

MORPHOLOGICAL CHARACTERISTICS OF CELLULOSE NANOFIBRIL-FILLED POLYPROPYLENE COMPOSITES

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Abstract. Nano-sized cellulose fillers (cellulose nanofiber [CNF] and microfibrillated cellulose [MFC]) and a micron-sized cellulose filler (microcrystalline cellulose [MCC]) were used as fillers in polypropylene (PP) composites. Cellulose-filled PP composite samples were manufactured and tested, and their morphological properties were examined to describe morphological characteristics of fracture surfaces at different filler loading levels after mechanical testing. Scanning electron microscopy analysis showed polymer stretching as the major component causing plastic deformation in fracture surfaces of CNF- and MCC-filled composites, whereas analysis of MFC-filled composites exhibited brittle deformation. Individual CNF and MFC fibers were separated and dispersed in the matrix polymer, although considerable agglomeration was observed beyond 6% (wt) filler loading, which resulted in sustained tensile and flexural strength. Mechanical property test results showed that in the case of CNF and MFC, composites sustained considerable tensile and flexural strength up to 10% (wt) filler loading, whereas tensile and flexural strength of MCC-filled composites decreased continuously.

Keywords: Cellulose nanofiber, microfibrillated cellulose, microcrystalline cellulose, scanning electron microscopy, plastic deformation, brittle deformation.

INTRODUCTION

For decades, a combination of discrete materials has been used to obtain composite materials with properties superior to the individual components (Marcovich et al 2006), and there is simultaneous and growing interest in developing biobased products and innovative process technologies that can decrease dependence on fossil fuels and move to a sustainable materials basis (Espert et al 2004; Pandey et al 2005). More recently, there has been increased interest in use of naturally occurring materials because of more environmentally aware consumers, increased price of crude oil, and concerns about global warming (Petersson et al 2007). The need for materials with specific characteristics for spe-

cific purposes that are also nontoxic and environmentally friendly is increasing because of lack of resources and increasing environmental pollution (Yang et al 2007). Use of natural, rather than synthetic, reinforcing fillers in composite materials will have a less harmful effect on the environment (Petersson et al 2007). In particular, considerable effort has been devoted in recent years to research and development of materials that use cellulose fibers as the load-bearing constituents for various polymeric composites (Marcovich et al 2006). Nature provides wonderful examples of composite materials that involve cellulosic structures. Wood properties result from a unique interplay among nanoscale domains of cellulose, hemicelluloses, and lignin (Hubbe et al 2008). Among cellulose products, cellulose nanofibrils are becoming an important class of reinforcing materials. Cellulose is one of the most abundant materials in the natural

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world because it represents the primary structural component of plants (Eichhorn and Young 2001) and has positive attributes such as low cost, low density, high stiffness, renewability, and biodegradability, all of which constitute major incentives for exploring new uses (Goussé et al 2004).

Recently, researchers have focused their work on processing nanocomposites (composites with nano-sized reinforcement) to enhance mechanical properties (Bondeson et al 2006; Dufresne 2006). Nanocomposites are a relatively new generation of composite materials in which at least one of the constituent phases has one dimension in the nanometer range (1-100 nm) (Kvien 2007). This new family of composites is reported to exhibit remarkable improvements in material properties compared with conventional composite materials (Garces et al 2000). As with traditional microcomposites, nanocomposites use a matrix in which the nano-sized reinforcement elements are dispersed. This particular feature provides unique and outstanding properties not found in conventional composites (Azizi Samir et al 2005; Bondeson et al 2006). Size and dispersion of filler particles in the matrix can affect composite properties. The small size of the reinforcement leads to an enormous surface area and thereby to increased interaction with the polymer matrix on the molecular level, leading to materials with new properties. The reinforcing ability of cellulose nanofibrils lies in their high surface area and good mechanical properties. However, to obtain significant increases in material properties, cellulose nanofibril fillers should be well separated and evenly distributed in the matrix material (Kvien et al 2005). Small, well-dispersed particles generally give better properties (Inoue and Suzuki 1995). Well-dispersed nanoparticles can improve tensile properties and ductility because their small size does not create large stress concentrations in the matrix (Kvien 2007). The small size also increases probability of structural perfection, which renders it more efficient than micron-sized reinforcements (Kvien 2007). However, dispersing very fine particles is often

difficult because of their tendency to agglomerate (Oksman and Clemons 1998).

Generally, cellulose nanofibers are the elementary assemblies of distinct polymeric units based on glucopyranose, which can have diameters on the order of tens of nanometers and constitute a fiber of the strand. Their unique structural aspects give them unique tensile, optical, electrical, and chemical properties, unlike their macroscopic counterparts such as microfibers or larger structures (Hubbe et al 2008). Recently, new efforts have been made to obtain cellulose dispersions in organic nonpolar solvents using water-based processing and further incorporation into new polymeric matrices (Marcovich et al 2006) such as thermoplastics, yet no systematic study at each filler loading level on micron- and nanoscale morphological characterization has been reported in the literature on the use of cellulose nanofibrils as reinforcement in thermoplastics using a melt blending process. Therefore, in this study, a detailed morphological investigation was carried out on cellulose nanofibril-filled polypropylene (PP) composites with special reference to effects of different cellulose fillers and filler loadings.

Scanning electron microscopy (SEM) was used for structure determination of nanocomposites using various natural fillers as reinforcements (Kvien et al 2005). In all studies, fractured surfaces of cellulose nanofibril-filled PP composite samples were generated and coated to avoid charging. The word fibril has been used by various researchers to describe relatively long and very thin pieces of cellulosic material (Dufresne et al 2000; Dalmas et al 2006; Marcovich et al 2006; Abe et al 2007; Cheng et al 2007; Wu et al 2007). Meanwhile, the word nanofiber has come into increasing use, which helps to emphasize cases in which very small cellulosic fibrous materials can display behavior and functionality that differ from what has been observed with larger cellulosic fibers (Hubbe et al 2008). SEM provides information about dispersion and orientation of fillers in the matrix in addition to presence of aggregates and voids (Kvien et al 2005).

The aim of this study was to describe morphological characteristics and evaluate filler dispersion of PP composites using different cellulose nanofibril fillers at different filler loading levels. SEM was used to observe fracture surfaces of composite samples after tensile testing.

MATERIALS AND METHODS

Materials

Matrix polymer. The PP, commercially named FHR Polypropylene AP5135-HS, used as the thermoplastic matrix polymer was supplied by Polystrand Co. (Montrose, CO) in the form of impact-modified copolymer pellets with a density of 900 kg/m³ and melt flow index of 35 g/10 min (230°C/2,160 g).

Reinforcing fillers. Cellulose materials used as natural reinforcing fillers in composites were microcrystalline cellulose (MCC) for comparison purposes, cellulose nanofiber (CNF), and microfibrillated cellulose (MFC). The product name of the MCC supplied by Sigma-Aldrich Co. (St. Louis, MO) is Sigmacell[®] Cellulose Type 50; the CNF supplied by J. Rettenmaier & Söhne GMBH Co. (Rosenberg, Germany) is named Arbocel Nano MF 40-10; and the MFC supplied by EFTecTM Co. (Shelton, CT) is named Lycopell L010-4. CNF was a suspension with a solids content of 10% (wt); MFC was a wet fiber web with a solids content of 15% (wt). CNF was in the form of rod-like short-fiber 50-300 nm diameter and 6-8 aspect ratio, MFC was in the form of long fibrils 50-500 nm diameter and 8000-80,000 aspect ratio, and MCC was in the form of particles 50-μm average diameter and 1-2 aspect ratio. For this research, MCC was stored in sealed containers after being oven-dried for 24 h at 103°C; CNF and MFC were stored in the refrigerator in sealed packages.

Sample Preparation

MCC was dried to less than 1% (wt) MC using a forced-air oven at 103°C for at least 24 h and

then stored in sealed containers in an environmental chamber prior to compounding. CNF and MFC were stored in sealed containers in a refrigerator prior to compounding. A Brabender (Duisburg, Germany) Prep-mixer[®] was used to compound MCC, CNF, and MFC with PP, with the latter being used as the polymer matrix. As CNF and MFC were mixed with PP, the cellulose nanofibril suspension and wet fiber webs were slowly and carefully fed into the bowl mixer in low amounts for each attempt to prevent explosive and violent water evaporation. Process temperature and torque changes were measured in real time. The sample preparation procedure consisted of three general processes: melt blending, grinding, and injection molding. Compounding was performed at 190°C for 40 min with a screw speed of 60 rpm. The blended mixture was granulated using a laboratory-scale grinder. The ground particles were stored in sealed packs to avoid moisture infiltration after first being oven-dried for at least 24 h at 103°C. Five levels of filler loading (2, 4, 6, 8, and 10% wt) for MCC, CNF, and MFC were used in sample preparation. Ground particles were stored in sealed containers in an environmental chamber prior to injection molding. Samples used for tensile tests were injection-molded at 246°C with an injection pressure of 17.25 MPa. Width, length, and depth of tensile test samples were according to ASTM D 638-03 type I. After injection-molding, test samples were conditioned before testing at 23 ± 2°C and 50 ± 5% RH for at least 40 h according to ASTM D 618-99. MCC samples for SEM analysis were prepared by making a thin board using compressed MCC particles, and then fractured surfaces were taken for analysis. CNF and MFC samples for SEM analysis were prepared by drying a CNF suspension and MFC fiber webs on the surface of aluminum fans and then surfaces were taken for analysis.

Test Methods

Studies on morphology of composite tensile fracture surfaces were carried out using an AMR 1000 (AMRay Co., Bedford, MA) SEM.

Images were taken at 10 kV with 200, 2000, and 12,000 $\times$ SEM micrograph magnifications. All samples were sputtered with gold before microscopic observations were obtained.

RESULTS AND DISCUSSION

Fracture surfaces of neat PP tensile samples at 200, 2000, and 12,000 $\times$ magnification are shown in Fig 1a, b, and c, respectively. SEM micrographs exhibited stretched polymers on the surface of neat PP samples in Fig 1a and

sphere-like objects, attributed to air bubbles produced during melt blending and injection-molding processes, were observed in Fig 1b and c. This unique appearance helps identify the filler or matrix polymer in SEM micrographs of composite samples. Figure 2a and b exhibit CNF at 2000 and 12,000 $\times$ magnifications, respectively. Mixed sizes of rod-like short fibers smaller than 200-nm diameter were the major filler particle observed, although fibers larger than 5- μ m diameter occurred as well. Figure 2c and d exhibit MFC at 2000 and 12,000 $\times$ magnifications, respectively. Mixed sizes of long fibrils from 50-300 nm diameter and fibril bundles, which have a high aspect ratio, can also be observed. MFC fibrils can be easily agglomerated with each other during the melt blending process (Oksman and Clemons 1998). Figure 2e and f exhibit MCC at 200 and 2000 $\times$ magnifications, respectively. Most MCC particles observed were from 30-100 μ m diameter, which can be deemed micro-scale. Figure 3 exhibits tensile fracture surfaces of composites at 2% wt filler loading and different magnifications. Figure 3a and b exhibit CNF-filled PP composites at 200 and 12,000 $\times$ magnifications, respectively. A minor amount of agglomerated fibers is shown in Fig 3a, and individual rod-like short fibers that dispersed into the matrix are observed in Fig 3b. Figure 3c and d exhibit MFC-filled PP composites at 200 and 12,000 $\times$ magnifications, respectively. Even at 2% wt filler loading, there were agglomerated long fibrils in composites in Fig 3c. Individual fibrils from 50-300 nm diameter and fibril bundles are observed in Fig 3d. Agglomerated MFC fibrils generate stress concentrations, and these flaws cause nonuniform stress transfer during tensile fracture of samples (Kvien 2007). Figure 3e and f exhibit MCC-filled PP composites at 200 and 2000 $\times$ magnifications, respectively. MCC particles from 50-90 μ m diameter, which are larger than CNF and MFC particles, are observed in Fig 3e. Empty spaces (microcracks) between the MCC and PP matrix, which occurred during tensile failure, are observed in Fig 3f, and these cracks caused nonuniform stress transfer under tension

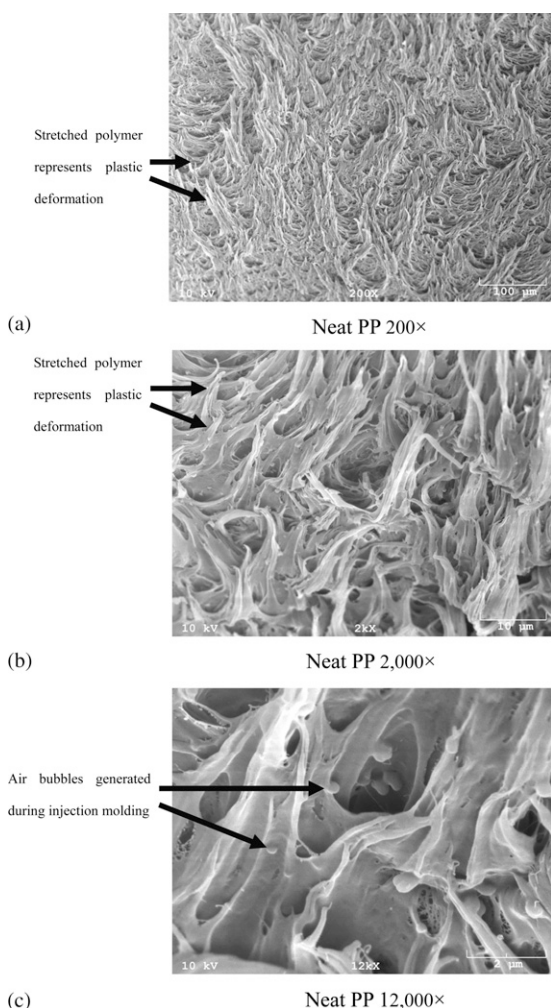


Figure 1. (a-c) Scanning electron micrographs of fracture surfaces of the neat polypropylene tensile samples.

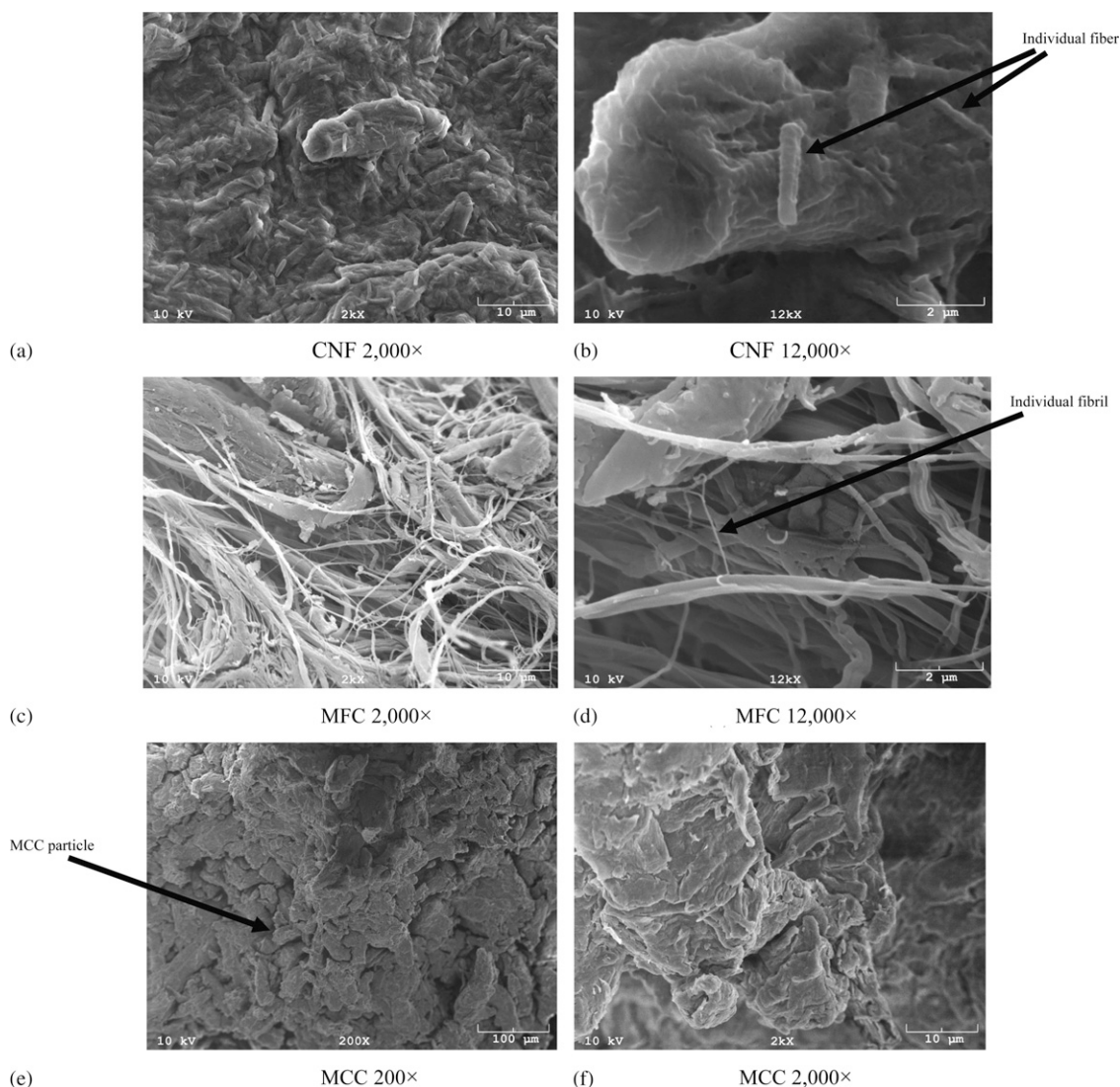


Figure 2. (a-f) Scanning electron micrographs of the cellulose fillers at different magnifications.

loading. Figure 4 exhibits tensile fracture surfaces of composites at 6% wt filler loading and different magnifications. An increased amount of agglomerated fillers is shown in Fig 4a, and individual rod-like short fibers can be observed in Fig 4b. Agglomerated MFC fibrils and fibril bundles are observed in Fig 4c, and individual fibrils can be observed among fibril bundles in Fig 4d. An increased amount of MCC particles as a logical sequence of increased filler loading

are observed in Fig 4e, and microcracks can be observed between the MCC and PP matrix in Fig 4f. Figure 5 exhibits tensile fracture surfaces of composites at 10% wt filler loading and different magnifications. Almost the same amount of agglomerated fibers as in the 6% wt filled sample is observed in Fig 5a, and this agglomeration could be the stress concentration point in composite samples as discussed previously in the mechanical properties study

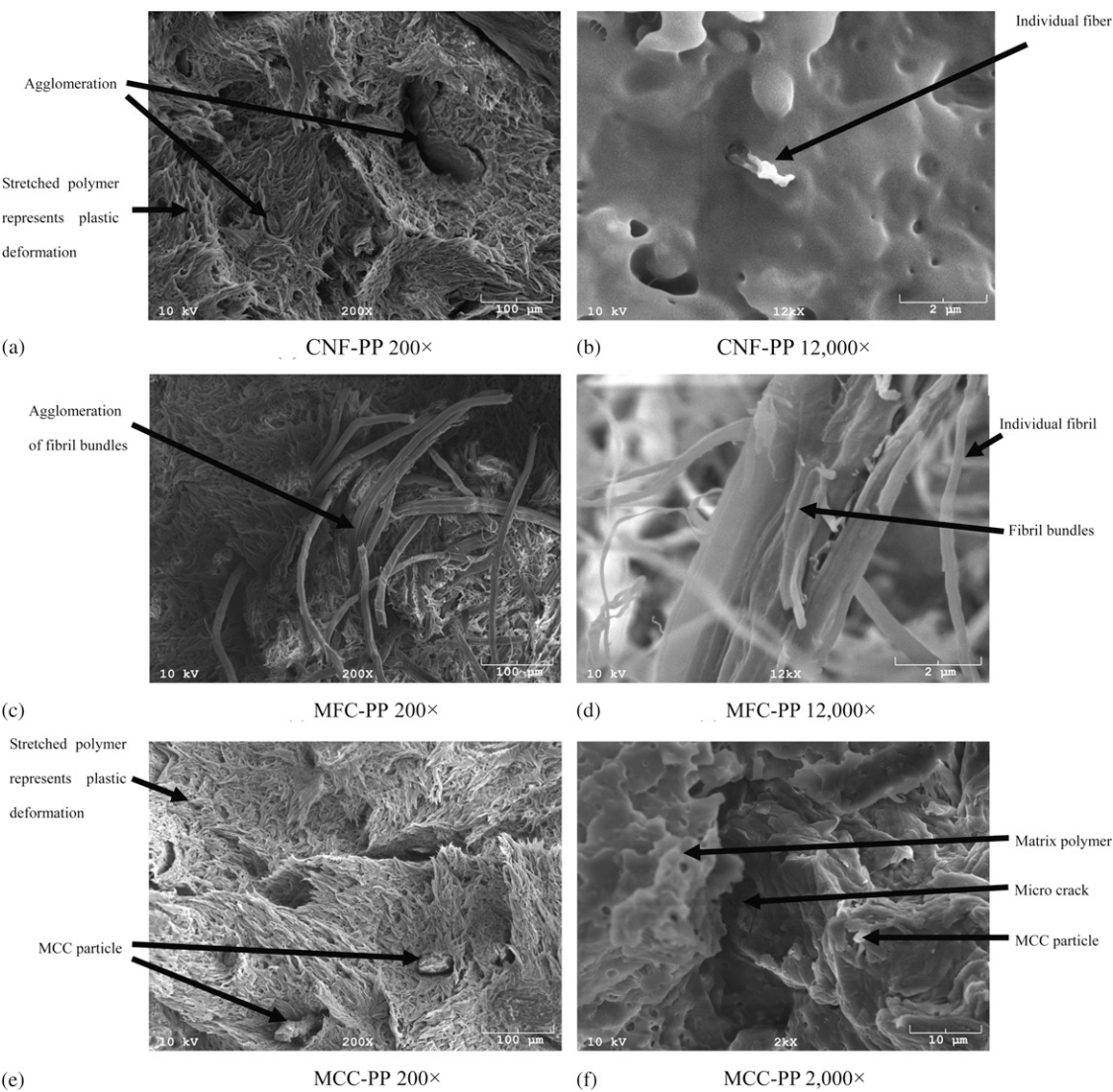


Figure 3. (a-f) Scanning electron micrographs of tensile fracture surfaces of the composite samples at 2 wt% filler loading and different magnifications.

(Yang and Gardner 2011). However, in addition to agglomerated fibers, many separated individual rod-like short fibers are observed in Fig 5b. A considerable amount of agglomerated MFC fibrils and fibril bundles are observed in Fig 5c. Also, an increased amount of individual MFC fibrils can be observed in Fig 5d. From Fig 5a to d, the amount of individual nanoscale fillers increased along with agglomerated particles as filler loading increased, and those

nanoscale fillers retarded tensile strength deterioration to some extent, as shown in Table 1 and mentioned previously in the mechanical properties study (Yang and Gardner 2011). Well-dispersed individual nanoscale fillers can play a positive role by increasing strength properties in the composite system in this case (Inoue and Suzuki 1995). MCC particles occupy quite a large portion of the fracture surface in Fig 5e, and microcracks can be

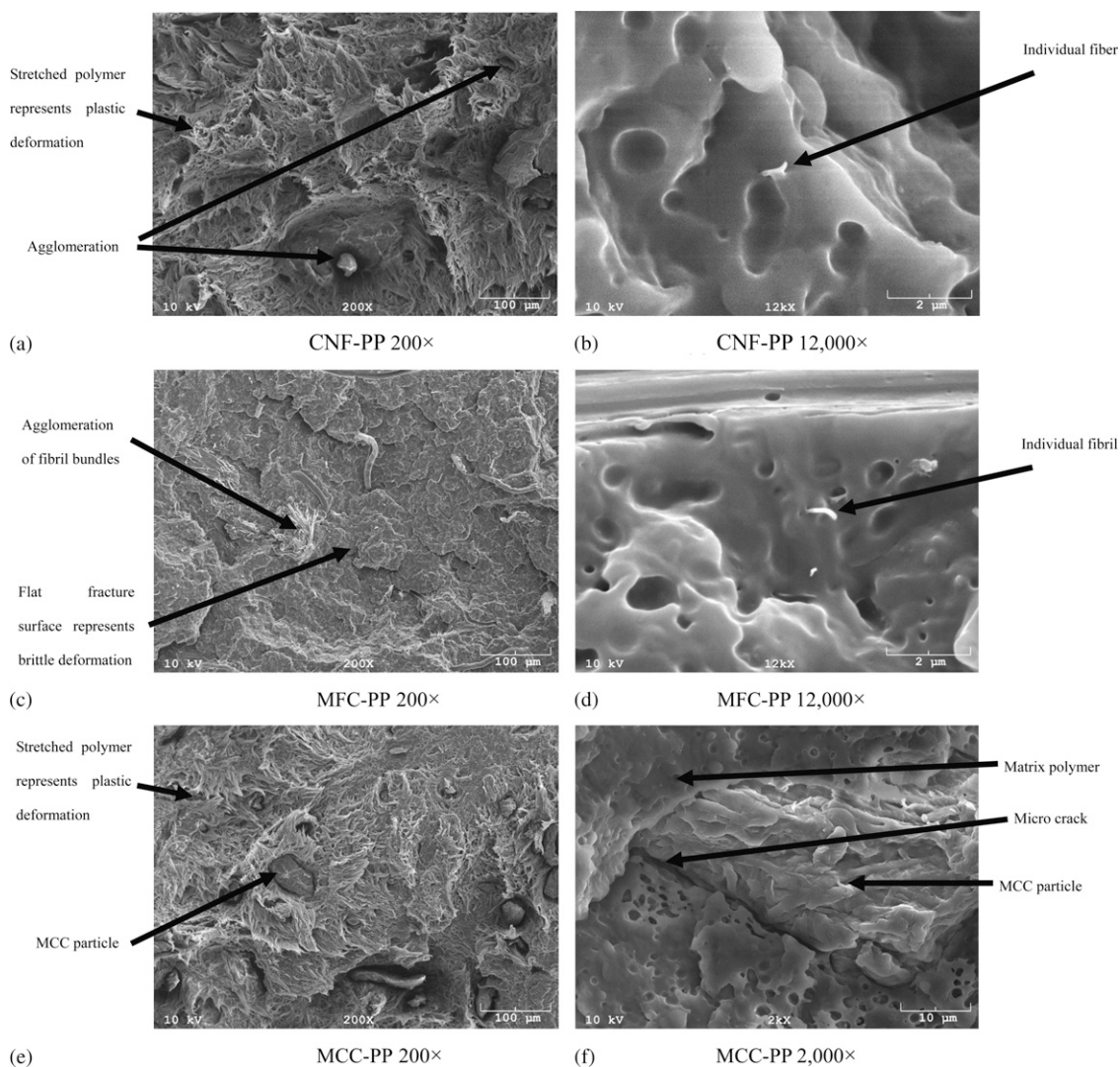


Figure 4. (a–f) Scanning electron micrographs of tensile fracture surfaces of the composite samples at 6 wt% filler loading and different magnifications.

observed between the MCC and PP matrix in Fig 5f. Microcracks, which can be observed between the MCC and PP matrix, clearly indicate a poor interaction between them. The polar nature of MCC and the nonpolar nature of the matrix can be cited as one of the possible causes for this observation (Yang et al 2007). Furthermore, different sizes and irregular shapes of fillers are evident in Fig 5. Stretched polymers can be observed in Fig 5a,

b, e, and f, which suggests plastic deformation of the matrix. Because adhesion of the matrix and MCC is poor, the matrix can deform independently until the filler particles restrict deformation. However, as filler loading increased, the observed plastic deformation characteristic appeared to decrease as deformability of the matrix was limited earlier during tensile test elongation. Therefore, SEM observations of composites provided visual evidence for

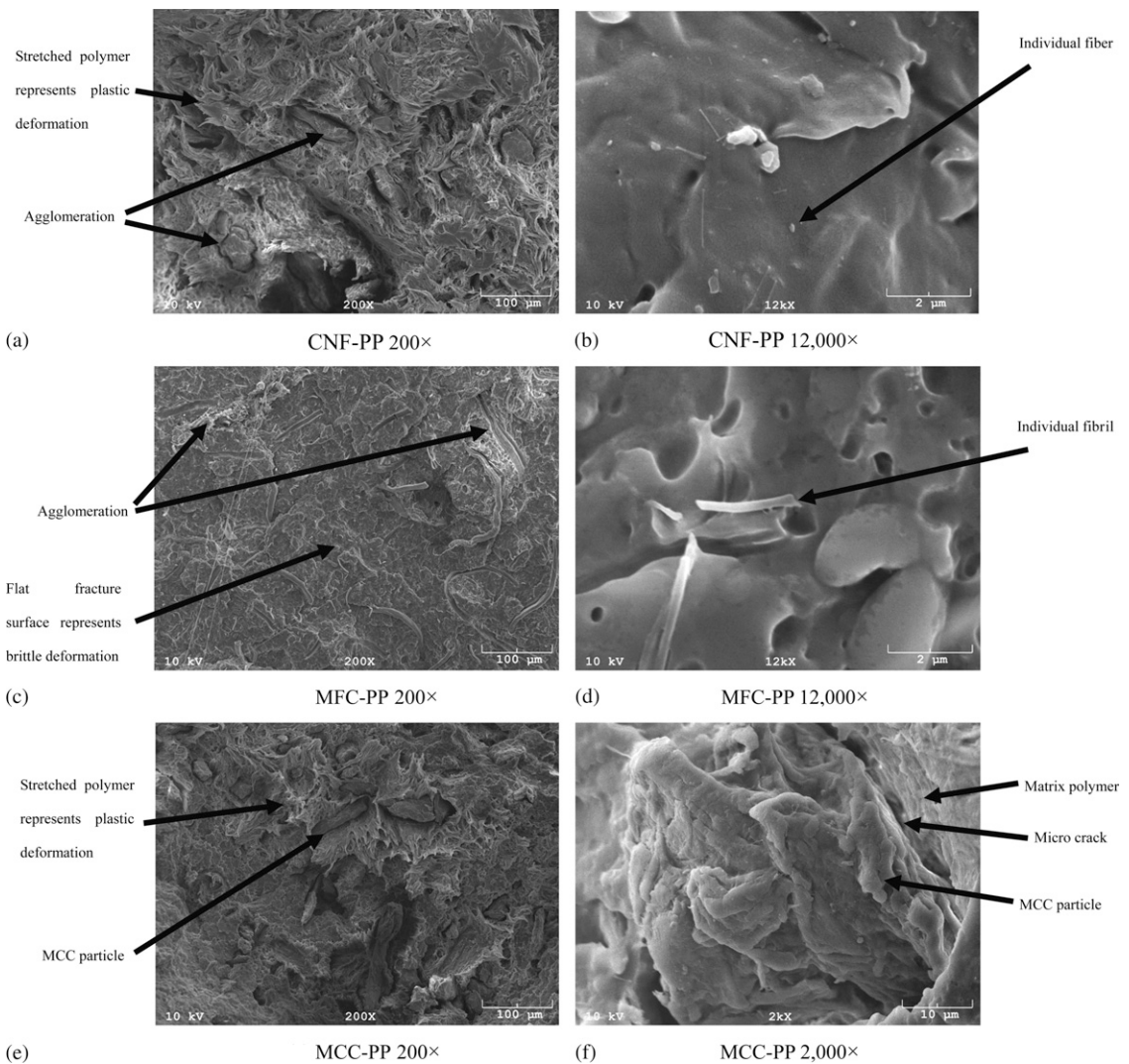


Figure 5. (a-f) Scanning electron micrographs of tensile fracture surfaces of the composite samples at 10 wt% filler loading and different magnifications.

decreased tensile strength and their trend against increased filler loading (Premalal et al 2002).

Generally, fracture surfaces of CNF- and MCC-filled composites appeared to be stretched polymers, whereas surfaces of MFC-filled composites represented brittle deformation. This means that CNF- and MCC-filled composites mainly represented plastic deformation (Yang et al 2004). This might be the reason why

elongations at the break of MFC-filled composites were lower than those of other composites as discussed previously in the mechanical properties study (Yang and Gardner 2011). Usually, fibers that have higher aspect ratios in reinforced composites must contribute higher tensile strength to the composite, but in the case of MFC-filled PP composites in this study, considerable agglomeration occurred during melt blending and kept tensile strength from improving.

Table 1. Tensile strength results and significance by Tukey-Kramer test^a (Yang and Gardner 2011).

Sample ID	Significance				Mean strength (MPa)	SD	COV (%)
Neat PP	A				21.97	0.44	2.00
CNF 2%		B			21.32	0.24	1.13
CNF 4%		B	C	D	21.02	0.47	2.24
CNF 6%		B	C	D	21.03	0.27	1.28
CNF 8%				D	20.55	0.27	1.31
CNF 10%				E	20.16	0.17	0.84
MFC 2%	A	B			21.47	0.32	1.49
MFC 4%		B	C	D	20.97	0.54	2.58
MFC 6%			C	D	20.69	0.49	2.37
MFC 8%		B	C		21.14	0.43	2.03
MFC 10%		B	C	D	21.04	0.50	2.38
MCC 2%		B	C	D	21.01	0.37	1.76
MCC 4%		B	C	D	21.02	0.31	1.47
MCC 6%				E	20.20	0.31	1.53
MCC 8%				F	19.32	0.22	1.14
MCC 10%				F	18.97	0.30	1.58

^a Means not followed by a common letter are significantly different one from another at $p = 0.05$.

PP, polypropylene; CNF, cellulose nanofiber; MFC, microfibrillated cellulose; MCC, microcrystalline cellulose.

Overall, individual CNF separated and dispersed into the matrix polymer, but considerable agglomeration was observed beyond 6% wt filler loading. Agglomerated MFC fibrils and fibril bundles can be observed in the SEM micrographs within the whole range of filler loading; this can contribute to a stress concentration point in MFC–PP composites and can result in nonuniform stress transfer between the filler and matrix polymer under tension loading and deterioration of tensile strength (Kvien 2007). As clearly evidenced by SEM observations, MFC fibrils formed more agglomerates than other cellulose fillers during melt blending and the presence of these agglomerates resulted in the generation of flaws, which became larger in size (Oksman and Clemons 1998). This causes elongations at the break of MFC-filled composites to be decreased compared with other cellulose fillers (Premalal et al 2002) as discussed previously in the mechanical properties study (Yang and Gardner 2011). Conversely, in the case of MFC-filled composites, a considerable amount of individual MFC fibrils was separated and dispersed into the matrix, which resulted in sustained tensile strength beyond 6% wt filler loading. Empty spaces (microcracks) nearby larger MCC particles caused nonuniform stress transfer between

MCC and matrix polymer under tension loading and caused lower tensile strength compared with CNF- and MFC-filled composite samples (Table 1). This was discussed previously in the mechanical properties study (Yang and Gardner 2011).

CONCLUSIONS

SEM analysis showed that individual CNF fiber and MFC fibrils were separated and dispersed in the matrix polymer, although considerable agglomeration generated during melt blending was observed beyond 6% wt filler loading, which resulted in sustained tensile and flexural strength. Fracture surfaces of CNF- and MCC-filled composites mainly represent plastic deformation, whereas surfaces of MFC-filled composites represent brittle deformation. In the case of MFC-filled PP composites, considerable agglomeration occurred during melt blending and kept tensile strength from improving. From SEM analysis, we can conclude that the observed microcracks nearby larger MCC particles could have caused nonuniform stress transfer between MCC and matrix polymer under tension loading and lower tensile strength compared with cellulose nanofibril filler-filled composite samples. From these observations, it can

be concluded that mechanical performance of cellulose nanofibril fillers was superior to that of microcrystalline cellulose. However, agglomeration of cellulose nanofibril fillers during processing is one of the most challenging tasks to overcome in the field of cellulose nanocomposites research.

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