EFFECT OF HYBRID MINERAL AND BAMBOO FILLERS ON THERMAL EXPANSION BEHAVIOR OF BAMBOO FIBER AND RECYCLED POLYPROPYLENE–POLYETHYLENE COMPOSITES

Runzhou Huang, a Yang Zhang, a Xinwu Xu, a Dingguo Zhou, a and Qinglin Wu a,b,*

The effect of bamboo and hybrid bamboo-precipitated calcium carbonate (PCC) fillers on thermal expansion behavior of filled plastic composites was investigated. The linear coefficient of thermal expansion (LCTE) of the filled composites decreased with increased PCC and bamboo filler loading levels. The composite system with refined bamboo fibers (RBFs) had smaller LCTE values compared with those from the systems with ground bamboo particles (GBPs). The use of silane treatment on bamboo fiber/particle surface helped enhance its bonding to the plastic matrix, leading to a further reduction of LCTE values for both GBP and RBF composite systems. The observed behavior of reduced LCTE is attributed to a small filler LCTE value, reduced overall plastic volume, and enhanced interfacial bonding with treated bamboo materials. Thus, hybrid bamboo and PCC fillers are suitable materials for reducing the thermal expansion of the composites caused by temperature changes.

Keywords: Bamboo; Thermal expansion; Recycled plastic; Composites

Contact information: a: College of Wood Science and Technology, Nanjing Forestry University, Nanjing, 210037, China; b: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA. *Corresponding author: qwusfm@gmail.com

INTRODUCTION

Wood and natural fiber plastic composites (WPCs) have attracted considerable attention in recent years. Many emerging applications for WPCs include decking, building, automobiles, and infrastructure (Klyosov 2007; Selke and Wichman 2004). Polyethylene (PE), polyvinylchloride (PVC), and polypropylene (PP) hold a major share of resins used in WPC. Compared with traditional glass fiber and mineral fillers, wood/natural fiber fillers are less expensive, lighter, sustainable, and less abrasive to processing machines. To enhance product performance, significant effort has been made to study WPC’s properties as affected by raw material compositions, wood-plastic interfacial bonding, and composite processing parameters (Mohanty et al. 2001, Lu et al. 2000). One of the important performance properties for WPC is thermal expansion and contraction caused by external temperature variation (Kim et al. 2007; Singh and Mohanty 2007; Klyosov 2007).

Thermal expansion and contraction of materials are usually measured by the linear coefficient of thermal expansion (LCTE), which is a vital engineering property for the composites’ structural applications. A low LCTE value is a desirable property in order to achieve dimensional stability. LCTE of crystalline polymers depends on various
parameters, including processing conditions, thermal history, and degree of crystallinity and crystallite size. Filler-aspect ratio, volume fraction, orientation, and distribution in the matrix also play a deciding role in determining the LCTE of composites (Luo and Netravali 1999; Tan et al. 1990).

LCTE values for wood (along the grain) and mineral (e.g., calcium carbonate) fillers are about 20 times lower than those of plastics and about 10 times lower than those of WPCs (Klyosov 2007). LCTE measured across the grain (radial and tangential) is proportional to wood specific gravity and is about 5 to 10 times higher than those along the grain. Thus, the use of filler can help reduce LCTE of WPCs. However, the effect of fillers on the LCTE is far from being understood. It appears that the largest effect is caused by the degree of anisotropy of the filler and the filler orientation in the flow (and in the final product). The characteristics of high-density PE (e.g., density and degree of crystallinity) and extrusion conditions (e.g., speed, pressure, and temperature profile) are also important for controlling the LCTE values.

As an important renewable resource, bamboo accounts for approximately 25% and 20% of the total biomass in the tropics and sub-tropical areas, respectively (Han et al. 2008), and its overall mechanical properties are comparable to or even surpass those of wood. Furthermore, bamboo can be renewed much more rapidly compared with wood. Thus, these advantages make it a highly competitive natural reinforcement in polymeric composites. In several preliminary reports, bamboo fibers or flours have been utilized as natural reinforcements of thermosetting resins, biodegradable polyesters, poly (vinyl chloride) (PVC), and PP (e.g., Okubo et al. 2004).

Among the mineral fillers, precipitated calcium carbonate (PCC) from chemical processes has characteristics of very fine and regular particle size (Wypych 2010; Echeverria and Holst 2005). Thus, its uses in plastic composites have led to improved mechanical properties. Kim et al. (2012) investigated the technical feasibility of using PCC of sugar origin as a reinforcing filler for bamboo fiber plastic composite. It was shown that air-dry PCC particles were in an agglomerated form made of individual cubic particles of about 1.2 micron in diameter. Compounding with plastic resin helped separate the PCC into smaller individual particles. The use of PCC led to a significant increase of flexural strength and flexural modulus of PCC-filled composites after 10 wt% PCC loading level. For bamboo-filled composites with PCC, tensile modulus and flexural modulus were improved with the increase of PCC content and with the use of surface-treated bamboo filler. The thermal expansion behavior of the filled composites was, however, not studied.

The objectives of this study were to elucidate the effect of PCC and bamboo fiber loadings on thermal expansion properties of filled plastic composites.

**EXPERIMENTAL**

**Materials and Preparation**

Recycled-PP/PE (R-PP/PE) resin, ground bamboo particle (GBP, ≤ 20 mesh), thermo-mechanically refined bamboo fiber (RBF, ≤ 20 mesh), and PCC were used as raw materials (Kim et al. 2012). Originally, R-PP/PE (about 95% PP and 5% PE) was a
Commingled plastic in a fluffy form, and it was pelleted using a twin-screw extrusion machine before being blended with other raw materials. GBP was prepared from bamboo flakes through grinding and screening, using a Model S10/9GF Granu-Grinder (C.W. Brabender, Instruments Inc., South Hackensack, NJ) with a 20-mesh screen. RBF was produced by refining bamboo chips at 160°C for 10 min using a KRK-2503 steam-aided disc refining system (Kumagai Riki Kogyo, Tokyo, Japan). Silane coupling agent (Z-6094) from the DOW Corning Co. (Midland, MI, USA) was utilized to treat the prepared GBP and RBF. The composition of silane was aminoethyl-aminopropyl-trimethoxysilane (> 60 wt%), and the density of this organo-silane was 1.02 g/cm³. Silane treatments of GBP and RBF were made by immersion methods. Before treatments, the silane aqueous solution was pre-hydrolyzed for over 30 min. GBP and RBF were first oven-dried at 85°C for 24 hr to reduce moisture content level to less than 2%. They were immersed in an aqueous solution (methanol:water = 9:1 by weight) including a silane coupling agent (3% of the weight of bamboo fiber) at 25°C for 1 hr. After immersion, silane-treated GBP and RBF (TGBP and TRBF) were dried at 85°C for 24 hr again. PCC in powder form was obtained from Domino Sugar Company (New Orleans, LA, USA). It was dried at 85°C for 24 hr and screened with a 100-mesh screen.

**Experimental Design**

The experiment design included three factorial experiments. The first experiment was designed to study the effect of PCC loading levels consisting of six PCC loading rates (i.e., 0, 3, 7, 10, 15, and 30 wt%). The second experiment was designed to study the effect of combined PCC and GBP consisting of eight blends covering three material types (GBP, TGBP, and PCC) and four loading rates for PCC (0, 6, 12, and 18 wt%). The third experiment was designed to investigate the effect of combined PCC and RBF, consisting of eight blends covering three material types (i.e., RBF, TRBF, and PCC) and four loading rates for PCC (0, 6, 12, and 18 wt%). All composite blends had 40 wt% GBP or TGBP based on the total composite weight. The neat R-PP&PE samples were also made as a control.

**Composite Manufacturing**

The R-PP/PE plastic, bamboo fiber, and PCC hybrid composites were prepared with a CW Brabender Intelli-Torque Twin-Screw Extruder (CW Brabender Instruments Inc., South Hackensack, NJ). R-PP/PE and PCC (50 wt% of plastic and 50 wt% of PCC) were blended first as a base material (Kim et al. 2012). After that, the pellets were diluted in the variation of PCC of 6, 12, and 18 wt%, which were re-compounded with bamboo fiber (40 wt%) in the blends of R-PP/PE and PCC (60 wt%) and then extruded in the second step.

The blending temperature profile was 155, 175, 180, 180, and 170°C from the feeding zone to the strand die, and the extruder rotation speed was 90 rpm. The extruded blends were pelletized and then dried in an oven at 85°C for 24 hr. Standard test samples were made through a Battenfeld 35-Ton Plus Injection molding machine (Wittmann Battenfeld GmbH, Kottingbrunn, Austria) at an injection temperature of 175°C.
Characterization

(1) Thermal expansion

Thermal expansion samples were machined with a miniature table saw along the long direction of injection molded samples with a dimension of 5.1 x 12.7 x 1.6-mm. Special attention was made to ensure that the sample ends were parallel. The test was done with a TA Q400 Thermo Mechanical Analyzer (TMA). The sample was placed on a quartz base, and an extension quartz probe was then placed on the top surface of the sample. A loading of 5-g force was applied to the probe to ensure the proper contact of the probe and the sample. The change in the length of the sample with temperature was measured using a linear variable differential transformer (LVDT) with a sensitivity of ±0.02 µm. The length and temperature data were recorded and analyzed with TA’s Universal Analysis software. All tests were done with three heating cycles: 1) 20°C to 60°C; 2) 60°C to –30°C; and 3) –30°C to 20°C. The heating and cooling rates were kept constant at 5°C /min. The LCTE \( (\alpha_L, 1/°C) \) was calculated as,

\[
\alpha_L = \frac{1}{L} \frac{dL}{dT}
\]

where \( L \) is the linear dimension of the test sample and \( dL/dT \) is the rate of change in the linear dimension per unit temperature.

(2) Composite morphology

The morphologies of selected composite samples were analyzed by a Hitachi S-3600N VP Scanning Electron Microscope (SEM) (Hitachi Ltd., Tokyo, Japan). The samples were coated with Pt to improve the surface conductivity before observation and observed at an acceleration voltage of 15 kV.

(3) Data analysis

Duncan’s multiple range tests for pairwise comparisons were used to test the effect of various treatments using statistical analysis software SPSS (version 10.0). Statistical ranking at the 5% significance level was provided among the treatments for each property.

RESULTS AND DISCUSSION

Dimension Change-Temperature History

Typical dimension changes in relation with temperature for the composite system are shown in Fig. 1 (neat resin and RBF-PCC-Resin systems). The sample dimension increased as the temperature increased and decreased as temperature decreased. The LCTE is represented by the slope of the linear portion of each curve. The neat plastic had an obvious larger dimension change than that from filled composites for a given temperature change. A significant residual deformation is seen for the neat plastic at the end of the final heating cycle. The dimension change of neat resin seemed to be more significant at lower temperature ranges (< 20°C) than that at higher temperature range (> 20°C) compared with filled composites. This could be due to complex stress development.
in the mixed plastics during cooling process. Composites with bamboo and combined bamboo-PCC fillers had much smaller dimensional changes, showing the restricting effect of the fillers in response to temperature changes. And residual deformation of filled composites was also significantly lowered.

![Graph showing dimension change vs. temperature]

**Fig. 1.** Typical dimension change-temperature history for PCC/Bamboo fiber filled R-PP&PE composite systems. RBF40PCC6 represents 40% RBF and 6% PCC in the composite.

**Effect of PCC Loading Level on Composite LCTE**

Table 1 and Fig. 2 show measured LCTE values as a function of PCC content for PCC-filled R-PP/PE polymer. The first heating cycle from 20 to 60°C had the largest LCTE values at all PCC content levels. The second heating cycle from -30 to 20°C had the smallest LCTE values. The cooling cycle (60 to -30°C) had the values in between. This behavior is related to the thermal history built into the samples, leading to heating-history dependent LCTE values. Obviously, LCTE decreased with increased PCC content for various composite systems. Statistical ranking shows a significant effect of PCC on measured LCTE values. The neat plastic had LCTE values of 149.8 x 10^-6/°C, 125.4 x 10^-6/°C, and 108.7 x 10^-6/°C for the three temperature ranges (i.e., 20 to 60°C, 60 to -30°C, and -30 to 20°C), respectively. The reported LCTE values for PP and PE neat resin are, respectively, 100-200 x 10^-6/°C and about 200 x 10^-6/°C (The Engineering ToolBox, 2012). Thus the measured LETC values for the neat PP/PE resin used are closer to the reported values for PP resin due to its large proportion in the mix. The values decreased by 20.1, 17.6, and 19.6%, respectively, at the 30% PCC loading level. The linear regression equations fit the LCTE-PCC content data well, as shown in Fig. 2. The second heating cycle from -30°C to 20°C had the smallest absolute slope value from the LCTE-PPC content plots.
### Table 1. Effect of PCC Content on Thermal Expansion Coefficient of Filled R-PP&PE Composites

<table>
<thead>
<tr>
<th>System</th>
<th>PCC&lt;sup&gt;a&lt;/sup&gt; (wt %)</th>
<th>Linear Coefficient of Thermal Expansion ($10^{-6}/^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 to 60°C&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>R-PP&amp;PE /PCC</td>
<td>0</td>
<td>149.8(5.0)E</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>143.17(4.7)D</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>140.6(1.5)CD</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>135.9(2.3)BC</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>131.9(1.4)B</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>119.8(5.0)A</td>
</tr>
</tbody>
</table>

<sup>a</sup> The content of each filler was based on the total composite weight.

<sup>b</sup> Mean values with the same capital letter for each property are not significantly different at the 5% significance level.

<sup>c</sup> Numbers in the parenthesis are standard deviation based on five specimens.

![Graph showing linear regression fits for thermal expansion](image)

**Fig. 2.** Effect of PCC content on Measured LCTE values for PCC-filled R-PP/PE composites. Lines show linear regression fits.

![Morphology images](image)

**Fig. 3.** Morphology of PCC particles (Left), PCC-filled R-PP&PE 7% (Middle); and PCC-Filled R-PP&PE 30% (Right).

---

The averaged individual PCC particle size estimated from SEM micrographs was 1.16 ± 0.37 μm (Fig. 3 left). The R-PP/PE blended with 7 wt% PCC (Fig. 3 middle) had some well-dispersed PCC particles in the polymer matrix (mean diameter 1.25 ± 0.43 μm). For the R-PP/PE blended with 30 wt% PCC (Fig. 3 right), some aggregated PCC particles were seen in the polymer matrix (estimated mean particle diameter = 1.66 ± 1.24 μm). The presence of well-dispersed PCC particles with small LCTE values reduced the overall plastic volume in the composite, leading to reduced overall composite LCTE.

Effect of Hybrid Bamboo and PCC Fillers on Composite LCTE

Table 2 (GBP) and Table 3 (RBF) summarize the measured LCTE data for composites with bamboo and hybrid bamboo-PCC fillers. Figures 4 and 5 show selected data plots. As shown in Table 2 and Fig. 4, the use of 40% GBP in the composite reduced the LCTE values of filled R-PP&PE by 56.5, 52.6, and 55.7% for the three temperature ranges of 20 to 60°C, 60 to -30°C, and -30 to 20°C, respectively. Treating bamboo particles with silane further reduced LCTE values due to the enhanced bonding between bamboo particles and plastic matrix. Similar behavior is observed with the use of 40% RBF in the composites (Table 3 and Fig. 5). The corresponding reduction from the base resin is 48.8, 51.8, and 55.8% for the three temperature ranges, respectively. Further reduction of LCTE is seen with silane-treated RBF in the composites. Kim et al. (2012) showed that the increased intensities of the peaks at 1604 cm⁻¹ and 1510 cm⁻¹ wavelengths from the FTIR spectra from silane treated bamboo filler, indicating the existence of silane crosslinks on the surface of TRBF after silane treatment. These changes probably resulted from the traces of NH₂ in silane coupling agent. It was shown that the small peak existed around 1203 cm⁻¹ wavenumber, arranged as Si-O-C or Si-O-Si band, which was associated with silane crosslinks. The results also suggest that the silane coupling agent more effectively interacted with RBF than with GBP (Kim et al. 2012). Thus, bamboo material, especially after being treated with silane coupling agent, is an effective filler in controlling thermal expansion of the filled plastic composites.

### Table 2. Effect of PCC Content on Thermal Expansion of PCC-GBPFilled Composites

<table>
<thead>
<tr>
<th>System</th>
<th>PCC a (wt %)</th>
<th>Linear Coefficient of Thermal Expansion (10⁻⁵ /°C)</th>
<th>20 to 60°C bc</th>
<th>60 to -30°C</th>
<th>-30 to 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-PP&amp;PE</td>
<td>0</td>
<td>149.8(5.0)G</td>
<td>125.4(4.7)F</td>
<td>108.7(3.1)F</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>76.72(2.9)F</td>
<td>60.49(0.9)E</td>
<td>48.05(1.1)E</td>
<td></td>
</tr>
<tr>
<td>R-PP&amp;PE/GBP/PCC</td>
<td>6</td>
<td>67.33(1.0)E</td>
<td>54.52(3.2)D</td>
<td>44.58(1.5)CD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>53.41(0.4)CD</td>
<td>51.48(0.7)BC</td>
<td>42.72(0.4)A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>49.91(2.7)BC</td>
<td>48.51(0.9)BC</td>
<td>40.12(1.6)A</td>
<td></td>
</tr>
<tr>
<td>R-PP&amp;PE/TGBP/PCC</td>
<td>0</td>
<td>64.06(0.5)E</td>
<td>56.07(1.0)D</td>
<td>46.83(0.8)DE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>56.23(1.2)D</td>
<td>49.75(1.0)BC</td>
<td>42.49(2.1)BC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>46.75(5.2)AB</td>
<td>48.13(2.1)B</td>
<td>40.47(0.4)AB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>44.05(0.7)A</td>
<td>43.35(2.5)A</td>
<td>38.93(2.3)A</td>
<td></td>
</tr>
</tbody>
</table>

a The content of each filler was based on the total composite weight.
b Mean values with the same capital letter for each property are not significantly different at the 5% significance level.
c Numbers in the parenthesis are standard deviation based on five specimens.
d R-PP&PE/GBP(TGBP) = 60 : 40 (wt %) fixed for all composites.
Table 3. Effect of PCC Content on Thermal Expansion of PCC-RBF Filled Composites

<table>
<thead>
<tr>
<th>System</th>
<th>PCC (^{a}) (wt %)</th>
<th>Linear Coefficient of Thermal Expansion (10(^{-6})/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 to 60°C(^{bc})</td>
</tr>
<tr>
<td>R-PP&amp;PE(^{b})</td>
<td>0</td>
<td>149.8(5.0)G</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>65.15(1.7)F</td>
</tr>
<tr>
<td>R-PP&amp;PE/</td>
<td>6</td>
<td>56.49(0.7)E</td>
</tr>
<tr>
<td>RBF/PCC</td>
<td>12</td>
<td>51.78(1.1)D</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>46.17(4.4)C</td>
</tr>
<tr>
<td>R-PP&amp;PE/</td>
<td>0</td>
<td>62.59(0.9)F</td>
</tr>
<tr>
<td>TRBF/PCC</td>
<td>6</td>
<td>54.04(0.9)DE</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>44.24(4.1)C</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>38.22(0.9)A</td>
</tr>
</tbody>
</table>

\(^{a}\) The content of each filler was based on the total composite weight.

\(^{b}\) Mean values with the same capital letter for each property are not significantly different at the 5\% significance level.

\(^{c}\) Numbers in the parenthesis are standard deviation based on five specimens.

\(^{d}\) R-PP&PE/RBF(TRBF) = 60:40 (wt%) fixed for all composites.

Fig. 4. Effect of ground bamboo particle (GBP) on thermal expansion coefficient of filled R-PP&PE composite systems (40% bamboo filler)
Figure 6 shows LCTE-PCC content plots for the composite systems with hybrid bamboo (40%) and PCC (varying percentages) fillers. For both GBP and RBF systems, measured LCTE values decreased linearly with increased PCC content. At the 18% PCC loading levels, the LCTE reductions for the temperature ranges of 20 to 60°C, 60 to -30°C, and -30 to 20°C are 34.9, 19.8, and 16.5%, respectively for the GBP system and 31.2, 22.7, and 16.9%, respectively, for the TGBP system. The corresponding values are, respectively, 29.1, 25.8, and 22.7% for the RBF system, and 38.9, 24.7, and 19.3% for the TRBF system. This is attributed to a small LCTE of PCC and reduced overall plastic volume in the composite.

Among the four bamboo material types (i.e., GBP, RBF, TGBP, and TRBF), the GBP system had the highest LCTE, and TRBF had the smallest LCTE values at all PCC loading levels. In comparison with RBF, GBP contained more lignin and hemicellulose (Kim et al. 2012) as the fiber refining processes under high temperature and pressure effectively reduced lignin and hemicelluloses parts of bamboo fibers for RBF material. RBF with higher cellulose content and more hydroxyl groups (Salmen et al. 2011) helps enhance bonding between bamboo fiber and plastic matrix and helps induce more silane crosslinks after silane treatment (Belgacem et al. 2004; Kim et al. 2012). The net effect is an overall improvement of composite properties, including LCTE values. This argument is further supported through morphological properties. Figure 7 shows a morphological comparison of TGBP and TRBF composite systems. The interfacial gaps between bamboo filler and polymer matrix are seen in TGBP-filled composite (Left), and the enhanced interfacial adhesions are observed in TRBF-filled composites (Right).
**Fig. 6.** Effect of PCC contents on thermal expansion (20 to 60°C) of GBP (Upper) and RBF (Lower) filled R-PP&PE composite systems (40% bamboo filler). Lines showing linear regression fits.
CONCLUSIONS

1. Thermal expansion of the composites decreased with increased PCC and bamboo filler loading levels.

2. The composite system with RBFs had smaller LCTE values than those from systems with GBPs.

3. The use of silane treatment on bamboo fiber/particle surface helped with their bonding to the plastic matrix, leading to further reduction of LCTE values for both GBP and RBF systems.

4. The observed behavior of reduced LCTE is attributed to a small filler LCTE value, reduced over-plastic volume, and enhanced interfacial bonding with treated materials.

5. Thus, hybrid bamboo and PCC fillers are suitable materials for controlling the thermal expansion of the composite materials caused by temperature changes.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from Louisiana Board of Regents [Contract Number: LEQSF-EPS(2011)-OPT-IN-04], from the United States Department of Agriculture Grant (68-3A75-6-508), and from the Department of Education, Jiangsu, China.

REFERENCES CITED
