Comparison of polyolefin biocomposites prepared with waste cardboard, microcrystalline cellulose, and cellulose nanocrystals via solid-state shear pulverization

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ABSTRACT

As a significant part of municipal solid waste (MSW), waste cardboard (CB) is a sustainable, inexpensive, and rich source of cellulose. Previous studies of polyolefin/CB composites have reported modest enhancement to major reduction in modulus and major reduction in elongation at break values relative to neat polymer. Here, green hybrids of low density polyethylene (LDPE) and polypropylene (PP) with 5–25 wt% CB are made by solid-state shear pulverization (SSSP), which achieves both size reduction of 2–3 cm sized CB pieces to the micron level and dispersion in polymer. The properties obtained with CB incorporation in LDPE and PP are compared and contrasted with those obtained with incorporation of microcrystalline cellulose (MCC) and cellulose nanocrystal (CNC). Polyolefin composites with CB made by SSSP exhibit major enhancement in Young’s modulus (63% and 71% increases for 10 wt% CB in LDPE and 15 wt% CB in PP, respectively). The PP/CB composites exhibit a broad range of property enhancements relative to neat PP, including a nearly 50% nucleating efficiency, as much as an 8% increase in PP crystallinity, and a factor of ~3 decrease in crystallization half-time. Well-dispersed CB particles improve LDPE and PP thermo-oxidative stability as shown by thermogravimetric analysis (~5–20 °C increase in 20% mass loss temperature in air with 15–20 wt% CB addition) and isothermal shear flow rheology. Similarly, post-SSSP high-temperature, long-time melt mixing results in no apparent degradation of LDPE/CB and MCC composites whereas LDPE/CNC composites show major degradation. When incorporated into polyolefin composites, low cost, cellulose-rich MSW can often produce reinforcement similar to glass fibers and thus has potential as filler for structural composite applications.

1. Introduction

The last two decades has witnessed rising interest in using nanofillers for the preparation of polymer nanocomposites [1–12]. Such nanoscopic fillers have the potential to improve material properties of the composite at much lower filler loadings (typically <10 wt%) when compared to microscopic or macroscopic fillers. Recent literature studies have thus focused on reducing filler size to the nanoscale, with the aim of achieving better property enhancements in composites [7–12]. Environmental concerns over depleting petrochemical resources have also prompted researchers to explore alternative, greener fillers [12–19]. Green polymer composites based on polyolefins that employ renewable sources as reinforcements offer sustainable ecological and structural benefits. Studies have thus investigated incorporating cellulose and lignocellulosic materials including wood flour, natural fibers, soy flour, rice husks and lignin into polymers as greener alternatives to synthetic fillers [20–30]. Green fillers offer benefits such as biodegradability, reduced reliance on fossil fuel-based raw materials, and reduced part weight, carbon footprint and wear to processing equipment [27–30]. Such advantages make biocomposites attractive for structural applications in the automotive industry, while adding value to waste materials obtained from agricultural and municipal sources [14–19].

In this regard, cellulose has good potential as a green reinforcing filler for polymers. It is the most abundant renewable material accounting for 50–90% of all plant matter [31]. Single cellulose nanocrystals (CNCs) possess excellent modulus with values of
and/or compatibilizer addition for the preparation of polyolefin composites incorporating cellulose fillers ranging from nanocellulose to macroscale cellulose-rich municipal solid waste (MSW) materials [32–58]. Corrugated cardboard (CB) and waste paper account for almost one-third of the total MSW generated in the United States [59]. Kraft pulping of wood employed for the production of cardboard results in the partial elimination of hemicellulose and lignin [58,60,61]. Corrugated cardboard is chemically made up of ~75% cellulose, ~15% lignin, and the rest being binders/adhesives such as starch and acrylamides [60,61]. The hemicellulotic part is primarily made up of mannose, galactose and xylose.

Despite advancements in recycling technologies, with increasing number of recycling operations the quality of cellulose fibers in CB decreases. As a result, almost 25 million tons of CB waste are discarded annually into landfills in the United States [59]. Lack of effective processing techniques results in extremely low valuation of ~$85/ton for paper scrap [62]; in contrast, the highly refined form of cellulose known as microcrystalline cellulose (MCC) that is used in the pharmaceutical industry is priced at ~$2500/ton [63]. Cardboard fibers are known to possess numerous attractive properties like high specific strength and high aspect ratio (~100) [44]. Similar to wood-based polymer composites, thermoplastic composites with waste CB are speculated to be useful in load-bearing applications, frames, car interiors, etc [44].

Despite their potential, the majority of studies producing such composites via melt processing have reported poor or mixed results. Yuan et al. [45] noted, “Because of the poor compatibility of polypropylene (PP) and paper flour, it is nearly impossible to prepare... PP/paper flour blends with good mechanical properties.” (The presence of hydroxyl groups on cellulose makes it inherently incompatible with the hydrophobic polyolefin matrices.) Thus, all literature reports attempting to produce such composites have utilized surface modification, particle size reduction, extraction and/or compatibilizer addition for the preparation of polyolefin/CB composites [42–58], Chibani et al. [46] reported no improvement in tensile modulus with incorporation of up to 28 wt% unmodified CB in PP composites prepared via melt processing. They further suggested the addition of maleated PP as a compatibilizer to improve material properties. Salma et al. [47] utilized intensive grinding to obtain waste paper particles that were an average of 31 μm in size. Incorporating 20 wt% of this filler in low density polyethylene (LDPE) resulted in a 125% increase in modulus but a 90% decrease in elongation at break compared to neat LDPE. Ashori and Nourbakhsh [56] incorporated 10–40 wt% of old corrugated cardboard fiber into PP by melt mixing; all composites exhibited tensile modulus values well below (as much as 50% below) that of neat PP. Drzal and coworkers incorporated recycled cellulose fiber (average 20 μm diameter) extracted from waste paper into PP via melt processing and observed a 64% increase in modulus for 30 wt% filler content [49–51]. The extra steps employed in these studies such as particle size reduction, extraction and compatibilization not only add to the time and cost of processing but also reduce the green aspect of the filler.

We previously reported on property enhancements achieved by incorporating CNC in polyolefins via solid-state shear pulverization (SSSP) [39]. For example, in 90/10 wt% LDPE/CNC composites made by SSSP, there was a 70% increase in tensile modulus and no reduction within error in elongation at break relative to neat LDPE [39]. The ambient conditions and solid-state nature of SSSP enabled high shear and compressive forces to be imparted to the materials, resulting in excellent CNC dispersion and strong suppression of filler degradation that accompanies high-temperature melt processing of cellulose-based fillers [39]. Past studies have shown the ability of SSSP to produce excellent dispersion of pristine fillers ranging from bundled carbon nanotubes and graphite to waste materials from natural sources [27–30,39,64–69]. Excellent dispersion of immiscible blends has also been achieved by SSSP [70–72]. Studies have also taken advantage of ambient conditions in SSSP to achieve functionalization and long-chain branching of PP without major molecular weight reduction [73–75].

Here, we compare the reinforcing ability of well-dispersed cellulose-rich CB waste to well-dispersed, synthetic sources of cellulose such as MCC and CNC in polyolefin composites. The CB is fed to the SSSP apparatus in several-centimeter-sized pieces with SSSP achieving both major particle size reduction and dispersion. For commercial viability of such composites as well as for sustainability considerations, it is important to compare low cost, cellulose-rich waste materials with much higher cost cellulose fillers. (At present, CNC production is at the pilot-plant scale rather than involving large-scale, commercial production.) We show that well-dispersed, cellulose-rich CB from MSW can often provide property enhancements similar to those achieved by highly refined, microcrystalline and nanocrystalline cellulose.

2. Experimental section

2.1. Materials

Two PP samples, PP1 (Total 3276) and PP2 (Total 3270) were used as received. As reported by the supplier (Total Petrochemicals), both samples had the same density (0.905 g/cm3) and melt flow index (MFI 2 g/10 min). Low density polyethylene (ExxonMobil LD 103) with density of 0.919 g/cm3 and MFI of 11.1 g/10 min (190 °C and 2.2 kg load) was supplied by ExxonMobil. Randomly chopped cardboard pieces (average size of ~2–3 cm) procured locally were used as-received without deinking. Microcrystalline cellulose (lattice NT with average particle size of ~50 μm and aspect ratio of ~1.4 as reported by the supplier) was supplied by FMC Biopolymers and used without modification. Unmodified cellulose nanocrystals were produced at the Forest Products Laboratory in Madison, WI as described in Ref. [76]. (Data related to polystyrene/CNC nanocrystals and used for comparative purposes are taken from Ref. [39].)

2.2. Preparation of polyolefin/cellulose composites

Polyolefin pellets were fed to a Berstorff ZE-25 pulverizer with a K-tron S-60 feeder at a ~100 g/h feed rate. (A commercial-scale apparatus has processed polyolefins at rates exceeding 150 kg/h [27,28].) The CB pieces (~2–3 cm) were fed to the pulverizer via the K-tron S-60 feeder whereas powdery MCC and CNC were added with a powder feeder (Brabender Technologies Inc. DDSR 12-1 volumetric feeder) at different feed rates to obtain desired filler content. The composites were produced using a 200 rpm screw speed and a screw design that yielded high specific energy (see Ref. [77] for a detailed description of screw design and energy inputs). The pulverizer barrels were cooled by a recirculating ethylene glycol/water mix (~7 °C, Budzar Industries WC-3 chiller). Other details and process conditions are available in Refs. [27–30,39].

2.3. Characterization of polyolefin/cellulose composites

Field-emission scanning electron microscopy (FE-SEM) samples were prepared by melting and extruding material obtained from SSSP with an Atlas Electronic Devices MiniMax molder (cup-and-rotor mixer). Morphologies of cryo-fractured sections were
obtained via an SU8030 instrument after sputtering with gold/palladium (Denton DeskIII). The FE-SEM images of as-received MCC were acquired after casting from water onto Si wafers. The morphologies of pristine CNC and polyolefin/CNC composites produced by SSSP have been reported [39].

Uniaxial tensile test samples of ~0.7 mm thickness were prepared by compression molding using a PHI (Model 0230C-X1) press at 180 °C or 140 °C depending on the matrix polymer for 5 min with 5 ton ram force. Dog-bone shaped specimens were cut using a Dewes-Gumbs die and tested using an MTS Sintech 25 tensile tester according to ASTM D1708 with a 5 kN load cell using a crosshead speed of 50 mm/min.

Polymer crystallization was characterized by differential scanning calorimetry (DSC; Mettler-Toledo 851e) under air. At least three samples were run to show reproducibility. (Neat PA11 molded discs (thickness 3.1 cm) were cooled in a desiccator, and immediately weighed (m).)

Water absorption measurements were performed on compression molded discs (thickness = ~0.125 inch and diameter = 2 inch) following ASTM D570. Specimens were dried at 80 °C for 24 h, cooled in a desiccator, and immediately weighed (w1). Specimens were then immersed in distilled water at ~23 °C. Samples were periodically removed, dried with absorbent paper, and weighed (w2). The percentage water absorption (WA) is calculated as follows:

\[
WA(\%) = \frac{(w2 - w1)}{w1} \times 100
\]

3. Results and discussion

3.1. Dispersion and morphology of polyolefin/cellulose composites

Fig. 1a shows ~2–3 cm sized CB pieces that were employed in the present study. The large shear and compressive forces imparted to the material during solid-state processing leads to major filler size reduction in the polymer composites. Fig. 1b and c shows SEM images of fractured surfaces of LDPE/CB and PP/CB composites with 10 wt% CB. The originally centimeter-sized CB pieces are reduced via a single-step SSSP process to particles in the range of 1–10 µm in size that are wetted into the polymer matrix. In addition, the fractured surfaces show no signs of pull-out, indicating the absence of major filler agglomeration. Fig. 1d shows SEM images of as-received MCC. Agglomerates of MCC can be as large as 100–200 µm due to the strong interparticle affinity arising from the numerous hydroxyl groups on the cellulose surface. Similar to polyolefin/CB composites, SEM images of LDPE/MCC and PP/MCC composites (Fig. 1e and f) show very good dispersion. The highly agglomerated MCC particles underwent major size reduction to particles no larger than 1 µm. In an earlier study, excellent filler dispersion was obtained in polyolefin/CNC composites made by SSSP [39].

Previous studies have reported challenges in achieving excellent dispersion of cellulosic fillers in polyolefinas via melt mixing. Chibani et al. [46] observed severe filler agglomeration, debonding and fiber pull-out, indicating poor adhesion between the CB fibers and PP matrix. In their study, 5 wt% PP grafted with maleic anhydride was used as compatibilizer to improve the interfacial adhesion which seemingly enhanced the filler dispersion. Gauster et al. [35] observed similar fiber pull-out and poor filler dispersion when MCC was incorporated in polyethylene by melt mixing. Wetting and dispersion similar to that achieved in our study were obtained only after the addition of maleated PP. In short, solid-state processes are able to achieve excellent filler dispersion and particle size reduction; this leads to the production of polyolefin/CB composites with morphologies similar to those observed by employing MCC or CNC fillers.

3.2. Mechanical properties of polyolefin/cellulose composites

3.2.1. Tensile properties of polyolefin/CB composites

Table 1 summarizes the effect of CB on the mechanical properties of LDPE/CB composites made by SSSP. Excellent dispersion and particle size reduction led to major improvements in Young’s modulus. For example, relative to neat LDPE, incorporation of 5 wt% CB results in a ~38% increase in modulus and 20 wt% CB results in a 190% increase. The yield strength of LDPE/CB composites shows a 22% increase relative to neat polymer for 5 wt% CB and values unchanged from that of neat LDPE at other CB loadings. These results compare well with those obtained by incorporating MCC and CNC into LDPE. The 63% increase in modulus seen with 90/10 wt% LDPE/CB is within error the same as that obtained with 90/10 wt% LDPE/MCC and LDPE/CNC (Fig. 2a and Table 1). Similarly, the 90/10 wt% LDPE/CB composites retain yield strength that is within error invariant from those of neat LDPE and the 90/10 wt% LDPE/MCC and only slightly lower than that of 90/10 wt% LDPE/CNC.

In addition, the excellent filler dispersion and particle size reduction achieved by SSSP processing led to unparalleled retention of elongation at break values in LDPE composites. As shown in Fig. 2b, 90/10 wt% LDPE/MCC and LDPE/CNC composites have elongation at break values that are within error unchanged from that of neat LDPE. Due to the slightly larger size scales of CB particles in the polymer matrix (yet less than 10 µm in size), the 95/5 and 90/10 wt% LDPE/CB composites exhibit reductions in elongation from 500% for neat LDPE to 390% and 280%, respectively. Notably, LDPE/CB composites produced by SSSP retain sufficient elongation at break to be viable for commercial applications at filler loadings as high as 20 wt%.

As shown in Table 2, relative to neat PP1 with a modulus of 910 MPa, PP1 composites with 5 and 25 wt% CB exhibit 24 and 92% increases in Young’s modulus, respectively. In addition, all PP1/CB
composites produced here show yield strength similar to neat PP1. Due to minor degradation of CB during compression molding, the 95/5 wt% PP1/CB composite retains an elongation at break of 40% while the 75/25 wt% PP1/CB composite has a value of 8%. Nonetheless, all composites exhibit ductile behavior except the 75/25 wt% PP1/CB composite with a barely ductile fracture. These results are comparable to those obtained with MCC and CNC composites; relative to neat PP2 with a 1200 MPa modulus, 90/10 wt% PP2/MCC and 90/10 wt% PP2/CNC composites show ~33% and ~53% increases in modulus, respectively.

3.2.2. Comparison with literature data for polyolefin/cellulose based composites

Few literature studies have investigated the fabrication of polyolefin/CB composites via melt mixing, all of which have employed particle size reduction steps prior to melt processing in order to achieve CB particles that are less than 50 μm in size [46,47]. Salmah et al. [47] utilized intensive grinding to produce, on average, 31-μm-sized waste paper particles, that were subsequently incorporated into LDPE via melt mixing. The LDPE composites with 23 wt% filler showed a ~100% increase in modulus relative to neat LDPE (modulus of 80 MPa). In contrast, the 80/20 wt% LDPE/CB composite produced via SSSP shows a 190% increase in modulus. The severe filler agglomeration and void formation during melt processing result in dramatically reduced elongation at break values in the composite. Salmah et al. [47] reported major reduction in elongation at break from 400% for neat LDPE to only 50% for composites with 9 wt% filler produced via melt processing. Dramatically superior performance is observed with an SSSP processed composite of similar filler content, showing a 260% elongation at break (neat LDPE has 500% elongation). Chibani et al. [46] incorporated up to 15 wt% CB fibers in PP via melt mixing and observed no improvement in tensile modulus. In comparison, in the present study, an 85/15 wt% PP/CB composite shows a ~71% increase in Young’s modulus relative to neat PP.

Poor outcomes have also been reported when synthetic cellulose fillers were incorporated in composites prepared via melt processing or solution mixing. Spoljaric et al. [36] produced a 90/10 wt% PP/MCC composite using ultrasonication in solution and reported a ~30% increase in modulus relative to neat PP. Our study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus E (MPa)</th>
<th>Yield strength σ (MPa)</th>
<th>Elongation at break ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat LDPE</td>
<td>160 ± 5</td>
<td>10.0 ± 0.3</td>
<td>500 ± 30</td>
</tr>
<tr>
<td>95/5 wt% LDPE/CB</td>
<td>220 ± 10</td>
<td>12.2 ± 1.0</td>
<td>390 ± 30</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CB</td>
<td>260 ± 20</td>
<td>10.7 ± 0.6</td>
<td>260 ± 15</td>
</tr>
<tr>
<td>80/20 wt% LDPE/CB</td>
<td>465 ± 35</td>
<td>10.1 ± 0.2</td>
<td>33 ± 10</td>
</tr>
<tr>
<td>90/10 wt% LDPE/MCC</td>
<td>260 ± 20</td>
<td>11.0 ± 0.1</td>
<td>485 ± 20</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CNC</td>
<td>270 ± 10</td>
<td>13.0 ± 1.0</td>
<td>460 ± 30</td>
</tr>
</tbody>
</table>

Note: Data for LDPE/CNC composites are from Ref. [39].
reports a similar 33% increase for the same MCC loading using the industrially scalable, solventless, continuous SSSP process. As shown in Ref. [39], polyolefin/CNC composites produced by SSSP have the highest reported enhancement in modulus relative to similar composites produced via melt or solution mixing in literature studies. Moreover, no study has produced PP/CNC composites using industrially scalable, melt processing techniques due to concerns with CNC thermal degradation. Alternatively, such composites can be manufactured by using ambient temperature, solid-state processes that are able to achieve very good dispersion. We further demonstrate here that effective agglomerate breakup and superior dispersion of macroscopic cellulose rich MSW achieved by SSSP give rise to property enhancements that are comparable to those seen with microscale or nanoscale cellulose. Well-dispersed cellulosic fillers thus provide excellent reinforcement to polyolefins, making the plastic stiffer and more durable.

3.3. Water uptake of polyolefin/cellulose based composites

Water absorption behavior is important in applications related to structural materials for outdoor use. The overall water absorption of a composite depends on moisture content of the filler, void fraction, quality of dispersion, permeability, filler hydrophilicity, etc [46]. Fig. 3 shows the percentage weight gain as a function of the square root of time with increasing filler content in composite samples (thickness = 0.125 inch and diameter = 2.0 inch, following ASTM D570). Neat LDPE and PP show no appreciable water absorption after 300 h immersion. Hence, water uptake in these composites is a result of filler incorporation.

Under the same conditions, LDPE composites show marginal water absorption. For example, after 24 h immersion, LDPE composites with 10 wt% CNC, MCC, and CB show 0.12, 0.15, and 0.19 wt% water gain, respectively; none of the composites reaches a constant, equilibrium sorption value after 300 h immersion. Similarly, after 24 h immersion, PP composites with 10 wt% CNC, MCC and 15 wt% CB show 0.09, 0.13, and 0.08 wt% water absorption; none of the PP composites reaches equilibrium after 300 h immersion. Via melt mixing, Tajvidi et al. [54] incorporated 15 wt% waste paper in PP and observed ~0.50% water absorption after 24 h, a factor of six greater than that observed with 85/15 wt% PP1/CB produced via SSSP (samples were tested according to ASTM D570 in their study). The very low water absorption reported in the current study is consistent with excellent filler dispersion and absence of voids within the composites. In addition, increasing the cellulose crystallinity by extraction of microscopic and nanoscopic crystallite does not significantly reduce water absorption in the composite. Overall, the very low moisture absorption with cellulose-based composites makes them appealing in load bearing and outdoor applications.

Table 2
Mechanical properties of PP/cellulosic filler composites produced by SSSP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus E (MPa)</th>
<th>Yield strength σ (MPa)</th>
<th>Elongation at break ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP1</td>
<td>910 ± 50</td>
<td>32.0 ± 0.7</td>
<td>740 ± 40</td>
</tr>
<tr>
<td>95/5 wt% PP1/CB</td>
<td>1130 ± 90</td>
<td>31.2 ± 1.0</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>85/15 wt% PP1/CB</td>
<td>1560 ± 80</td>
<td>32.6 ± 1.7</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>75/25 wt% PP1/CB</td>
<td>1750 ± 90</td>
<td>32.7 ± 0.9</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>Neat PP2</td>
<td>1200 ± 20</td>
<td>36.0 ± 1.0</td>
<td>700 ± 40</td>
</tr>
<tr>
<td>90/10 wt% PP1/MCC</td>
<td>1600 ± 50</td>
<td>35.6 ± 1.1</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>90/10 wt% PP1/CNCa</td>
<td>1830 ± 70</td>
<td>38.0 ± 1.0</td>
<td>12 ± 3</td>
</tr>
</tbody>
</table>

Note. PP1 and PP2 samples employed in this study had different tensile properties despite having the same MFI values (as reported by suppliers).

a Data for PP/CNC composites are from Ref. [39].
3.4. Nucleating efficiency of polyolefin/CB composites

Fig. 4 and Table 3 summarize the effects of well-dispersed CB, MCC and CNC on the crystallization of LDPE and PP. Cellulosic fillers are often good nucleating agents for polymer crystallization. However, the extent of enhancement in crystallization depends strongly on filler dispersion and size reduction and the inherent crystallizability of the polymer. The LDPE used in this study has a very fast crystallization rate, and hence incorporating cellulosic fillers provides no additional benefit. Within error, all LDPE/CB composites retain crystallization behavior similar to that of neat LDPE. On the other hand, excellent particle size reduction and very good dispersion of CB pieces lead to major increases in PP crystallization rate. Relative to neat PP1 with an onset temperature of crystallization ($T_c$) of 117.1 °C, incorporating 5 wt% and 15 wt% CBresults in 10.2 °C and 11.4 °C increases in $T_c$, respectively. Enhancements are also seen in overall crystallinity of PP in the composite; neat PP1 is 44.7% crystalline whereas in a 75/25 wt% PP1/CB...
The neat PP2 used in preparing MCC and CNC composites has $T_c = 121.4^\circ$C. Relative to neat PP2, both composites with 10 wt% filler show a 7.8 $^\circ$C increase in $T_c$. (See Supplementary information for isothermal and nonisothermal crystallization curves.) $t_{1/2}$ decreases from 54 min for neat PP2 to 17 and 13 min for 90/10 wt% PP2/MCC and 90/10 wt% PP2/CNC, respectively. To compare the effectiveness of different fillers as nucleating agents, we calculated their nucleating efficiency. Using Eq (1) and $T_{c,\text{max}} = 140.2^\circ$C, 95/5 wt% PP1/CB composite has a nucleating efficiency of 44% whereas the 85/15 wt% PP1/CB composite has a 50% efficiency. Synthetic, highly crystalline cellulose such as MCC and CNC are known to be effective nucleating agents: 90/10 wt% PP2/MCC and PP2/CNC have efficiencies of 42%. These results show that well-dispersed, cellulose-rich MSW such as waste CB can offer nucleating efficiency that is equal to or better than that obtained with expensive sources of cellulose.

Relatively poor or mixed results have been reported in the nucleating ability of CB in PP composites produced via melt mixing or solvent processing. For example, Chibani et al. [46] observed no improvement in crystallization rates of PP with the incorporation of CB particles. Addition of maleated PP was indicated as necessary to improve the crystallization rate. Huda et al. [51] reported an 11 $^\circ$C increase in $T_c$ with the incorporation of 30 wt% cellulose fibers extracted from recycled newspaper. Spoljaric et al. [36] produced 90/10 wt% PP/MCC composites via ultrasonication in solution that showed an 8 $^\circ$C increase in $T_c$ but an 11 $^\circ$C decrease in crystallinity relative to neat polymer. In contrast, the 90/10 wt% PP/MCC produced in this study by SSSP shows a 7.8 $^\circ$C increase in $T_c$ relative to neat PP and similar crystallinity to that of neat PP. Overall, the fine filler dispersion and agglomerate breakup achieved by SSSP maximize the nucleating efficiency of fillers.

3.5. Thermal degradation of polyolefin/CB composites-thermogravimetric analysis

Understanding thermo-oxidative degradation behavior of a composite is important in determining the processing and end-use conditions of the material. Fig. 5 and Table 4 show degradation behavior of LDPE and PP composites with CB, MCC and CNC as measured by TGA at a heating rate of 10 $^\circ$C/min in air. We define $T_{10\%}$ and $T_{20\%}$ as temperatures corresponding to 10% and 20% mass loss. Cellulosic fillers susceptible to oxidative degradation [39,81]. For example, CB shows $T_{10\%} = 291^\circ$C and $T_{20\%} = 312^\circ$C; MCC shows $T_{10\%} = 314^\circ$C and $T_{20\%} = 321^\circ$C. In comparison, the CNC particles possess lower thermal stability, with $T_{10\%} = 265^\circ$C and $T_{20\%} = 277^\circ$C due to the higher susceptibility of sulfate end groups to oxidative degradation. (Sulfate groups are incorporated as a result of acid hydrolysis for CNC extraction [39,81].)

Neat LDPE employed in this study has $T_{10\%} = 345^\circ$C and $T_{20\%} = 365^\circ$C. Incorporation of 5 wt% CB in LDPE results in a 9 $^\circ$C decrease in $T_{10\%}$ but a 5 $^\circ$C increase in $T_{20\%}$, and identical results within error are obtained in 90/10 and 80/20 wt% LDPE/CB composites. The thermo-oxidative degradation behavior of polyolefin/CB composites compares mostly favorably with those of polyolefin/ MCC and polyolefin/CNC composites made by SSSP. 90/10 wt% LDPE/MCC composites exhibit the same $T_{10\%}$ value and an 11 $^\circ$C decrease in $T_{20\%}$ value as compared to 90/10 wt% LDPE/CB.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature for crystallization, $T_c$ ($^\circ$C)</th>
<th>Percent polymer crystallinity, $X_c$ (%)</th>
<th>Isothermal crystallization half-time, $t_{1/2}$ (min)</th>
<th>Nucleating efficiency, NE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat LDPE</td>
<td>97.1</td>
<td>30.1</td>
<td>83</td>
<td>87</td>
</tr>
<tr>
<td>95/5 wt% LDPE/CB</td>
<td>97.4</td>
<td>29.7</td>
<td>83</td>
<td>87</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CB</td>
<td>98.3</td>
<td>29.5</td>
<td>83</td>
<td>87</td>
</tr>
<tr>
<td>80/20 wt% LDPE/CB</td>
<td>98.5</td>
<td>30.9</td>
<td>83</td>
<td>87</td>
</tr>
<tr>
<td>90/10 wt% LDPE/MCC</td>
<td>98.2</td>
<td>30.1</td>
<td>28</td>
<td>44</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CNC</td>
<td>98.3</td>
<td>32.1</td>
<td>27</td>
<td>50</td>
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<tr>
<td>Neat PP1</td>
<td>117.1</td>
<td>44.7</td>
<td>83</td>
<td>87</td>
</tr>
<tr>
<td>95/5 wt% PP1/CB</td>
<td>127.3</td>
<td>48.2</td>
<td>28</td>
<td>44</td>
</tr>
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<td>85/15 wt% PP1/CB</td>
<td>128.5</td>
<td>47.1</td>
<td>27</td>
<td>50</td>
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<tr>
<td>75/25 wt% PP1/CB</td>
<td>128.5</td>
<td>52.3</td>
<td>25</td>
<td>50</td>
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<tr>
<td>Neat PP2</td>
<td>121.4</td>
<td>51.5</td>
<td>54</td>
<td>84</td>
</tr>
<tr>
<td>90/10 wt% PP2/MCC</td>
<td>129.2</td>
<td>53.2</td>
<td>17</td>
<td>42</td>
</tr>
<tr>
<td>90/10 wt% PP2/CNC</td>
<td>129.2</td>
<td>56</td>
<td>13</td>
<td>42</td>
</tr>
</tbody>
</table>

Note. The two different PP samples employed in this study had different crystallization behavior.

- $T_c$ values reported here have a maximum one standard deviation error of ±0.5 $^\circ$C.
- $X_c$ measurements reported here have a maximum one standard deviation error of ±0.5%.
- Data obtained are from Ref. [39].

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{10%}$</th>
<th>$T_{20%}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat LDPE</td>
<td>316</td>
<td>370</td>
</tr>
<tr>
<td>95/5 wt% LDPE/CB</td>
<td>316</td>
<td>370</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CB</td>
<td>335</td>
<td>370</td>
</tr>
<tr>
<td>80/20 wt% LDPE/CB</td>
<td>335</td>
<td>370</td>
</tr>
<tr>
<td>90/10 wt% LDPE/MCC</td>
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<td>359</td>
</tr>
<tr>
<td>90/10 wt% LDPE/CNC</td>
<td>328</td>
<td>417</td>
</tr>
<tr>
<td>Neat PP1</td>
<td>291</td>
<td>301</td>
</tr>
<tr>
<td>95/5 wt% PP1/CB</td>
<td>295</td>
<td>316</td>
</tr>
<tr>
<td>85/15 wt% PP1/CB</td>
<td>303</td>
<td>321</td>
</tr>
<tr>
<td>75/25 wt% PP1/CB</td>
<td>298</td>
<td>320</td>
</tr>
<tr>
<td>Neat PP2</td>
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<td>307</td>
</tr>
<tr>
<td>90/10 wt% PP2/MCC</td>
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<td>304</td>
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<tr>
<td>90/10 wt% PP2/CNC</td>
<td>281</td>
<td>299</td>
</tr>
<tr>
<td>CB</td>
<td>291</td>
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<td>MCC</td>
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<td>321</td>
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<tr>
<td>CNC</td>
<td>265</td>
<td>277</td>
</tr>
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</table>

Note. Two different PP samples employed in this study had different thermal degradation behavior.

- Data for LDPE/CNC and PP/CNC composites are from Ref. [39].
composites. Relative to neat LDPE, 90/10 wt% LDPE/CNC composites show an 18 °C decrease in $T_{10\%}$ but a dramatic 62 °C increase in $T_{20\%}$. This increase can be attributed to preferential degradation of cellulose filler. The enhancements seen with polyolefin/CB composites made by SSSP are also superior to those reported in similar composites prepared via melt processing. For example, Salmah et al. [47] observed similar $T_{20\%}$ values for LDPE/waste paper composites and neat LDPE.

The neat PP1 employed in PP1/CB composites shows $T_{10\%} = 291$ °C and $T_{20\%} = 301$ °C, whereas the neat PP2 used to produce MCC and CNC composite shows $T_{10\%} = 297$ °C and $T_{20\%} = 307$ °C. Markedly improved thermal stability to oxidative degradation is observed in PP1/CB composites, with an 85/15 wt% PP1/CB composite showing 12 and 20 °C increases in $T_{10\%}$ and $T_{20\%}$, respectively, relative to neat PP1. Unlike CB fillers, incorporation of MCC and CNC into polymers that have low stability to thermo-oxidative degradation (such as PP) results in 10–16 °C and 3–8 °C decreases in $T_{10\%}$ and $T_{20\%}$, respectively. In addition to cellulose, CB contains ~15% lignin [60,61]. Lignin is an effective antioxidant for polyolefins [25,30]. For example, past studies have demonstrated up to ~35 °C increase in $T_{20\%}$ over neat polymer (LDPE or PP) with the incorporation of lignin via SSSP [30]. Due to the excellent dispersion of CB achieved by SSSP, composite materials made by SSSP possess superior thermal stability compared to neat polymer.

3.6. Thermal degradation of polyolefin/CB composites—melt mixing and rheology

Thermal degradation is a strong function of temperature and time. Shear forces and stresses imparted to polymer melts also influence degradation. Material properties can be significantly affected by molecular weight reduction and crosslinking that accompany melt processing at elevated temperature. Hence, to better illustrate the effect of CB and other synthetic cellulose fillers on thermal stability, we employed isothermal shear flow experiments to monitor the time-dependent evolution of microstructure in the polymer melt. Fig. 6 shows normalized shear storage modulus for neat LDPE and composites with 10 wt% CB, MCC and CNC measured at 200 °C. (Storage modulus values are normalized by their respective values at the start of the shear flow experiment.) Under oxidative conditions, LDPE undergoes degradation via chain scission and subsequent branching. From Fig. 6, LDPE exhibits a significant increase in storage modulus at ~1350 s due to chain branching. Interestingly, both 90/10 wt% LDPE/CB and 90/10 wt% LDPE/MCC hybrids made by SSSP display an onset time for chain branching that is within error similar to that of neat LDPE. This is consistent with TGA results that show small changes in $T_{10\%}$ from the neat polymer for both composites. In comparison, 90/10 wt% LDPE/CNC composites prepared by SSSP exhibit a major increase in shear storage modulus beginning at ~870 s under isothermal shear flow conditions, indicating reduced thermal stability; this is consistent with reductions in $T_{10\%}$ seen from TGA.

In order to better emphasize and understand the differences in thermal stability, SSSP-processed LDPE composites with 10 wt% cellulose fillers were further melt mixed using an ATLAS Electronic Devices MiniMax molder for 15 min at 200 °C. Fig. 7a–c shows images of compression molded (140 °C for 5 min) films (~0.7 mm thickness) prepared from SSSP-processed LDPE composite powder; Fig. 7d–f shows compression molded films from pellets obtained via melt mixing of SSSP-processed LDPE composite powder. No film shows visible agglomerates or distortion of the image underneath the film. The additional long, high-temperature melt processing does not result in any sign of degradation in either LDPE/CB or LDPE/MCC composite films. This observation is consistent with isothermal shear flow experiments in which no degradation is detected up to ~1350 s. However, LDPE/CNC composites change from a clear film after SSSP to a tan/brownish color after further melt processing at 200 °C, which is in line with the onset time for degradation of ~870 s at 200 °C measured by isothermal shear flow measurements. The sulfate end groups on CNC undergo degradation at temperatures as low as 150 °C [81]. Overall, CB waste rich in
cellulose brings considerable benefit to industrial melt processing of polyolefin composites. Additionally, as shown in Section 3.5 above, incorporation of some lignin with the cellulose, as is the case with CB, can lead to further benefits in thermal stability.

4. Conclusions

The effectiveness of low cost, cellulose-rich MSW in acting as reinforcing filler in polyolefin composites has been compared to that of highly refined versions of cellulose. Solid-state shear pulverization is employed for the first time to produce polyolefin/CB composites with 5–25 wt% filler, and the property enhancements are compared to those achieved with the incorporation of more expensive MCC and CNC. Microscopy reveals that excellent size reduction and dispersion of ~2–3 cm sized CB is achieved via SSSP without the need for compatibilizer or surface treatment. Furthermore, micrographs reveal CB particles of ~1–10 μm, comparable to those seen with composites incorporating MCC. Such polyolefin/CB composites exhibit improvements Young’s modulus improvement (63% and 71% increases relative to neat LDPE and PP for 10 wt% CB, respectively) that is comparable or superior to those seen with synthetic MCC or CNC. In addition to the excellent retention of elongation at break (260% for 10 wt% CB in LDPE), particle size reduction of CB to levels similar to MCC and CNC results in tensile strength similar to or better than neat polymer. Thus, well-dispersed CB can be used to produce durable polyolefin composites with enhanced modulus that may be attractive for applications as structural materials in the automotive and other industries.

The PP/CB composites exhibit a broad range of other property enhancements including a nearly 50% nucleating efficiency, a significant increase in PP crystallinity and a major decrease in $\tau_{1/2}$. These enhancements compare favorably with those achieved with MCC and CNC. Thermogravimetric analysis in air reveals that CB incorporation results in a 5–20 °C increase in 20% mass loss temperature relative to neat polyolefin. Composites with CB or MCC show superior thermal stability compared to CNC-based...
composites as ascertained from isothermal shear flow measurements. Additional long, high-temperature melt mixing of SSSP-processed composites results in no apparent visual sign of degradation in either CB or MCC composites. These properties indicate that polyolefin composites reinforced with appropriately size-reduced and well-dispersed CB (with CB available at ~$95/ton) can rival the enhancements achieved with more costly, highly refined forms of cellulose.

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Appendix A. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.08.029.

References