

MECHANICAL PROPERTIES OF CELLULOSE NANOFIBRIL-FILLED POLYPROPYLENE COMPOSITES

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Abstract. Cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC) filled-polypropylene (PP) composite samples were manufactured using a melt mixing technique. Mechanical testing was conducted to investigate tensile and flexural properties of the composites at different filler loading levels. Test results showed that in the case of cellulose nanofibril fillers, the composites sustained considerable tensile strength up to 10% (w/w) filler loading whereas the tensile strength of the MCC-filled composites decreased continuously. Moreover, tensile modulus increased as filler loading increased for all cellulose fillers. CNF and MCC-filled composites demonstrate plastic deformation and longer elongation at break than MFC-filled composites while MFC-filled composites exhibited a quasi-brittle behavior under tensile deformation. Flexural strength of cellulose nanofibril-filled composites decreased slightly as a function of filler loading up to 6% (w/w) and increased beyond 6% (w/w). The 10% (w/w) cellulose nanofibril-filled composite samples exhibited sustained flexural strength as compared with neat PP. The trend of increased flexural modulus of elasticity behavior was identical to the tensile modulus of elasticity behavior.

Keywords: Cellulose nanofiber, microfibrillated cellulose, microcrystalline cellulose, tensile strength, plastic deformation, flexural strength.

INTRODUCTION

In the past few decades, research and engineering interest has been shifting from monolithic materials to reinforced polymeric materials (Wambua et al 2003). Nowadays, various synthetic polymers are being prepared and combined with various reinforcing fillers to generally improve mechanical properties as well as to obtain desired properties for particular applications (Yang et al 2004). Reinforced composite materials now dominate the aerospace, leisure, automotive, con-

struction, and sporting industries (Wambua et al 2003). Newer materials and composites have both economic and environmental benefits. For instance, mineral fillers and synthetic fibers are used frequently in the plastics industry to achieve desired properties or to reduce the cost of the final products (Sanadi et al 1995). In the field of reinforced composites, the fiber reinforcement of matrices was initially developed using synthetic fibers such as glass, carbon, aramid, etc. to take advantage of their high tensile moduli (Joseph et al 1999). Composites based on thermoplastic polymers are very popular because of their processing advantages (Rana et al 1998). Among commodity thermoplastics,

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polypropylene (PP) possesses outstanding properties such as low density, high softening point, good fatigue resistance, sterilizable, good surface hardness, scratch resistance, very good abrasion resistance, and excellent electrical properties (Rana et al 1998). The utilization of fillers from various sources with polypropylene has been an accepted route to enhance material properties or provide cost savings. Fillers can be categorized as inorganic and organic. In terms of inorganic fillers, carbon black, silica, calcium carbonate (CC), and talc are used in PP composites (Premalal et al 2002). In recent years, rapid growth occurred in the consumption of reinforced polymer composites, yielding a unique combination of high performance, great versatility, and processing advantages at favorable cost (Amash and Zugenmaier 2000). However, the need for materials having special characteristics for specific purposes, while at the same time being nontoxic and environmentally friendly, is increasing because of a lack of resources and increasing environmental pollution (Yang et al 2007). Among the fillers used for polymeric composites, cellulose nanofibers are becoming an important class of reinforcing materials. Cellulose fibers exhibit many advantages, including low density, low damage during processing, low energy requirements on processing equipment, biodegradability, high stiffness, and relatively low price compared with inorganic fillers (Amash and Zugenmaier 2000). The main purpose of adding cellulose-based fillers to thermoplastics is to reduce the cost per unit volume and improve stiffness. Low-price cellulose-based fillers such as wood flour, wood fibers, and cellulose fibers have high stiffness, low density, and are recyclable (Oksman and Clemons 1998). A thermoplastic nanocomposite is a reinforced composite material consisting of nano-scale reinforcing fillers and a thermoplastic matrix polymer. A nanocomposite is a two-phase material where one of the phases has at least one dimension in nanometer range (1-100 nm) and usually results in composites with superior thermal, barrier, and mechanical properties (Oksman et al 2006). There is great appeal in the study of cellulose

nanofiber-filled PP composites in an attempt to achieve comparable properties with synthetic fiber/inorganic material-filled PP composites and cellulose nanofibril-filled bio-based composites can result in significant material cost savings as plant-based materials are cheaper than the pure polymer and far less expensive than inorganic fillers. The three different cellulose fillers, which are cellulose nanofiber (CNF), microfibrillated cellulose (MFC) and microcrystalline cellulose (MCC), have been used in this study to evaluate the effect of filler type. CNF is in the form of short fiber, MFC is in the form of long fiber, and MCC is in the form of particle. Each filler type has a different effect on the mechanical properties, for example, longer fiber could better contribute to the tensile strength than shorter fiber as reinforcement. The objectives of this study were to obtain selected mechanical properties of PP composites using different cellulose nanofibril fillers at different filler loading levels, to describe mechanical performance, and to determine the suggested filler loading for further study about surface-modified cellulose nanofibril filler-filled PP composites.

EXPERIMENTAL PROCEDURE

Materials

Matrix polymer. The PP used as the thermoplastic matrix polymer was supplied by Polystrand Co. and is marketed under the commercial name of FHR Polypropylene AP5135-HS. This PP, in the form of impact-modified copolymer pellets with a density of 900 kg/m^3 and a melt flow index of 35 g/10 min (230°C /2,160 g), was stored in sealed packages.

Reinforcing fillers. The cellulose materials used as natural reinforcing fillers in the composites were MCC for comparison purposes, CNF, and MFC. The product name of the MCC was Sigmacell[®] Cellulose Type 50 supplied by Sigma-Aldrich Co., CNF was Arbocel Nano MF 40-10 supplied by J. Rettenmaier and Söhne GMBH Co., Germany, and the MFC was

Lyocell L010-4 supplied by EFTec™ Co. CNF was in the form of a suspension with a solids content of 10% (w/w). MFC was in the form of wet fiber web with a solids content of 15% (w/w). CNF is in the form of rod-like short fiber 50-300 nm in diameter and 6-8 in aspect ratio, MFC is in the form of long fiber 50-500 nm in diameter and 8,000-80,000 in aspect ratio, and MCC is in the form of particle 50 μm in average diameter and 1-2 in aspect ratio. The MCC was stored in sealed containers after being oven-dried for 24 h at 103°C. The CNF and MFC were stored in a refrigerator at 5-10°C in sealed packages before being used.

Sample Preparation

The MCC was dried to a moisture content of less than 1% (w/w) 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. The CNF and MFC were stored in sealed containers in a refrigerator prior to compounding. A Brabender Prep-mixer® was used to compound the MCC, CNF, and MFC with the PP with the latter being used as a matrix polymer. During the CNF and MFC mixing 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, otherwise the water would evaporate explosively and violently. This procedure took 8 min. The process temperature and torque changes were measured in real time. The sample preparation procedure consisted of three general processes, viz. melt blending, grinding, and injection molding. Compounding was performed at 190°C for 40 min including cellulose filler feeding time with a screw speed of 60 rpm. After being oven-dried for at least 24 h at 103°C, the blended mixture was granulated using a lab scale grinder and the ground particles were stored in sealed packs to avoid unexpected moisture infiltration. Five levels of filler loading (2, 4, 6, 8, and 10% [w/w]) for MCC, CNF, and MFC were used in the sample preparation. Ground particles were stored in sealed containers in an environmental chamber prior to

injection molding. The samples used for the tensile and flexural tests were injection molded at 246°C using an injection pressure of 17.25 MPa. The width, length, and depth of the tensile and flexural test samples were according to ASTM D 638-03 type I and D 790-07, respectively. After injection molding, the test samples were conditioned before testing at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ RH for at least 40 h according to ASTM D 618-99.

Test Methods

Tensile tests. Tensile tests were performed to examine static tensile strength and modulus of elasticity of the composite samples using the ASTM D638-03 standard and under a displacement control of loading (loading rate = 5 mm/min). An extensometer was employed to determine elongation of the samples. Tests were performed in an environmentally conditioned room maintained at 21.1°C and 50% RH. A 4,448-N, a load cell attached to a servohydraulic universal testing machine (Instron 8872) was used to collect stress-strain data of the corresponding samples. Static tensile loads were applied to 12 replicate samples for each series of prepared samples and then average and standard deviation were calculated.

Flexural tests. Flexural tests were performed to examine static 3-point bending strength and modulus of elasticity of the composite samples using the ASTM D790-07 standard and under a displacement control of loading (loading rate = 1.27 mm/min). Tests were performed in an environmentally conditioned room maintained at 21.1°C and 50% RH. The applied spans were 50.8 mm long for a length vs depth (L/D) ratio of 16. A 222.4-N load cell attached to a servohydraulic universal testing machine (Instron 8872) was used to collect stress-strain data of the corresponding samples. The ultimate flexural strength values were calculated from maximum load, and the flexural modulus of elasticity values were calculated from the stress vs strain data between 20 and 40% of ultimate

stress level. Static flexural loads were applied to six replicate samples for each series of prepared samples and then average and standard deviation were calculated.

RESULTS AND DISCUSSION

Tensile Strength

The tensile stress–strain curves of the CNF, MFC, and MCC-filled composites are shown in Fig 1. CNF and MCC-filled composites demonstrate plastic deformation which represents a typical yielding process and ductile nature followed by strain hardening. In contrast, MFC-filled composites exhibit a quasi-brittle behavior under tensile deformation (Premalal et al 2002). A closer examination of the coupon sample showed a large amount of agglomerated fibers among the MFC-filled composite samples, which might explain the brittle behavior due to stress concentrated points and nonuniform stress transfer. From Fig 1, it was found that yield stress, elongation at yield, and elongation at break generally tended to decrease as filler loading increased while tensile modulus increased as filler loading increased. Figure 2 shows tensile strength of the composites. Generally, a reduction of tensile strength after mixing cellulose fillers with PP was caused by incompatibility between the hydrophilic cellulose filler and hydrophobic matrix polymer but in the case of under 10% (w/w) filler loading, it appears not to be a significant strength reduction. It is hypothesized that tensile strength could be improved significantly by using a compatibilizing agent but before incorporation, filler agglomera-

tion issue needs to be solved first. From the tensile results, 4% (w/w) seems to be best recommended filler amount for the future study about the compatibilizing agent because there is less agglomeration than higher filler loading and the composites still sustained considerable strength. In the case of CNF and MFC, the composites sustained considerable tensile strength up to 10% (w/w) filler loading whereas the tensile strength of MCC-filled composites decreased continuously after 6% (w/w) filler loading. From this figure, it might be perceived that there is a huge amount of agglomerated fibers or particles generated in the composites during melt blending up to 6% (w/w) filler loading and this caused nonuniform stress transfer when the sample was under tension loading. However, in the case of CNF- and MFC-filled composites, there are also increasing amounts of separated individual nanoscale fibers beyond 6% (w/w) filler loading (detailed evidence from SEM micrographs addressed in the morphological characteristics study [Yang and Gardner 2011]) so that composite samples sustained considerable tensile strength up to 10% (w/w) filler loading while the tensile strength of MCC-filled composites decreased continuously as shown in Table 1. From 2-6% (w/w) filler loading, generating agglomerated particles is dominant for the cellulose nanofibers during the melt blending process. However, from 6-10% (w/w) filler loading, the number of agglomerated particles does not increase and individual filler separation becomes more dominant. This assumption also will be discussed in the morphological characteristics study (Yang and Gardner 2011). Figure 3 exhibits

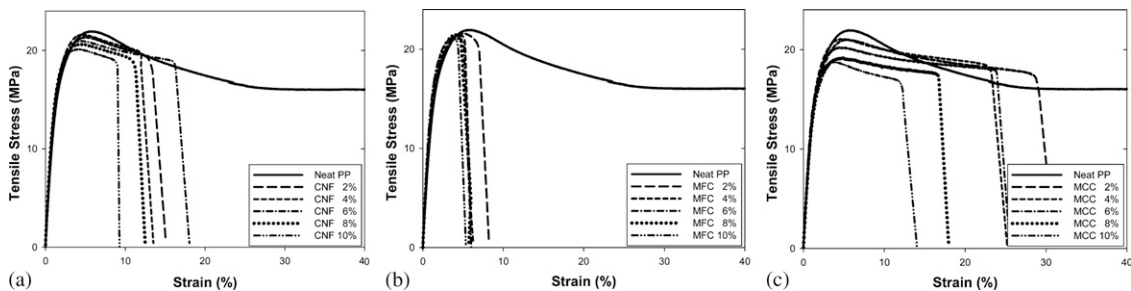


Figure 1. Tensile stress–strain curves of the composites at different filler loadings.

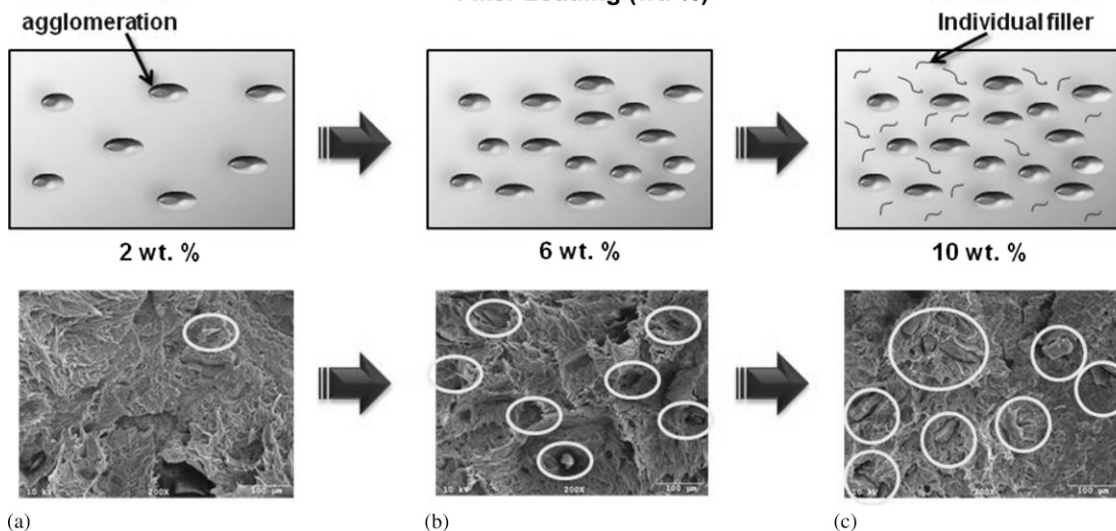
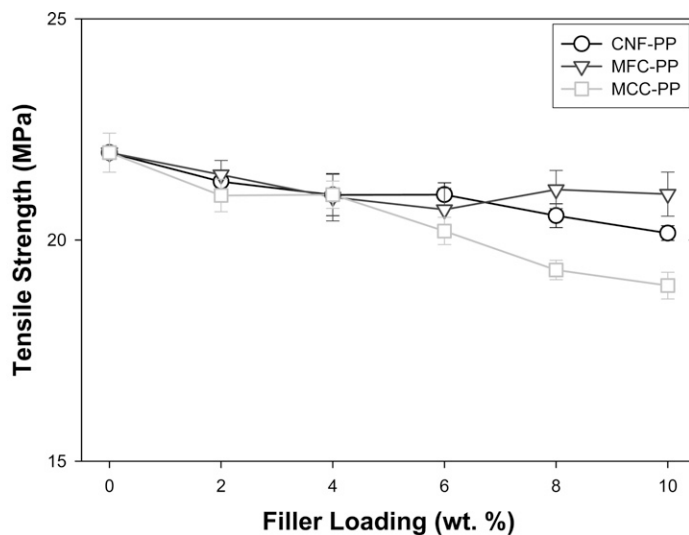


Figure 2. Tensile strength of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites, and schematic representations of CNF-filled PP composites. (a) 2% (w/w), (b) 6% (w/w), and (c) 10% (w/w) filler loading.

tensile Young’s moduli of the composites. The increase in filler content restricted the mobility of the PP chain and this was reflected in the tensile Young’s modulus values (Rana et al 1998). The tensile Young’s modulus values continuously increased as filler loading increased because the filler is more brittle than the matrix polymer (Yang et al 2007). Figure 4 shows tensile elongations at yield of the composites. The elongation at yield values continuously decreased as filler loading increased because of the increased

brittleness as described in Fig 3. The elongation at yield of the MFC-filled PP composite was slightly lower than others because of the larger fiber size and greater amounts of agglomerated fibers in the composite. Figure 5 shows tensile elongations at break of the composites. Incorporation of the filler resulted in an abrupt drop in elongation at break compared with that of neat PP which was unmeasured (many samples did not break beyond the maximum limit of the extensometer). Increase in filler loading restricted the

Table 1. Significance in tensile strength results by Tukey-Kramer test.^a

Sample ID					Mean strength (MPa)	Standard deviation
Neat PP	A				21.97	0.44
CNF 2%	B				21.32	0.24
CNF 4%	B	C	D		21.02	0.47
CNF 6%	B	C	D		21.03	0.27
CNF 8%			D	E	20.55	0.27
CNF 10%				E	20.16	0.17
MFC 2%	A				21.47	0.32
MFC 4%	B	C	D		20.97	0.54
MFC 6%		C	D	E	20.69	0.49
MFC 8%	B	C			21.14	0.43
MFC 10%	B	C	D		21.04	0.50
MCC 2%	B	C	D		21.01	0.37
MCC 4%	B	C	D		21.02	0.31
MCC 6%				E	20.20	0.31
MCC 8%				F	19.32	0.22
MCC 10%				F	18.97	0.30

^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.

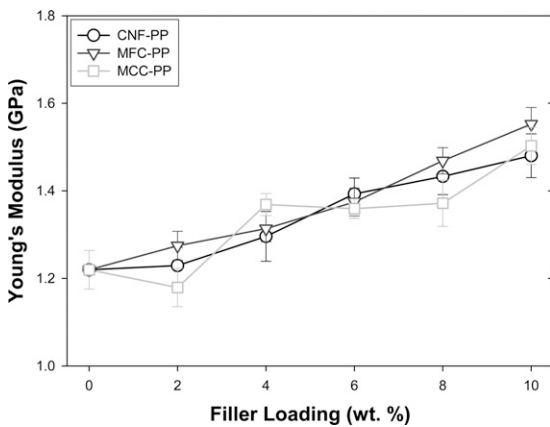


Figure 3. Tensile moduli of elasticity of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

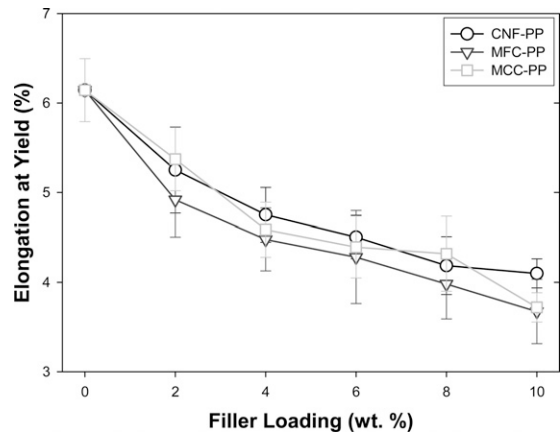


Figure 4. Tensile elongations at yield of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

mobility of the polymer chains and this presumably caused a decrease in the elongation at break (Rana et al 1998). The elongation at break values of the composite continuously decreased as the filler loading increased. This result is in good agreement with previous research results that the agglomerated fillers caused reduced elongation at break (Qiu et al 2000; Premalal et al 2002; Siqueira et al 2009). The agglomeration of fillers leads to numerous irregularly shaped microvoids or microflaws in the composite structure. Because

of these microflaws, the stress transfer from the matrix to the filler is poor and the mechanical properties of the MFC fillers are not fully utilized. The brittleness of the material is accentuated by the probable aggregation of the MFC fillers that leads to the formation of weak points. Filler entanglements are not likely to occur with CNF fillers that occur as straight rod-like nanoparticles and then the behavior at break of the ensuing nanocomposites is mainly governed by the matrix (Siqueira et al 2009).

The elongation at break values of MFC-filled composites were lower than the other filled composite samples at all filler loadings because of the large amount of agglomerated fibers even at lower filler loadings. It appears that the single batch mixer cannot prevent agglomeration of fibers, which exhibit a high aspect ratio during mixing with the thermoplastic matrix polymer. This trend might be changed if the samples are manufactured by other blending systems rather than a single batch mixing system. Further work will address this.

Flexural Strength

Figure 6 exhibits flexural stress–strain curves of the CNF, MFC, and MCC-filled composites.

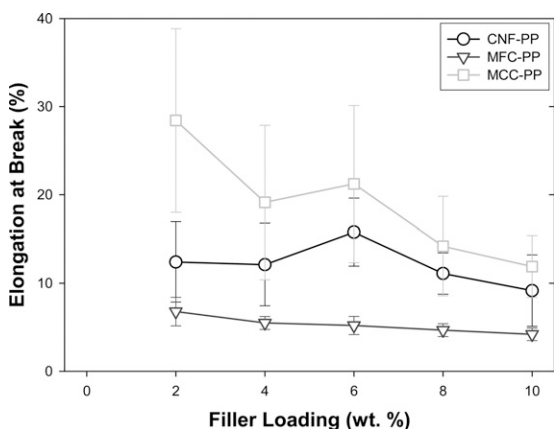


Figure 5. Tensile elongations at break of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

CNF- and MCC-filled composites demonstrate plastic deformation while MFC-filled composites exhibit a quasi-brittle behavior under flexural deformation at 8 and 10% (w/w) filler loading which is the same trend as tensile behavior. Figure 7 and Table 2 exhibit flexural strength of the composites. In the case of CNF and MFC, flexural strength slightly decreased with filler loading increasing up to 6% (w/w) but flexural strength increased beyond 6% (w/w). Finally, 10% (w/w) CNF- and MFC-filled composite samples exhibit the same strength level as compared with neat PP. This figure also proves the assumption described earlier that there is a considerable amount of agglomerated fibers or particles generated during the melt blending up to 6% (w/w) filler loading, and there are also increasing amounts of separated individual nanoscale fillers beyond 6% (w/w) filler loading so that flexural strength of the composite samples are improved as detailed in the SEM micrographs in the morphological characteristics study (Yang and Gardner 2011). The variation in flexural modulus of elasticity of the composites is depicted in Fig 8. The trend of the flexural modulus of elasticity (MOE) behavior was identical to the tensile modulus described earlier where the effect of the filler content was obvious (Rana et al 1998). The MOE is increased by the increase of filler loading for all composites. The MOE of the CNF- and MFC-filled composites are higher than that of MCC-filled composites at higher filler loading such as 8 and 10% (w/w). This may be because of the increased number of smaller particles and the greater surface area of individual cellulose nanofibril fibers or particles

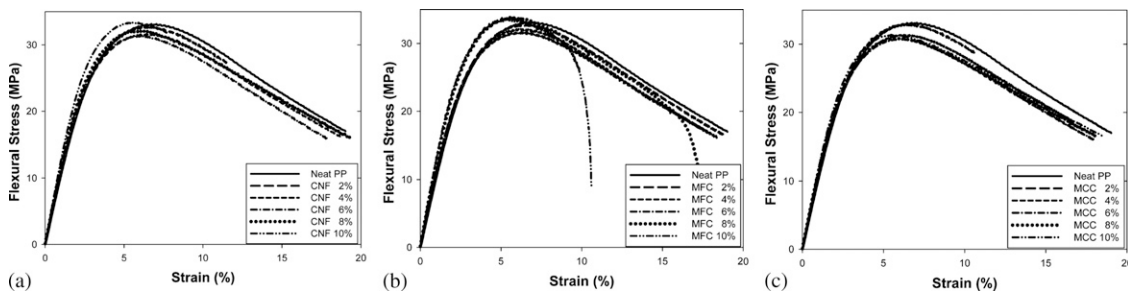


Figure 6. Flexural stress–strain curves of the composites at different filler loadings.

as mentioned in the tensile strength section. As the surface area is increased, the filler–matrix interface area also increased resulting in a decrease in mobility of the polymer macromolecules (Premalal et al 2002). The flexural MOE results were comparatively lower than the corresponding tensile modulus. These two loading conditions exhibited different kinds of stresses in the samples being tested. Whereas the stresses in a tensile test are uniform throughout the sample cross-section, the stresses in flexural tests

vary from zero in the middle to maximum in the top and bottom surfaces (Folkes 1985). The simple tension and flexural MOE measurements can hence differ significantly when the material is heterogeneous and anisotropic. A flexural test is highly influenced by the properties of the sample closest to the top and bottom surfaces, whereas a simple tension test reflects the average property through the thickness (Folkes 1985). Figure 9 exhibits flexural strains at yield of the composites. The strain at yield values continuously decreased as filler loading increases which is the same trend as tensile elongation at yield results.

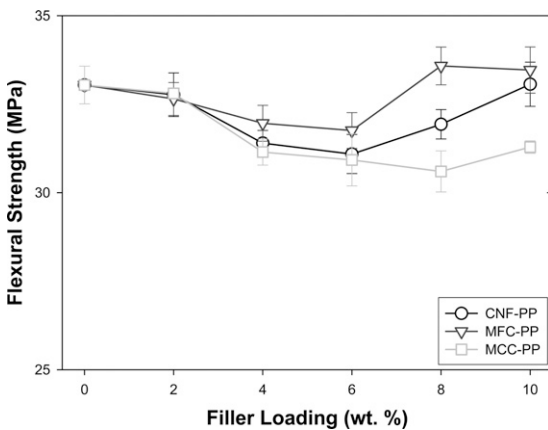


Figure 7. Flexural strength of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

Overall, the MFC showed the best of the three cellulose fillers studied; CNF is the second best in terms of mechanical performance of the cellulose filler–PP systems because MFC is in the form of longer fiber than CNF and MCC is in the form of particle. In the case of the tension test, the whole composite volume is critically loaded, sensitive to the properties of fiber reinforcement and yielding a higher stress until failure occurs. In the case of flexural testing, the outer fibers at the midspan of the beam are loaded up to their maximum stress and also sensitive to the properties of fiber reinforcement (Rijsdijk et al 1993). The longer fiber maintains better mechanical strength and modulus in both cases.

Table 2. Significance in flexural strength results by Tukey-Kramer test.^a

Sample ID	Mean strength (MPa)	Standard deviation				
Neat PP	A	33.04	0.53			
CNF 2%	A	B	C	32.77	0.62	
CNF 4%			D	E	31.40	0.36
CNF 6%			D	E	31.09	0.55
CNF 8%		B	C	D	31.93	0.42
CNF 10%	A				33.06	0.62
MFC 2%	A	B	C		32.65	0.46
MFC 4%		B	C	D	31.96	0.51
MFC 6%			C	D	31.76	0.51
MFC 8%	A				33.58	0.53
MFC 10%	A				33.46	0.65
MCC 2%	A	B			32.80	0.13
MCC 4%			D	E	31.15	0.37
MCC 6%			D	E	30.96	0.73
MCC 8%				E	30.60	0.58
MCC 10%			D	E	31.29	0.18

^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.

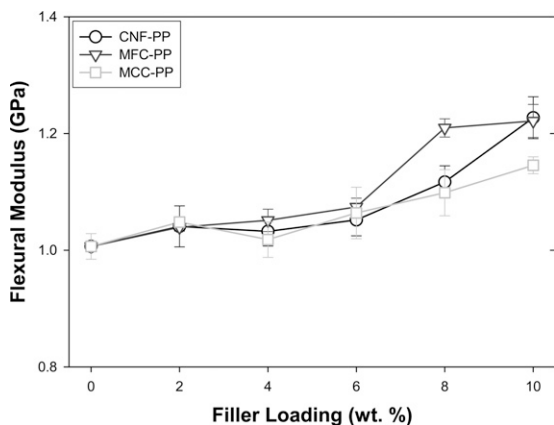


Figure 8. Flexural moduli of elasticity of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

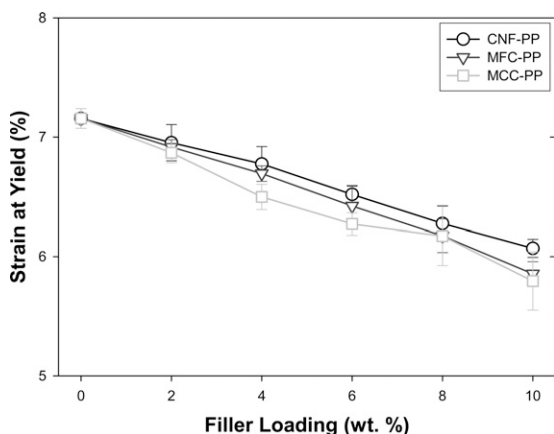


Figure 9. Flexural strains at yield of the cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC)-filled polypropylene (PP) composites.

CNF and MFC have great potential for use as reinforcing fillers for thermoplastic polymers to enhance mechanical performance. Another important point to note is the lower cost of cellulose nanofibril filled bio-based composites compared with the cost of inorganic-filled systems. This can result in significant material cost savings as agricultural and forest-based materials are cheaper than the pure polymer and far less expensive than inorganic fillers (glass fibers, graphites, clays, zeolites, etc.).

Environmental and energy savings realized by using a natural material instead of the high energy-utilizing glass fibers or mined inorganic fillers are benefits that cannot be ignored, although a thorough study needs to be conducted to evaluate these benefits (Sanadi et al 1995). However, as far as material costs are concerned, cellulose nanofibrils can be regarded as comparable to an inorganic material as a filler and the less expensive material cost may enhance the acceptability of cellulose nanofibrils as fillers in thermoplastic composites (Premalal et al 2002).

CONCLUSIONS

In the case of cellulose nanofibrils (CNF and MFC), the composites sustained considerable tensile and flexural strength up to 10% (w/w) filler loading. Tensile and flexural MOE increased continuously as filler loading increased for all cellulose fillers. The mechanical strength of the cellulose nanofibril-filled composites reduced slightly up to 6% (w/w) filler loading but this trend was ameliorated beyond 6% (w/w) because of the increased amount of separated individual nanoscale fillers. Four percent (w/w) seems to be best recommended filler amount for the future study about the compatibilizing agent because the composites still sustained considerable strength with less agglomeration. Cellulose nanofibril fillers are better than microcrystalline cellulose in terms of mechanical performance. CNF and MFC have great potential for use as reinforcing fillers for thermoplastic polymers in terms of mechanical performance. Therefore, cellulose nanofibrils can be regarded as comparable to inorganic material as fillers for thermoplastic polymers.

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