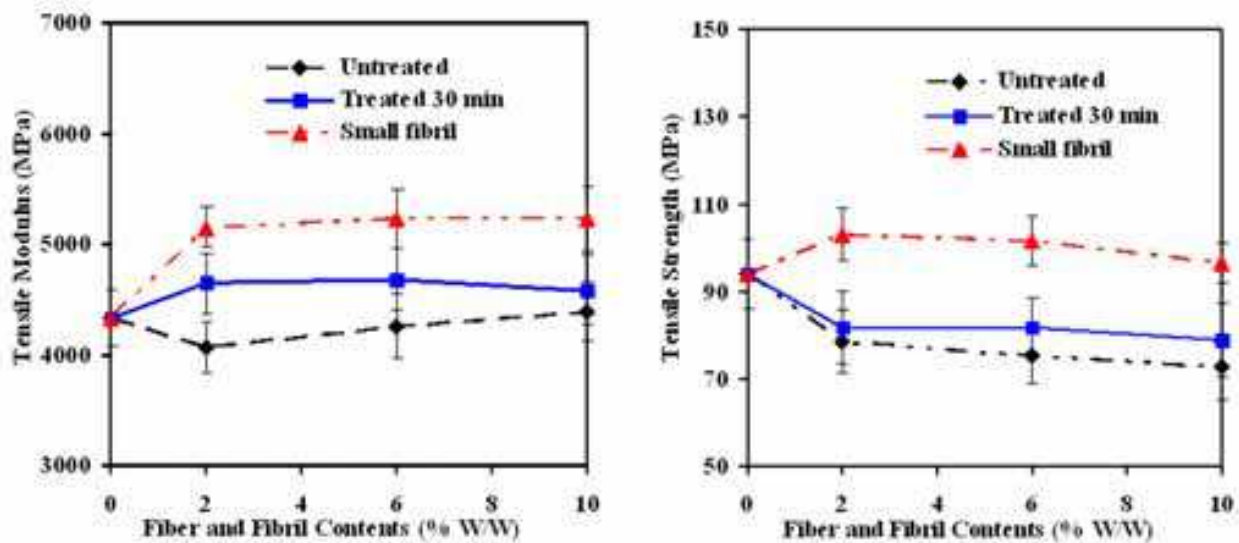
Fig. 8. Tensile modulus and strength of PVA and its composites reinforced by untreated and treated MCC, and small MCC fibrils (Reprinted from Cheng et al., 2009b with permission from Elsevier)
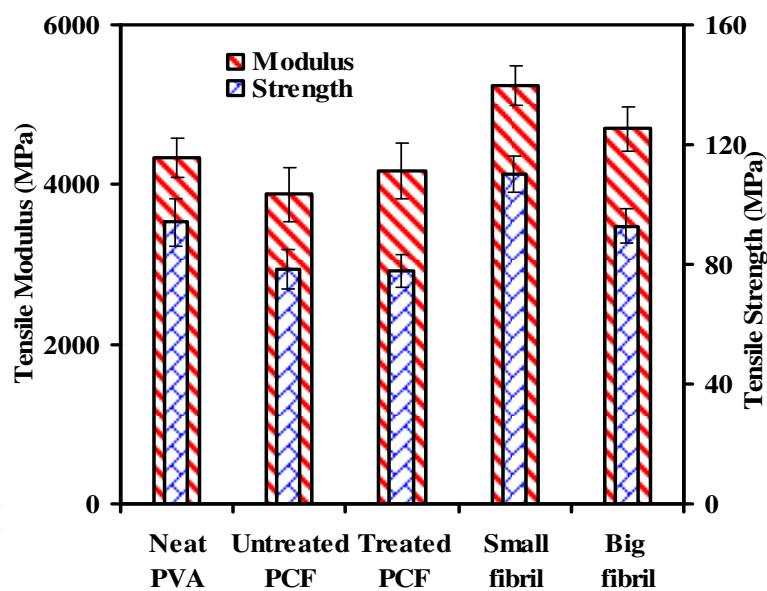

Fig. 9. Tensile modulus and strength of PVA and its composites reinforced by untreated and treated PCF, and small and big PCF fibrils (Reprinted from Cheng et al., 2009b with permission from Elsevier)

Table 1 shows the tensile modulus and strength of neat PVA and its composites reinforced by untreated and treated RCF fibers, small RCF fibrils, and commercial microfibrillated cellulose (MFC, used as a reference material) of 2%, 6%, and 10% by weight. PVA tensile modulus was increased significantly by all the fibers, fibrils, and MFC except 2% and 6% of untreated RCF, but the modulus changes were not significant among the filler loadings of 2%, 6%, and 10%, except between the 2% and 6% of MFC. PVA tensile strength was not significantly changed by untreated RCF and MFC except 10% of MFC. However, PVA

tensile strenth was increased significantly by only 2% of treated RCF fibers and all the small fibrils. Adding more fiber and fibrils did not increase strength due to the dispersion problem for higher filler loadings as mentioned above. Again, small RCF fibrils had better reinforcement for PVA strength than the treated fiber; and the treated fiber had better reinforcement for both the modulus and strength of PVA than untreated fibers. The RCF fibrils had much better reinforcement for PVA than that of MCC and PCF fibrils, and again, possibly because the aspect ratio of RCF fibrils was higher and the elastic modulus of RCF fibrils was higher than that of natural fibers.

	Modulus (GPa) (PVA: 5.7±0.2)			Strength (MPa) (PVA: 112±6)		
Materials	2%	6%	10%	2%	6%	10%
Untreated	6.0±0.4	6.1±0.3	6.3±0.4	108±6	107±7	105±8
Treated	6.6±0.2	6.7±0.2	6.5±0.4	125±6	118±7	115±7
Small	6.5±0.4	6.8±0.4	6.8±0.3	127±6	124±7	130±7
MFC	6.3±0.3	7.1±0.3	7.2±0.4	112±10	113±8	101±7

Table 1. Tensile modulus and strength with standard deviations of PVA and its composites reinforced with untreated and treated RCF fibers, small RCF fibrils, and MFC (Reprinted from Cheng et al., 2009b with permission from Elsevier)

SEM images of fracture surface after tensile testing and AFM images of cross-sections after cutting by microtome from the PVA nanocomposites reinforced by small RCF fibrils are shown in Figs. 10 and 11, respectively. The dispersion of small fibrils was not perfectly uniform observed from the cross-sections. Some pulled out holes after tensile test were detected. These results indicated that the increments of tensile strength and modulus of the composites were not as high as expected, especially for higher fibril loadings because the fibril dispersion of 10% fibril loading composite was much worse than 2% fibrils loading samples, which possiblly was the main reason why increased amounts of filler did not further reinforce the PVA composites.
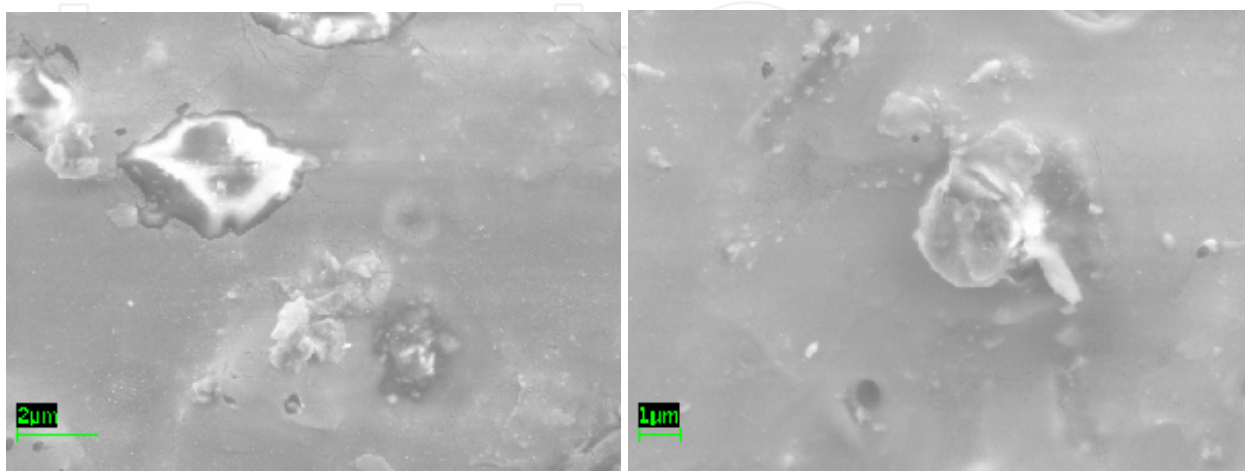

Fig. 10. SEM images of the fractured cross-sections of PVA composites reinforced with small RCF fibrils (Reprinted from Cheng et al., 2009b with permission from Elsevier)
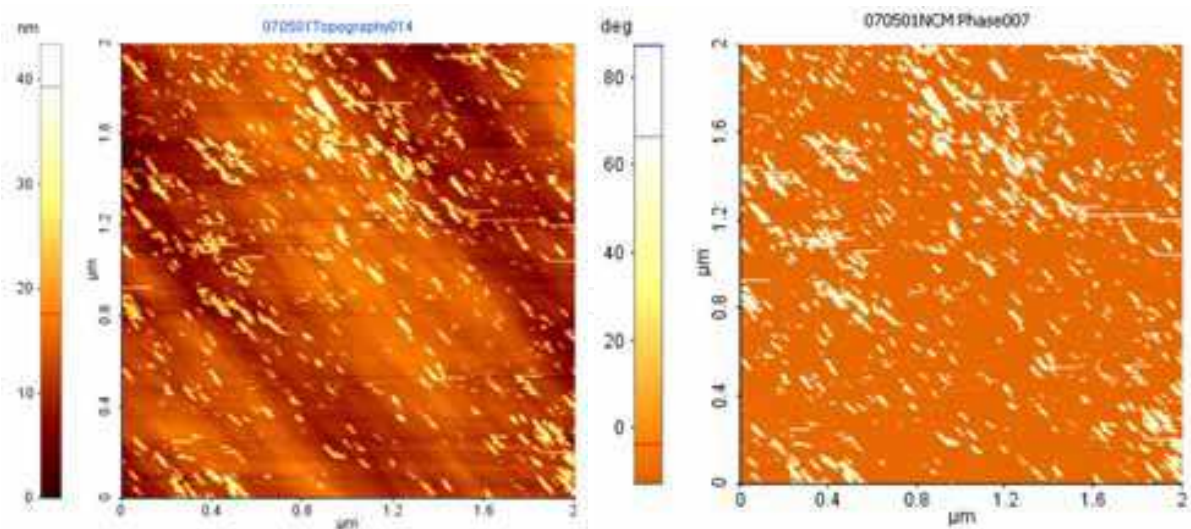
Fig. 11. AFM topography and phase images of the cross-sections of PVA composites reinforced with small RCF fibrils (Reprinted from Cheng et al., 2009b with permission from Elsevier)

4.4 PLA and PP cellulosic composites reinforced with fibril aggregates

Fibril aggregates were generated from a regenerated cellulose fiber (RCF, Lyocell fiber) by ultrasonication treatment. Composites of poly(lactic acid) (PLA, biodegradable) and polypropylene (PP, non-biodegradable) reinforced with fibril aggregates were prepared by compression molding. For PLA composites, the fibril aggregates and the PLA polymer were combined together using multiple layers followed by compressive molding (Fig. 12) (Cheng et al., 2007b). The PP composites were made from filtered mats of cellulose fibril aggregates and PP fibers by compression molding. The mats were made from the well-stirred mixture of cellulose fibril aggregates and PP fibers by a filtration system using the same setup above for fibrils mats. The formed mixture mats were oven dried, put in a round metal mold with a nominal thickness of 254 µm, and hot pressed at a temperature of 170 °C and a pressure of 5 MPa for approximately 5 minutes. The physical and mechanical properties of these composite materials were evaluated by SEM and tensile tests, respectively (Cheng et al., 2007a).

Fig. 12. Sandwich structure of PLA and fibril composites for compressive molding

The tensile modulus and strength of PLA and its composites reinforced by untreated and treated Lyocell fibers by loading of 10% and 20% indicated that all composites have a higher tensile modulus than that of pure PLA. The untreated and treated fibers of 10% loading did not change PLA tensile strength. The tensile strength of the 20% fiber loading composites with untreated fibers decreased 18%. However, the treated fibers increased the tensile strength about 14% compared to pure PLA, which may be attributed to the contribution of

the fibrils isolated from the fibers and microfibrillation on the fiber surface. Some gaps around big fibers were observed by SEM images, indicating the adhesion between the PLA and the mixture of fibers and fibrils was poor (Fig. 13).
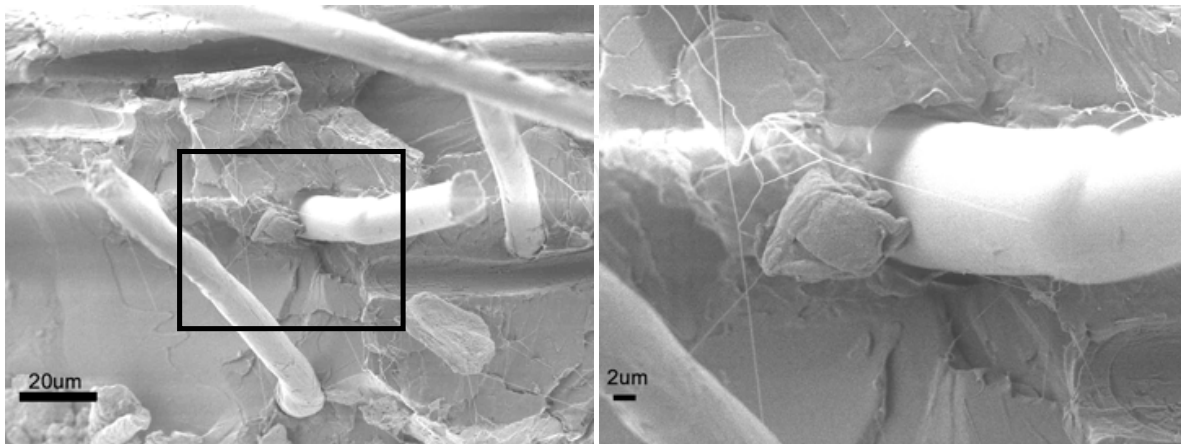

Fig. 13. The fractured cross-sections of PLA composites by SEM: (left) overview, and (right) detailed view

Some typical tensile curves of neat PP and its composites with 10% and 20% of untreated and treated Lyocell fibers are shown in Fig. 14. Higher fiber loading composites had higher tensile strength and lower elongation to break, indicating that the composites were becoming more brittle.
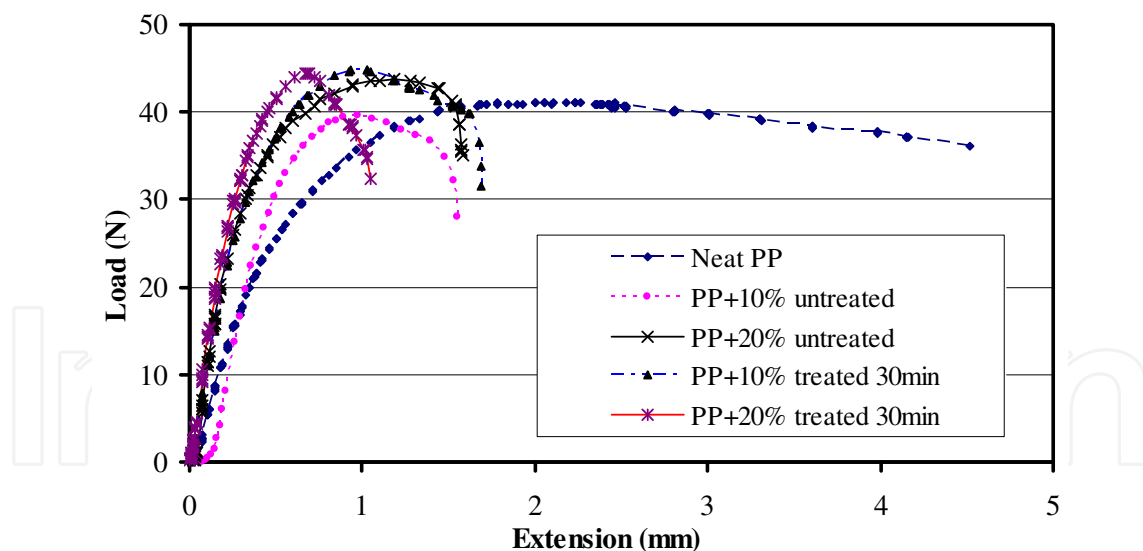

Fig. 14. Typical stress-strain curve of PP and its composites

The results of tensile modulus and strength of PP and its composites reinforced with untreated and treated Lyocell fibers indicated that all composites have higher tensile modulus and strength than those of neat PP. The treated fibers had higher mechanical reinforcement for PP composites. The PP tensile modulus was increased 81% and 96% by loadings of 10% and 20% untreated fibers, respectively. The PP tensile modulus was increased 93% and 130% by adding 10% and 20% of treated fibers, respectively. The fibers

and fibril aggregates had a good distribution observed from the thickness of the composites, but some holes in the PP matrix and some gaps between fibers and PP matrix were observed. The presence of the discontinuities between the PP matrix and fibers from the selected broken cross-sections indicated that there was not good adhesion between the PP matrix and the fibrils and fibril aggregates (Cheng et al., 2007a).

5. Conclusions

Natural cellulosic fibers, particles, fibrils (in micro and nano scale), and crystals/whiskers are alternative reinforcement materials that are able to replace man-made fibers, such as glass and aramid fibers to make environmentally friendly products. Cellulose fibrils in micro and nano scales can be isolated from many resources, including wood particles, regenerated cellulose fiber, pure cellulose fiber, and pulp fiber by chemical and/or mechanical methods. Most current methods are low yield, not environmental friendly and/or not energy efficient. A method using high intensity ultrasonic (HIUS) was developed to isolate fibrils from several cellulose resources: regenerated cellulose fiber, pure cellulose fiber, microcrystalline cellulose, and pulp fiber. The obtained material is a mixture of fibrils in micro and nano scales. Small fibrils can be separated by centrifuge. Water retention values revealed that the cellulose fibrillation was significantly increased by HIUS treatment for all cellulose resources. The mixture, and separated small fibril aggregates, can be used to increase the tensile modulus and strength of PVA, PLA, and PP by fabrication methods of film casting and compression molding, respectively. Because there were not perfect adhesions between the polymers and the fibers and fibril aggregates without further modification of cellulose and/or polymers, the polymer reinforcements with these cellulosic fibrils were not as high as expected strength and stiffness. The small fibrils on the surfaces of big fibers and those isolated from the fibers reinforced the polymer composites with higher tensile modulus and strength compared with the composites with untreated fibers. Cellulose nanofibers/nanocrystals can be isolated from wood particles, such as poplar wood samples, using acid hydrolysis after lignin removel. Most nanofibers were bundles of single nanocrystals if the acid hydrolysis conditions are mild, e.g. lower temperature and/or lower acid concentration. These nanofibers can be used to reinforce PVA when fabricating bio-nanocomposites and had much better performance than commercial MCC for PVA reinforcement.

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7. References

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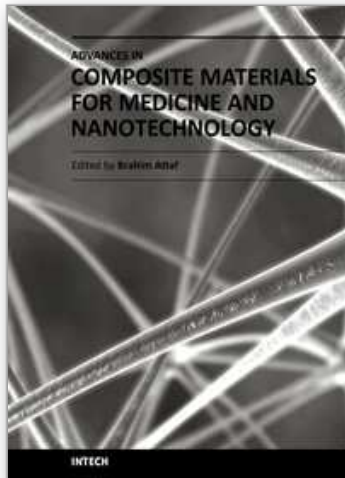
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Due to their good mechanical characteristics in terms of stiffness and strength coupled with mass-saving advantage and other attractive physico-chemical properties, composite materials are successfully used in medicine and nanotechnology fields. To this end, the chapters composing the book have been divided into the following sections: medicine, dental and pharmaceutical applications; nanocomposites for energy efficiency; characterization and fabrication, all of which provide an invaluable overview of this fascinating subject area. The book presents, in addition, some studies carried out in orthopedic and stomatological applications and others aiming to design and produce new devices using the latest advances in nanotechnology. This wide variety of theoretical, numerical and experimental results can help specialists involved in these disciplines to enhance competitiveness and innovation.

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