The Effect of Filler Type on the Mechanical, Thermal and Rheological Properties of Cellulose-filled Thermoplastic Composites

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Abstract

Over the past several decades, interest in the development of new composite materials derived from cellulose-based fillers and thermoplastic polymer matrices has received considerable attention. The mechanical and rheological properties of the composites are found to be a function of the particle size, filler loading, dispersion and the interfacial interaction between the fillers and polymer matrix. The role of cellulose-based filler type and size effect has not been studied in great detail. In this study, the effects of adding microcrystalline cellulose with variable particle sizes (15, 50 and 90 µm), alpha cellulose (60 µm), silicified microcrystalline cellulose (50 µm) and wood flour (70 µm) on the mechanical, thermal and rheological properties of polystyrene composites were investigated. High impact polystyrene (HIPS) composites with varying concentrations from, 5 to 20 wt. percent of cellulose-based fillers were prepared by thermal compounding followed by injection molding. It was observed that the larger sized fillers produced higher flexural modulus values than the smaller sized fillers. Also, the tensile strength increased with particle size. Particle size did not seem to have much influence on the thermal degradation behavior of the composites. Results show that MCC has increased thermal stability when compared to SMCC. SMCC also shows better mechanical properties than untreated MCC. Significant differences were found in size and shape of the AC and MCC filler materials. Alpha cellulose had the lowest circularity, aspect ratio and solidity values. The increased viscosity was more pronounced when smaller sized fillers were used. Because of the lower thermal mixing viscosities, future experiments may prove larger fillers sizes to have better dispersion with better matrix interactions than composites made from small sized fillers.

Keywords filler size, shape parameters, thermoplastic composite, cellulose-based fillers, rheological properties, mechanical properties and morphology
Introduction

Inorganic and organic fillers for example micro-/nano SiO₂, glass, talc, Al₂O₃, Mg(OH)₂, CaCO₃ particles, layered silicates, carbon nanotubes and cellulose-based fillers are generally used as fillers in polymer composites to address the obvious limitations of polymers such as low stiffness and strength, low creep resistance, high coefficient of thermal expansion and high cost (Fu et al. 2008). Cellulose-based fillers have several advantages in comparison with inorganic fillers based on their lower density, less abrasiveness to processing equipment, renewable character, biodegradability and lower price (Naurbakhsh et al. 2009; Dikobe and Luyt 2006; Stark and Rowlands 2003). Cellulose-based filled polymer composites are widely used in many areas such as building and structural applications and the automobile, aircraft, electronic and medical areas, but mostly in areas where they are exposed to the effect of external loads (Naurbakhsh et al. 2009, Pukanszky et al. 2000). The use of cellulose-based filler materials as fillers in polymer composites has attracted a significant interest over the past several decades. The increase in applications has been due to the fact that cellulose-based filled polymer composites usually have a high specific stiffness and strength properties compared to polymer composites with inorganic fillers (Dikobe and Layt 2006). Mechanical properties of these composites are strongly influenced by the presence of the filler and the characteristic of polymer composites which are determined by the properties of their components, composition, structure and interactions (Pukanszky et al. 2000). The stiffness or Young’s modulus can be readily improved by adding either micro- or nano cellulose-based fillers and always increases linearly with the amount of filler used (Fu et al. 2008; Pukanszky et al. 2000). However, tensile strength of cellulose-based fillers filled composites decreases with filler loading due to poor adhesion between the hydrophilic surface of cellulose-based fillers and the essentially hydrophobic polymers that are commonly used as the matrix (Pukanszky et al. 2000; Dikobe and Luyt 2006).

Other factors that influence the mechanical properties of cellulose-based filled polymer composites are characteristics of the particles such as particle size, particle origin, particle shape and particle size distribution, particle content and interactions (Pukanszky et al. 2000, Fu et al. 2008, Dikobe and Luyt 2006). Particle size has an obvious effect on the mechanical properties and Zaini et al. reported the effect of filler content and size on the mechanical properties of polypropylene/oil palm wood flour and they found that the composites filled with larger sized filler showed a higher modulus, tensile and impact strength, particularly at higher filler content (Zaini et al. 1999, Fu et al. 2008). Dikobe and Luyt studied effect of filler content and size on the properties of ethylene vinyl acetate copolymer-wood fiber composites and reported that the tensile strength of the composites decreased with increasing wood fiber content. Ismail et al studied the effect of filler content and size on oil palm wood flour reinforced epoxidized natural rubber composites and they found that the smaller particle size of oil palm wood flour provides better mechanical properties (Ismail et al. 1997). Particle size is not sufficient itself for the characterization of any filler, and for that reason, the knowledge of the size distribution is extremely important (Pukanszky et al. 2000). Particle size distribution rather than average particle size also affects rheology of dispersed systems and shear viscosity is lower for a filler system with a multimodal distribution of particle size than for a system with unimodal distribution of particle sizes at the same filler loading level (Zhou et al. 2000). The filler also makes processing of a polymer more difficult and the flow behavior of polymer composites can
be measured by capillary rheometry and melt flow index (Li and Salovery 2004). Li and Wolcott studied rheology of wood plastic melts with different sizes of maple and reported that the increased viscosity with maple loading was more pronounced with small particle sizes (Li and Wolcott 2005). Particle shape is another important factor in terms of mechanical properties and it is reported that plate-like fillers such as talc and mica reinforce the modulus of composites more than spherical fillers for example glass beads (Pukanszky et al. 2000 and Iisaka and Shibayama 2003).

In this study, the effects of cellulose-based filler type, size and shape and content on the mechanical, thermal and rheological properties of polystyrene composites was investigated. Tensile and flexural tests were used to evaluate the mechanical properties of the composites. Qualitative morphology of composites was determined using scanning electron microscopy (SEM). Quantitative morphology of cellulose-based fillers was determined using transmission optical microscopy based on shape parameters. Thermal stability of cellulose-based fillers and composites were characterized by thermogravimetric analysis (TGA).

Experimental procedure

Materials
The high impact polystyrene (HIPS, Styron 478) used as the thermoplastic matrix polymer, was kindly supplied by American Styrenics LLC, USA. HIPS had a density of 1.04 g/cm³ and melt flow rate of 6 g/10 min. The lubricant (TPW 113) used as an additives to improve processing conditions, was supplied by Struktol Co. Wood flour (WF), microcrystalline cellulose (MCC), alpha cellulose (AC) and silicified microcrystalline cellulose (SMCC) used as the reinforcement for composite materials. SMCC is 98% MCC manufactured from cellulose pulp obtained from softwood co-processed with 2% of colloidal silicon dioxide. WF was kindly supplied by J. Rettenmaier & Sohne (JRS) with 70-120µm particle size. Emcocel type SP15, 50M and 90M type with 15, 50 and 90 µm particle size MCC was kindly supplied by JRS. AC was supplied Creafill Fibers Corp. with average 60 µm fiber length. Prosolv SMCC 50 type SMCC was also kindly supplied by JRS with 50 µm particle size.

Sample Preparation
The reinforcing fillers and HIPS were dried to moisture contents less than one percent using an oven at 105°C for 16 hours. The HIPS was mixed with the cellulose-based fillers by thermal compounding using a Brabender Prep-mixer® equipped with a bowl mixer and the process temperature and torque changes were measured in real time. The basic processing parameters are listed in Table 1. Mixing was done for 10 min until the torque values stabilized. The HIPS – reinforcing fillers compounds were granulated using a lab scale grinder. The ground particles were dried in an oven at 105°C for 16 hours before being injection molded into ASTM test samples. All materials were injection molded using a barrel temperature of 240°C mold temperature of 240°C injection pressure of 2,500 psi. The compositions of composites are shown in Table 2.
Characterization
The tensile behavior of composites was measured using an Instron 8801 with a 10 kN load cell. All the tension tests were tested at a rate of 0.2 in/min. The flexure tests were conducted according to ASTM D 790-03, using an Instron 8801 with a 4.48 N load cell. The support span was 50 mm and tests were run at a test speed of 0.05 in/min. TGA measurements were carried out using a Mettler Toledo analyzer on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 600°C at a heating rate of 10°C/min under nitrogen with a flow rate 20 ml/min to avoid sample oxidation. A capillary rheometer (Gottfert Rheograph 2002) was used to characterize the rheological properties of the HIPS composites. Material about 40 – 50 grams was filled in the barrel for each test. From the testing, melt viscosities of different materials were obtained using a tungsten capillary die of length to diameter ratio \( L/D = 10 \) with \( D = 2 \text{ mm} \) at 240°C in the shear rate range of 1.44 to 144 S\(^{-1}\). Four minutes at melting temperature was applied for all the measurements. The rheological behavior of the composites was also studied by a melt flow index (MFI), manufactured by Dynisco (LMI 4000 Model D4004) at temperature 240°C and 2.16 kg load. Qualitative morphology of cellulose-based fillers filled composites was determined using scanning electron microscopy (SEM). Studies on the morphology of the tensile fracture surfaces of the composites were carried out using an AMR 1000 (AMRay Co.) scanning electron microscope. Images were taken at 10 kV with 200× SEM micrograph magnifications. Quantitative morphology of AC, 15 µm MCC, 50 µm MCC and 90 µm MCC were determined using transmission optical microscopy (Malvern Morphologi G3 with Automated Particle Characterization System) based on shape parameters.

Results and Discussion

Mechanical Properties
The effect of particle size and particle loading on the tensile properties of cellulose-based filled composites are shown in Fig.1. It was clear that tensile modulus of elasticity in general was strongly dependent on particle loading and filler size. When 20 wt. % fillers were added, the modulus increased by \( \approx 15-30\% \) with WF, AC, SMCC and 90 µm MCC fillers. Similar results were reported for other filler-polymer composites (Dikobe and Luyt 2006; Suprapakorn et al: Shevlova and Poloucek 1994, Fu et al. 2008). The highest tensile modulus of elasticity was observed for composites containing 90 µm MCC and the lowest tensile modulus of elasticity for those with 50 µm MCC. It can be also seen from Fig. 1 that the tensile strength of the composites in general decreased upon addition of cellulose-based fillers and the tensile strength was affected by particle size for these composites. When the filler content was the same, the tensile strength of composites filled with 90µm MCC was higher than that of composites filled with other sizes of particles. The better filler dispersion and filler-matrix interaction may be two main factors responsible for better tensile properties with larger particle size in this study. SMCC show better tensile modulus of elasticity and tensile strength compared to the same size 50 µm MCC because of better interfacial adhesion. Fig. 2 shows the flexural modulus of elasticity of composites filled with different cellulose-based fillers and different sizes of MCC. For all particles, flexural modulus of elasticity of the composites increased with increasing filler content. It can be concluded from Fig. 2 that when the filler content was the same, the flexural modulus of elasticity filled 90 µm MCC were obviously higher than those of composites filled with other sizes of particles. Considering treatment, the flexural modulus of elasticity of composites filled
with 50 µm MCC and the same size SMCC could be regarded as the same. The TGA and DTGA curves of the neat HIPS and HIPS-filled composites are shown in Fig. 3. Neat HIPS curve shows one degradation step with a Tmax (temperature at the maximum decomposition rate) around 431°C. HIPS filled composites are characterized by two Tmax temperatures. The first, related to the Tmax of cellulose-based fillers, starts at about 350°C. the second due to Tmax of HIPS, occurs at about 431°C. The results also show that the thermal stability of the composites decreased slightly as the cellulose-based filler content increased because of lower thermal stability of cellulose-based fillers compared to the neat HIPS. All cellulose-based filled composites degraded in a similar way, regardless of the particle size and type used. Therefore, particle size did not seem to have much influence on the thermal degradation behavior of the composites. A similar effect was reported by Dikobe and Luyt 2006.

In terms of controlling the mechanical properties of composites, flow or rheological behavior of melt is one of the key factors (Englund and Wolcott 2008). Fig. 4 shows the dependence of viscosity on the shear rate range analyzed for neat HIPS and different cellulose filler type- and size-filled HIPS composites at loadings of 20% by mass. As it can be seen, both neat HIPS and HIPS composites showed a shear thinning behavior. In other words, the viscosity decreases with increasing shear rate. Shear thinning behavior of neat HIPS and HIPS composites was stronger at a low shear rate range. While wood flour and 50 µm MCC showed higher viscosity compared to the neat HIPS at low shear rate, 90 µm MCC, SMCC and alpha cellulose showed lower viscosity in comparison with HIPS at a low shear rate. In general, a weak trend of increase in viscosity with decreasing filler size can be observed at all shear rates. However, the difference between different filler types and sizes was not large. A similar effect was also reported by other researchers (Wong et al. 2004; Zhou et al. 2000, and Li and Wolcott 2005). Because of lower viscosity, future experiments may prove that larger fillers sizes (90 µm MCC and AC) have better dispersion with better matrix interactions than composites made from small sized fillers. We observed that the effect of cellulose-based filler type and particle size on the morphology of the HIPS and HIPS composites in Fig. 5. The analysis of the cellulose-based filler dispersion, carried out by SEM, shows that the addition to HIPS of 20 wt. % of small size cellulose fillers appeared to suggest a higher number of agglomerations or clusters. Because of this behavior, poor dispersion probably occurred with the small sized fillers in the HIPS matrix. This result was in agreement with the mechanical and rheological results found in this study. Quantitative analysis of particle morphology through determination of particle CE diameter, circularity, aspect ratio, and solidity were also investigated. The quantitative and SEM indicated that using both observational and quantifiable methods, cellulose-based fillers had different morphologies.

Conclusions

HIPS and cellulose-based filled HIPS composites were prepared by melt compounding followed by injection molding. The mechanical properties of the composites were found to be a function of particle size and shape, the dispersion and the interfacial interaction between the cellulose–based fillers and the polymer matrix. Mechanical property studies showed that the composites filled with large sized fillers had higher mechanical properties. There was a significant increase in the flexural modulus of elasticity with an increase in the filler loading. Tensile strength also decreased with increased filler loading. TGA results indicated that particle size did not appear to
have much influence on the thermal degradation behavior of the composites. Isothermal TGA also showed that MCC was thermally more stable and has less weight loss in comparison with similar sized cellulose-based fillers in this study. A weak trend of increase in viscosity with decreasing filler size can be observed at all shear rate ranges. Because of lower viscosity, future experiments may prove larger fillers sizes to have better dispersion with better matrix interactions than composites made from small sized fillers. SEM showed that poor dispersion occurred with small sized fillers in the HIPS matrix. Significant differences in shape were found. AC had the lowest HS circularity, aspect ratio and solidity values in comparison with the MCC fillers.

References


Table 1. Basic operating parameters of the Brabender rheomixer for HIPS composites.

<table>
<thead>
<tr>
<th>Stage Level</th>
<th>Set Temp.</th>
<th>Melt Temp.</th>
<th>RPM</th>
<th>Mix Melt Temp.</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st stage (HIPS)</td>
<td>250</td>
<td>240</td>
<td>60-70</td>
<td>-</td>
<td>8 min</td>
</tr>
<tr>
<td>2nd stage (Fillers)</td>
<td>230</td>
<td>200-240</td>
<td>50</td>
<td>Cont. under 240</td>
<td>2 min</td>
</tr>
</tbody>
</table>

Temperature values are °C.

Table 2. Composition of cellulose-based filled HIPS composites.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>MCC/ WF/AC/SMCC Content</th>
<th>HIPS</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PS</td>
<td>0</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>PS+5% Filler Loading</td>
<td>5</td>
<td>92</td>
<td>3</td>
</tr>
<tr>
<td>PS+10% Filler Loading</td>
<td>10</td>
<td>87</td>
<td>3</td>
</tr>
<tr>
<td>PS+20% Filler Loading</td>
<td>20</td>
<td>77</td>
<td>3</td>
</tr>
</tbody>
</table>

Values are percentage by weight (wt. %).

Figure 1. Tensile properties of neat HIPS and cellulose-based filled composites.
Figure 2. Flexural modulus of elasticity of neat HIPS and HIPS composites.

Figure 3. TGA of neat HIPS and HIPS composites.

Figure 4. Rheological properties of neat HIPS and cellulose-based filled composites.
Figure 5. Scanning electron microscope images of HIPS and HIPS composites.