Effect of Environmental Conditions on the Mechanical Properties and Fungal Degradation of Polycaprolactone/ Microcrystalline Cellulose/Wood Flour Composites

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Polycaprolactone (PCL) filled with microcrystalline cellulose (MCC), wood flour (WF), or both were characterized before and after exposure to various environmental conditions for 60 days. PCL/WF composites had the greatest tensile strength and modulus compared to neat PCL or PCL composites containing MCC. Electron microscopy indicated better adhesion between WF particles and PCL than between MCC particles and PCL. Neither wood flour nor MCC cellulose appeared to significantly affect the crystallinity of PCL. Environmental conditioning resulted in only minor deterioration of mechanical properties, although samples soaked in water had greater deterioration of mechanical properties than those in high humidity or freezing environments. After a modified 12-week soil block test, specimens made with wood flour lost weight and showed signs of decay after exposure to the brown-rot fungus *Gloeophyllum trabeum*.

Keywords: Thermoplastic resin; Polycaprolactone; Wood flour; Microcrystalline cellulose; Composite; Environmental degradation; Mechanical properties

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INTRODUCTION

Biodegradable plastics have received growing attention in the last couple of decades because of increasing concern over plastic waste (Chandra and Rustgi 1998; Lee and Ohkita 2003; di Franco *et al.* 2004; Mathew *et al.* 2005; Zhao *et al.* 2008). Extensive research and product development has been done to reinforce polyolefins and other non-biodegradable plastics, but research on reinforcing biodegradable polymers is limited. The application of biodegradable polymers has primarily focused on the medical, agricultural, and consumer packaging industries (Chandra and Rustgi 1998). Challenges remain, however, with respect to the development of biodegradable polymer composites that can compete with synthetic and non-biodegradable plastics (Chandra and Rustgi 1998).

Polycaprolactone (PCL) is a synthetic, polyester-based biodegradable polymer with a melting point near 60 °C; it has been studied as a biodegradable plastic and biocomposite (Goldberg 1995; di Franco *et al.* 2004; Pandey *et al.* 2005; Balmayor *et al.* 2009). PCL is often blended with other polymers to improve the properties of plastic products (Jacob *et al.* 1998; Sarazin *et al.* 2008; Perstorp 2011). Improvements claimed by one manufacturer include low-temperature flexibility, excellent tear strength, hydrolytic stability, and faster crystallization rates (Perstorp 2011). The incorporation of natural fibers into PCL has been shown to enhance the biodegradability of the resulting composites (di Franco *et al.* 2004; Zhao *et al.* 2008). However, the biodegradability of

the resulting product is limited if all polymers are not biodegradable (Tilstra and Johnsonbaugh 1993; Goldberg 1995; Chiellini *et al.* 1996). Therefore, composites in which all or nearly all components are biodegradable are desirable.

Research has also shown that natural fibers, as well as other biobased materials, can be combined with biodegradable materials to make composites with enhanced properties and lower material costs (Averous *et al.* 2000; Nitz *et al.* 2001; Lee and Ohkita 2003; di Franco *et al.* 2004; Mathew *et al.* 2005; Zhao *et al.* 2008). Some of the biodegradable materials added to PCL include starch (di Franco *et al.* 2004; Averous *et al.* 2000; Matzinos *et al.* 2002), rice husk (Zhao *et al.* 2008), cellulose derivatives (Rosa *et al.* 2007), lignin (Nitz *et al.* 2001), wood flour (Nitz *et al.* 2001; Lee and Ohkita 2003), and nanocellulose (Habibi *et al.* 2008; Siqueira *et al.* 2009). Previous work has also shown that cellulose can be chemically coupled to polycaprolactone (Lönnberg *et al.* 2006; Krouit *et al.* 2008; Lönnberg *et al.* 2008). Although natural fibers are known to enhance biodegradability and mechanical properties of polycaprolactone, more work is needed to understand and develop viable biodegradable composites for widespread use.

The present research is focused on evaluating the influence of aging in different environments on the mechanical performance of polycaprolactone and lignocellulosic biocomposites. This study is also expected to provide the groundwork for understanding the mechanical properties and fungal biodegradability of natural fiber-reinforced polycaprolactone composites.

EXPERIMENTAL

Materials

Poly(ε-caprolactone) used in this study was CAPA 6500, a commercial product of Perstop Polyols, Inc. (Toledo, OH, USA). The melt flow index (MFI) of polycaprolactone at 160 °C using a 2.16 kg load was about 6.6 g/10 min. The weight average molecular weight (M_w) of the PCL was about 50,000 g/mol. Microcrystalline cellulose (FD100) was purchased from FMC BioPolymer (Philadelphia, PA, USA), and the average diameter was reported to be about 15 microns. The wood flour was a nominal 40-mesh ponderosa pine (AWF 4020) and was obtained from American Wood Fibers (Schofield, WI, USA).

Extrusion

Compounding for this work was carried out in a co-rotating twin-screw extruder (Davis Standard, LLC, Pawcatuck, CT, USA) with a 32 mm screw diameter. The barrel had a length/diameter ratio of 32:1 and seven zones with independent temperature control. The moisture content of the wood flour and microcrystalline cellulose after overnight drying at 105 °C was below 1.0 wt%. The screw speed was fixed at 50 rpm for all formulations. PCL/MCC blends were compounded using the following temperature profile: 70/74/74/77/77/80/80 °C from the barrel section just after the feed throat to the die. For the compounding of PCL with WF (with or without MCC), the temperature profile was: 70/85/85/90/100/100/110 °C. The molten extrudate was cooled in a water trough and pelletized for injection molding. The polymer blend formulations are listed below in Table 1.

Table 1. Summary of Blends Used in this Study

Blend #	PCL (%)	MCC (%)	WF (%)
1.) 100/0/0	100	0	0
2.) 90/10/0	90	10	0
3.) 80/20/0	80	20	0
4.) 70/30/0	70	30	0
5.) 60/40/0	60	40	0
6.) 60/0/40	60	0	40
7.) 60/10/30	60	10	30
8.) 60/20/20	60	20	20

Injection Molding

The compounded composite blends were dried for 72 h at 40 °C to a moisture content below 0.3 wt%. PCL/MCC and/or WF pellets obtained by extrusion processing were then molded into ASTM D638 (ASTM 2000) type I dog-bone specimens and ASTM D256 (ASTM 2006) impact specimens using a 33 ton Cincinnati Milacron (Batavia, OH, USA) reciprocating screw injection molder. The experimental molding conditions included melt temperatures of 110 to 177 °C, a peak injection pressure set to 16 MPa, and a mold temperature of 15 °C.

Conditioning

Specimens were placed in one of three different environments for 60 days: 1) water submersion at 21 °C, 2) a temperature of 27 °C and a relative humidity of approximately 90%, and 3) a temperature of -18 °C. Of these, half were tested for mechanical properties after 30 days. The remaining specimens were tested after 60 days.

Mechanical Properties

Conditioned specimens were dried for 72 h at 40 °C before testing to attain the same conditioning for specimens before and after aging. Tensile tests were carried out according to ASTM D638 (ASTM 2000) on a MTS 810 material test system (MTS Systems Corporation, Eden Prairie, MN, USA). The crosshead speed was 5 mm/min. Notched and unnotched Izod impact resistance tests were determined according to ASTM D256 (ASTM 2006) on an impact tester (Baldwin-Southwark Corporation, Philadelphia, PA, USA). Five replicate specimens were tested for each formulation.

Water Absorption

Five specimens from each blend formulation were dried in an oven for 72 h at 40 °C, and weighed to the nearest 0.001 g. These samples were immersed in deionized water at room temperature. Samples were then removed at specific intervals, wiped with paper tissue to remove the excess surface water, and weighed. Samples were dried and weighed at the end of the test.

Thermal Analysis

The Perkin–Elmer DSC 7 differential scanning calorimeter (Perkin-Elmer, Norwalk, CT, USA) was calibrated using indium. Samples of approximately 10 mg were sealed in aluminum pans. All measurements were conducted under nitrogen (20 mL/min) at a heating or cooling rate of 10 °C/min. Two heating cycles were used for each sample. The material was initially heated to 120 °C and held at 120 °C for 10 min to eliminate the

thermal history of the sample. The sample was then cooled to 20 °C and rescanned until it reached 120 °C. An empty pan followed the same process to obtain the baseline. The thermal effects shown refer to the second heating. The heat of fusion was determined by integrating the heating curves between 30 °C and 62 °C and dividing by the amount of PCL in the composite. The PCL crystallinity was determined by dividing the heat of fusion for each sample by the heat of fusion for 100% crystalline PCL, which was taken to be 157 J/g (Homminga *et al.* 2006).

Soil Block Test

Blends 1, 5, 6, and 8, as well as solid wood pine and sweet gum controls, were evaluated for fungal durability. The initial oven-dried weight was determined by drying for 48 h at 40 °C in a forced-draft oven, cooling in a desiccator for 1 h, and then weighing each specimen. Specimens were preconditioned by soaking in water for 2 weeks. They were then weighed and the moisture content was calculated. At the end of precon-ditioning, five specimens of each blend were air-dried for 24 h, oven-dried for 48 h in a forced-draft oven at 40 °C, cooled for 1 h in a desiccator, and then weighed. Percentage weight loss due to leaching during the water soaking was calculated.

A modified soil block test procedure based on ASTM D 1413 (ASTM 2007) was used to evaluate fungal durability. Five replicates of each blend were sterilized with propylene oxide and then placed in a soil bottle under one of three fungal exposure conditions:

1. No fungus (NF)
2. *G. trabeum*, a brown-rot fungus (BR)
3. *C. versicolor*, a white-rot fungus (WR)

After 12 weeks exposure, the specimens were removed, wiped to remove fungal mycelium if present, weighed, oven-dried for 48 h at 40 °C in a forced-draft oven, cooled in a desiccator for 1 h, and weighed again. Weight loss and moisture content were calculated.

Scanning Electron Microscopy

Specimen surfaces, fracture surfaces, and microtomed cross-sections of notched impact specimens were examined using a Zeiss EVO 40 scanning electron microscope (SEM) (Carl Zeiss SMT, Inc., Thornwood, NY, USA). Specimens were mounted on stubs using carbon tape or silver paste and then sputter-coated with a thin layer of gold using a Denton Desk-1 sputter coater (Denton Vacuum, LLC, Cherry Hill, NJ, USA) to provide adequate conductivity. SEM images were taken at ultrahigh vacuum.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the tensile strength for the samples tested before and after 60 days of environmental conditioning in the three previously described environments. The tensile strength of polycaprolactone decreased with the addition of microcrystalline cellulose from 16.8 MPa for the pure polycaprolactone to 10.5 MPa for the blend with 40 wt% microcrystalline cellulose (a 37.5% decrease). This strength decrease may be attributed to poor bonding of the microcrystalline cellulose to PCL as well as the low aspect ratio of the MCC particles, which are unfavorable for reinforcement. The addition

of 40% wood flour to PCL resulted in a modest strength increase of about 11%, but the substitution of MCC for WF resulted in a decrease in tensile strength of the composite. The lack of reinforcement from microcrystalline cellulose was probably due to poor adhesion, as no coupling agent was used.

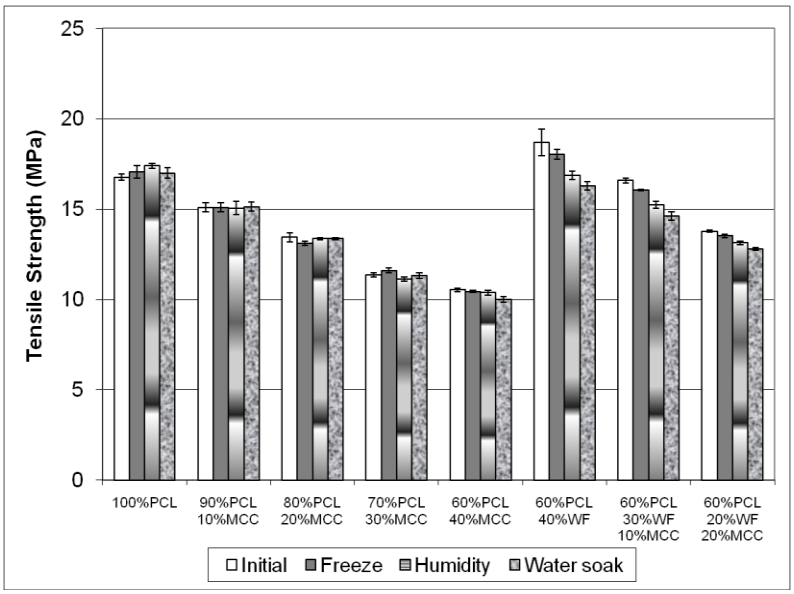

Fig. 1. The effect of environmental conditioning for 60 days on tensile strength; error bars represent standard error of the mean

The tensile strength of PCL/MCC blends after 60 days of aging did not significantly change from the initial value, whereas the value of PCL blended with 40 wt% WF decreased slightly when it was soaked in water. An analysis of variance (ANOVA) and pairwise Tukey test (Larsen and Marx 1986) revealed that, at a 0.05 level of significance, the tensile strength of samples conditioned in the freezer was not significantly different from the initial samples, whereas the tensile value of the water-soaked wood flour composites was significantly reduced. The pairwise analysis also showed that high humidity conditioning resulted in a significant decrease in all composites with wood flour, except the one with 40% WF. The tensile strength data for the initial 60/40 PCL/WF samples had unusually high variability, leading to a wider confidence interval than the other samples containing wood flour.

Figure 2 shows the tensile modulus for each of the blends before and after 60 days of environmental conditioning. Water-soaked PCL/MCC samples containing 30% or more MCC had significantly decreased moduli after 60 days according to a pairwise Tukey test at a 0.05 level of significance. Both high humidity-conditioned and water-soaked composites containing 30% or more WF had decreased moduli after 60 days. In general, moisture appeared to have a significant effect on tensile modulus for PCL composites containing large amounts of cellulose or wood flour.

Figures 3 and 4 show impact energies for notched and unnotched samples, respectively, for each of the blends before and after 60 days of conditioning in the three previously described environments. Addition of microcrystalline cellulose and/or wood significantly reduced the impact resistance of the specimens. However, exposure to moisture through both high humidity conditioning and water soaking resulted in increased impact resistance for the PCL/MCC composites containing 30% or more MCC.

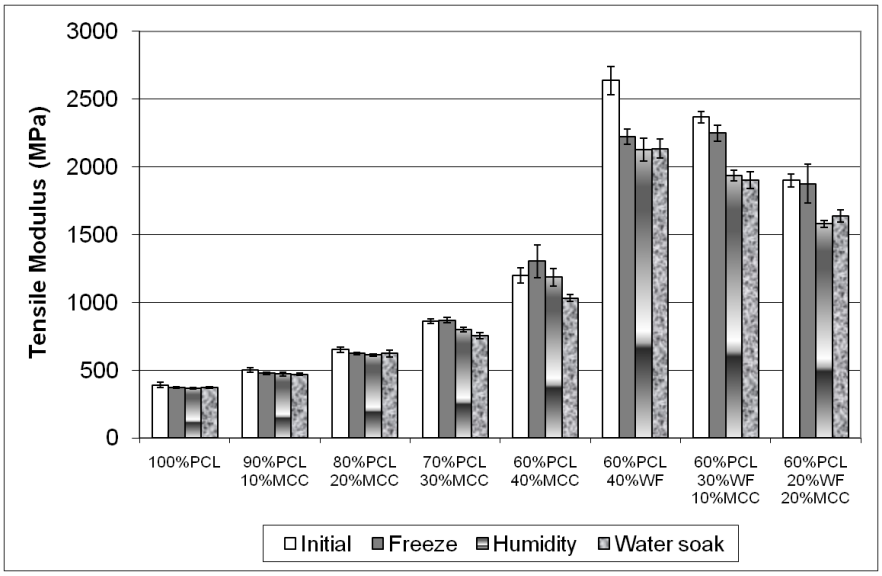

Fig. 2. The effect of environmental conditioning for 60 days on tensile modulus; error bars represent standard error of the mean

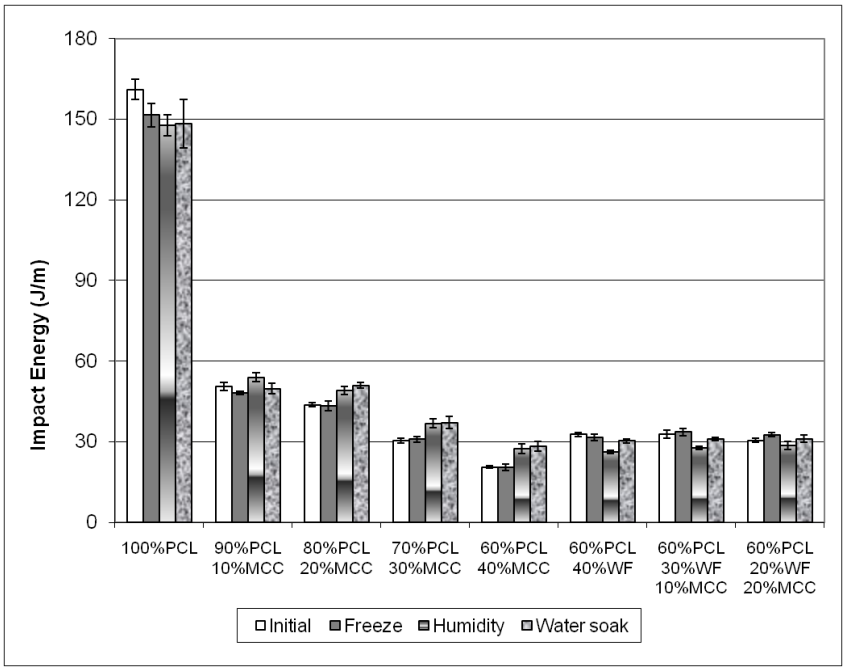

Fig. 3. The effect of environmental conditioning for 60 days on notched impact resistance; error bars represent standard error of the mean

Moisture treatments resulted in increased notched impact resistance for the PCL/MCC composites containing as little as 20% MCC. Similar results of impact strength in the presence of moisture were previously reported (Sombatsompop and Chaochanchaikul 2004). Water may create a plasticizing effect in these composites, but it is unclear why those containing WF did not exhibit similar behavior. Because the evaluation of mechanical properties after environmental conditioning is not common, it is difficult to compare such results to previous work. Overall, the conditioning did not have a negative effect on impact resistance of the composites in this study.

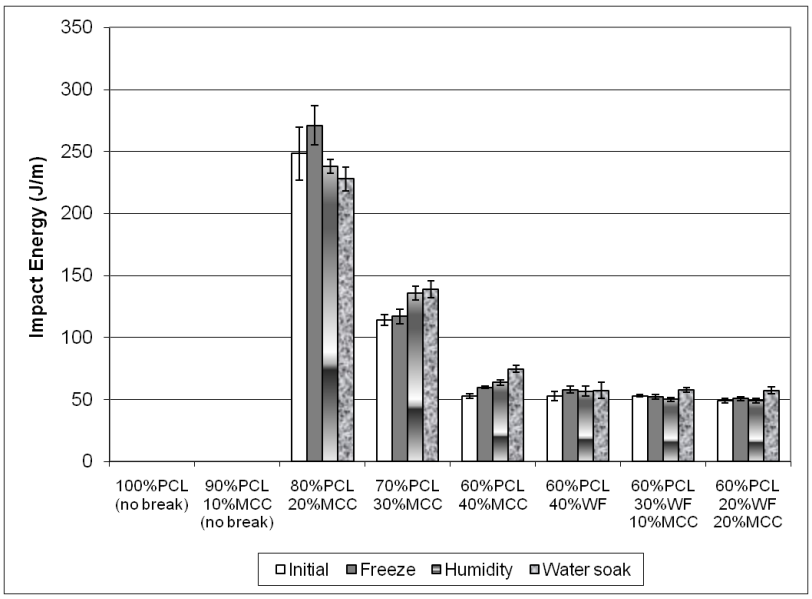

Fig. 4. The effect of environmental conditioning for 60 days on unnotched impact resistance; error bars represent standard error of the mean

Samples conditioned for 30 days typically showed less change in mechanical properties than those conditioned for 60 days. Therefore, any changes in mechanical properties appear to be gradual. However, the mechanical property data after 30 days are not shown because they do not significantly contribute to the analysis in this work.

Water Absorption

The weight gain of samples soaked in a water bath is shown in Fig. 5. The four formulations monitored for water absorption were pure PCL, 60/40 (PCL/MCC), 60/40 (PCL/WF), and 60/20/20 (PCL/MCC/WF).

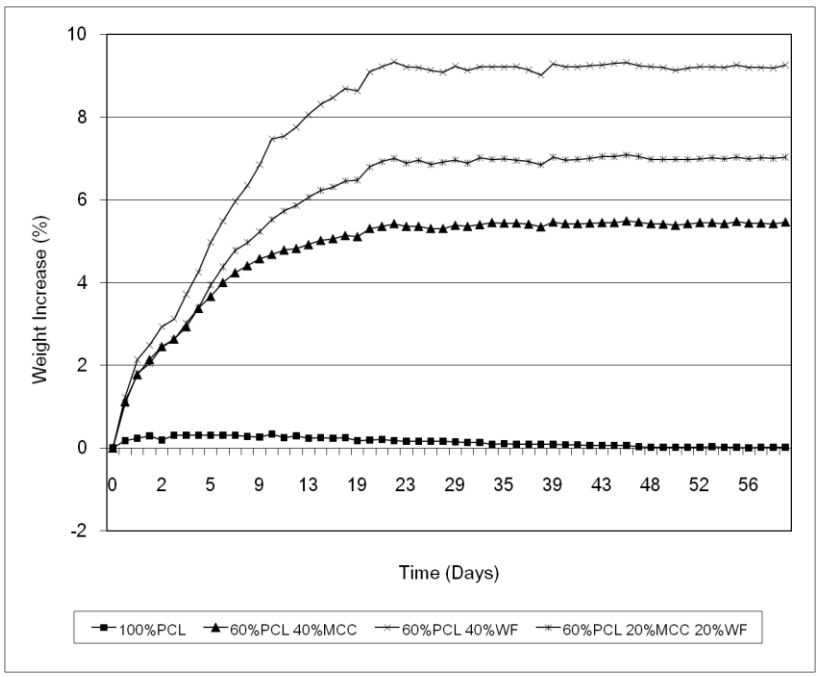

Fig. 5. The weight gain of composites in a water soak test

The composites with wood flour showed the largest moisture absorption, with the 40% WF composite gaining more than 9% of its original weight, nearly twice the weight gain of the 40% MCC composite. The moisture content of pure PCL reached a peak value in three days, but gradually lost weight and fell to its initial weight after 45 days. The lack of moisture gain of the PCL was attributed to its hydrophobicity, but the initial weight increase followed by a decrease was unexpected. It is possible that slight degradation of the polymer occurred, but no significant degradation in mechanical properties was observed.

Crystallization Behavior

Figure 6 displays the second heating scans from the DSC tests. All samples exhibited only one endothermic peak, which corresponded to the melting behavior of the crystalline PCL phase. The incorporation of MCC or WF did not significantly influence the arrangement of PCL chains. The enthalpies of fusion, represented by the area of the melting peak (Hatakeyama *et al.* 2000), and crystallinity are shown in Table 2.

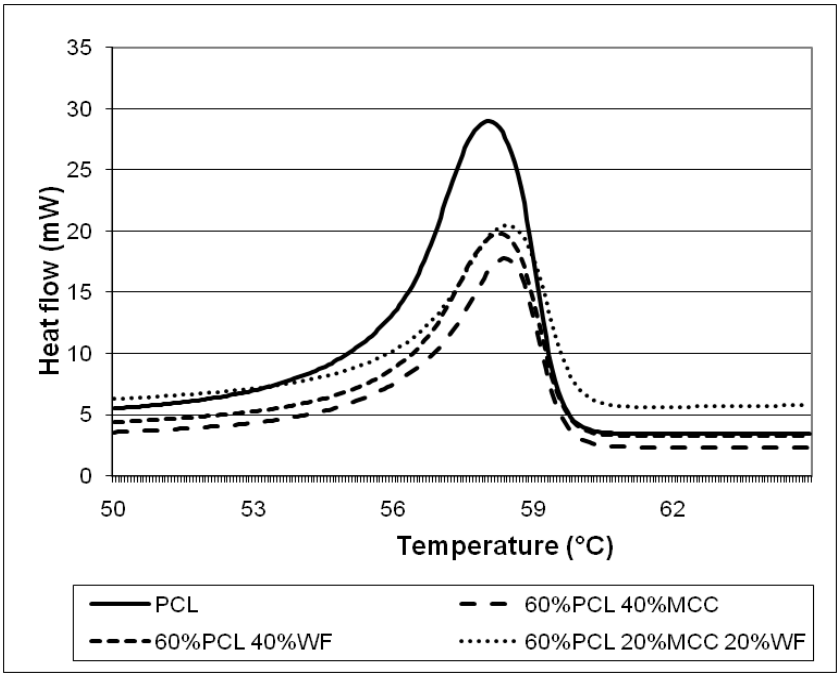

Fig. 6. DSC thermograms of composites

Table 2. Differential Scanning Calorimetry Results

Blend	Peak temperature (°C)	Heat of fusion (J/g)	Crystallinity (%)
100% PCL	58.0	59.5	37.9
60% PCL, 40% MCC	58.4	59.2	37.6
60% PCL, 40% WF	58.3	60.7	38.9
60% PCL, 20% MCC, 20% WF	58.5	60	38.2

Electron Microscopy

Based on electron micrographs (Fig. 7 and 8), wood flour appears to have had greater adhesion to the PCL matrix than did the microcrystalline cellulose. In Fig. 7a, several wood fibers can be seen coated with or adhered to the PCL matrix. Figure 7b

shows the strong interaction between PCL and wood fibers at a higher magnification. By contrast, MCC particles are seen in Fig. 8 to have poor adhesion to the PCL matrix. Here, gaps can be readily seen between distinct MCC particles and the polymer matrix. The greater adhesion between PCL and WF compared to PCL and MCC explains why the tensile strength of PCL/WF composites was much greater than that of the PCL/MCC composites.

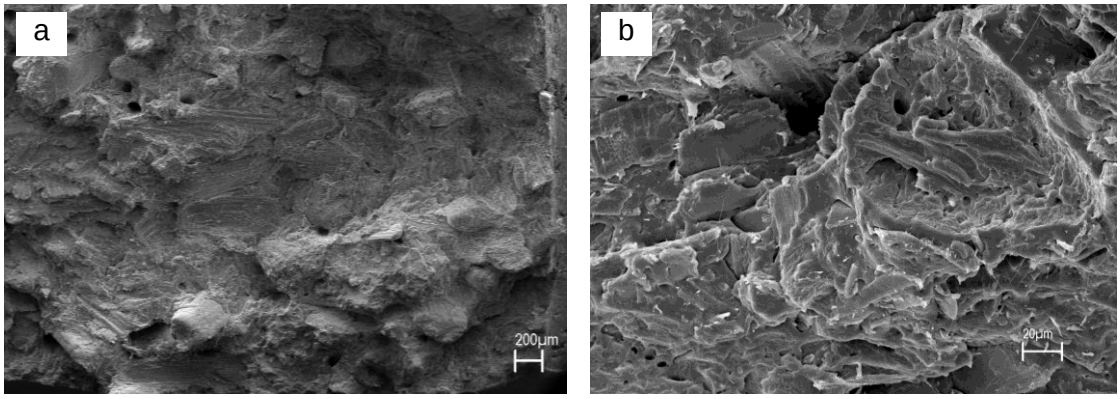

Fig. 7. Scanning electron micrographs of PCL/WF composite (blend 60/0/40)

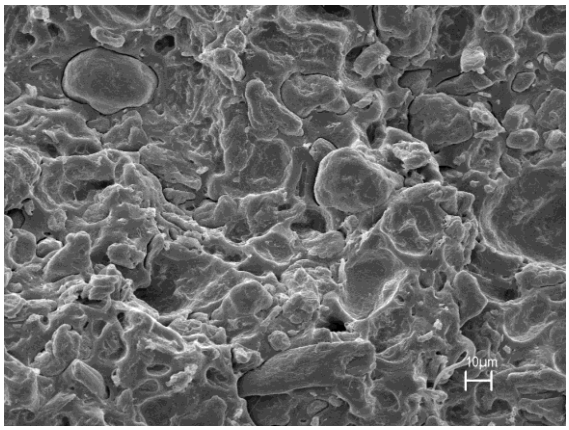

Fig. 8. Scanning electron micrograph of PCL/MCC composite (blend 60/40/0)

Fungal Durability

Table 3 presents the average moisture content of the specimens before and after the soil block test, along with the weight loss after decay testing and the weight loss after water leaching for 2 weeks. Overall weight losses from decay were low, which was expected due to the fact that the specimens were injection molded (Clemons and Ibach 2004). Injection-molded WPCs absorbed the least amount of moisture, followed by compression-molded WPCs. The most moisture sorption was found with extruded WPCs.

For wood to decay, the moisture content needs to be greater than the fiber saturation point (>25%). The moisture contents from water-soaked specimens indicated that there was sufficient moisture present in the specimens with 40% wood flour for decay to occur (15.99 ± 2.30% MC). The moisture content of WPCs was nearly all in the wood component, and therefore exceeded the critical value for decay. The other blends had less moisture at the beginning of the test, but after the soil block test, the moisture contents showed the same trend, except that the overall levels were lower.

Table 3. Results of Fungal Evaluations

Blend	Exposure	Before SBT MC (%)	After SBT MC (%)	After SBT Wt. Loss (%)	Water Leaching Wt. Loss (%)
100% PCL	Water soaking	**5.64** 1.43			**0.11** 0.04
100% PCL	No Fungus		**0.50** 0.20	**0.19** 0.04	
100% PCL	BR Fungus		**0.03** 0.04	**0.46** 0.05	
100% PCL	WR Fungus		**0.19** 0.12	**0.25** 0.08	
60% PCL, 40% MCC	Water soaking	**8.81** 0.80			**-0.66** 0.05
60% PCL, 40% MCC	No Fungus		**5.64** 0.11	**-0.42** 0.09	
60% PCL, 40% MCC	BR Fungus		**5.51** 0.17	**0.13** 0.17	
60% PCL, 40% MCC	WR Fungus		**5.61** 0.21	**-0.26** 0.19	
60% PCL, 40% WF	Water soaking	**15.99** 2.30			**-1.20** 0.15
60% PCL, 40% WF	No Fungus		**9.37** 0.31	**-0.01** 0.09	
60% PCL, 40% WF	BR Fungus		**8.80** 0.33	**1.98** 0.32	
60% PCL, 40% WF	WR Fungus		**9.40** 0.18	**-0.23** 0.11	
60% PCL, 20% MCC, 20% WF	Water soaking	**12.98** 0.74			**-1.07** 0.03
60% PCL, 20% MCC, 20% WF	No Fungus		**7.43** 0.07	**-0.62** 0.11	
60% PCL, 20% MCC, 20% WF	BR Fungus		**6.87** 0.10	**1.26** 0.13	
60% PCL, 20% MCC, 20% WF	WR Fungus		**7.55** 0.07	**-0.09** 0.14	
Pine solid wood	BR Fungus			**47.14** 4.37	
Gum solid wood	WR Fungus			**42.86** 1.60	

MC=Moisture content; SBT=soil block test; BR=brown-rot fungus; WR=white-rot fungus
(Numbers in **bold** are averages; unbolded numbers are standard deviations)

As a biopolymer, 100% PCL had some weight loss with both a brown-rot (0.46 ± 0.05) and a white-rot (0.25 ± 0.08) fungi, but adding wood pine wood flour enhanced the brown-rot degradation. There was little to no weight loss from decay in the case of the 60% PCL/40% MCC blend. However, two blends with wood flour had weight losses after brown-rot fungus exposure (*i.e.*, 60% PCL/20% MCC/20% WF (1.26 ± 0.13% weight loss) and 60% PCL/40% WF (1.98 ± 0.32% weight loss)). Although these are small weight losses, they show that decay is possible under these conditions. Examination of these specimens under SEM shows deterioration and loss of the wood flour on the surface of the specimens (Fig. 9a and 10a), and decay of the wood flour by the presence

of fungal hyphae in the cross-sections (Fig. 9b and 10b). These findings are similar to previous research with WPCs made with wood flour and either the polymer high density polyethylene (HDPE) or the biobased plastic, polylactate (PLA), instead of PCL (Ibach and Clemons 2007; Ibach *et al.* 2004; Segerholm *et al.* 2012a and 2012b).

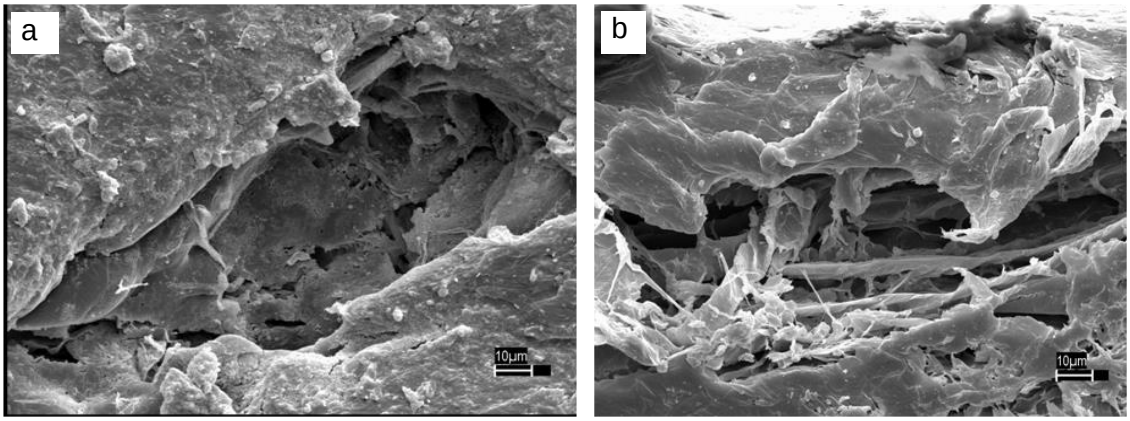

Fig. 9. Scanning electron micrographs showing decay from *G. trabeum* of PCL/WF composite (blend 60/0/40) of the a) surface and b) cross-section

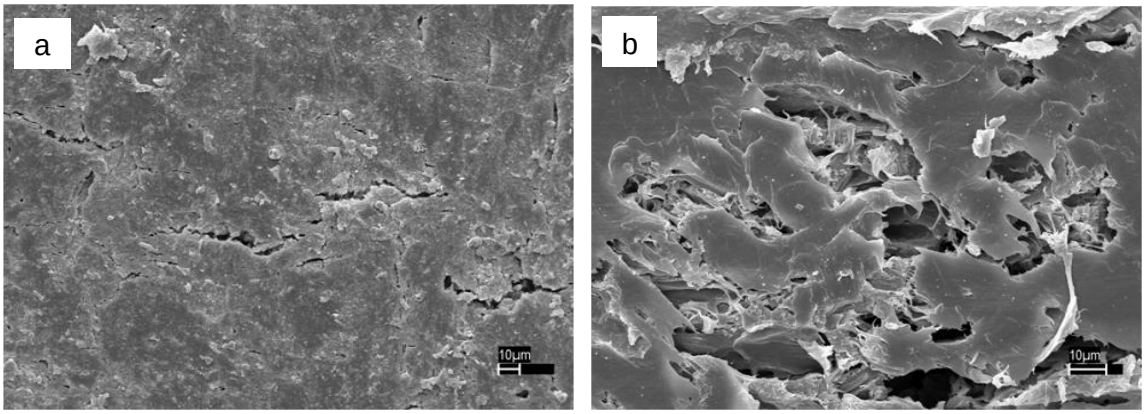

Fig. 10. Scanning electron micrographs showing decay from *G. trabeum* of PCL/MCC/WF composite (blend 60/20/20) of the a) surface and b) cross-section

There were no weight losses from the white-rot fungus *C. versicolor* with the blends containing wood flour. This was expected because the wood flour used was from a softwood species (ponderosa pine), and white-rot fungi prefer hardwoods. Both the solid wood pine (47% wt. loss) and sweet gum (43% wt. loss) had high weight losses, indicating the viability of the test fungi.

Wood is normally oven dried at 105 °C, but, because of PCL's low melting point (58 °C), the composites had to be dried at 40 °C. However, weight losses were followed by weight gains after water leaching for all except the 100% PCL, indicating that the wood must not have been completely dried at 40 °C.

CONCLUSIONS

1. In the absence of coupling agents or modifiers, wood flour generally performed better than microcrystalline cellulose as reinforcement for polycaprolactone. Blending of microcrystalline cellulose with polycaprolactone increased the tensile modulus, but decreased the tensile strength of the composites.
2. Compared to pure PCL and all other formulations, the composite with 40 wt% WF had improved tensile strength and modulus. The modulus of 60/40 PCL/WF composite was about six times that of pure PCL. As expected, the addition of WF, MCC, or both to PCL also resulted in reduced impact resistance compared to pure PCL.
3. Despite being comprised of biodegradable polymers and fillers, PCL-MCC-WF composites did not experience extensive deterioration of mechanical properties after being conditioned at high humidity, frozen, or soaked in water for 60 days.
4. Neat PCL showed minimal weight loss after exposure to either a brown-rot or a white-rot fungus, The addition of pine wood flour to PCL increased the biological decay (>1% weight loss) by the brown-rot fungus *Gloeophyllum trabeum*.

ACKNOWLEDGMENTS

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