Mechanical properties and extended creep behavior of bamboo fiber reinforced recycled poly(lactic acid) composites using the time–temperature superposition principle

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HIGHLIGHTS

- Mechanical and creep properties of BFRPCs with various fiber loadings were studied.
- BFRPC with 60 wt% fiber exhibited the best flexural properties and creep resistance.
- The $E'$ of BFRPCs above the $T_g$ of rPLA increased with increasing fiber loading up to 60 wt%.
- Nearly perfect superposition of master curves was obtained using the TTSP method.
- The modulus of all BFRPCs reduced in the range of 27–40% over a 30-year period.

GRAPHICAL ABSTRACT

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ABSTRACT

The present study investigates mechanical properties and creep resistance of bamboo fiber reinforced recycled PLA composites (BFRPCs). The results revealed that the modulus of rupture and modulus of elasticity of BFRPCs increased with increasing bamboo fiber loading up to 60 wt% and then declined sharply as the fiber increased further. Short-term accelerated creep tests on BFRPCs were conducted at a series of elevated temperatures by time–temperature superposition principle. As a result, the BFRPC with 60 wt% fiber exhibited the best creep resistance among all the BFRPCs, and then decreased when the fiber loading was more than 70 wt%.

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1. Introduction

In recent years, the depletion of fossil fuels and the growth of environmental awareness have motivated many researchers to develop bio-materials. Consequently, natural fiber biocomposites, such as wood plastic composites (WPCs), have become important in composite science. WPCs are of great interest in construction applications due to their advantages, including dimensional stability, moisture resistance, mechanical properties, and durability [1–4]. However, one of their disadvantages is the change in WPC mechanical properties with temperature, leading to limits in wider applications. Therefore, it is also important to investigate the temperature sensitivity of WPC properties, such as creep behavior, because WPCs exhibit a strong time–temperature dependent response. On the other hand, it is time-consuming and...
expensive to conduct full-scale creep tests in a normal time scale. In this study, an accelerated creep test based on the time–temperature superposition principle (TTSP) was implemented to predict the long-term creep response. Methods using this principle have been employed to confirm that TTSP is applicable to various WPCs [5–8].

Among bio-based polymers, poly(lactic acid) (PLA), which is made from renewable raw agricultural materials, is a versatile biodegradable polymer used in many applications. PLA has great potential to replace petroleum-based plastics due to its high stiffness and strength compared with polystyrene. However, the drawbacks of PLA include its brittleness, low thermal resistance, and slow crystallization rate, which limit wider applications. To overcome these drawbacks and reduce fossil fuel consumption, natural fiber reinforced PLA has been studied to improve the characteristics of PLA and obtain fully bio-based composites [9–11]. Compared with inorganic fillers, natural fibers such as wood, bamboo, flax, ramie, jute, kenaf, and hemp have numerous advantages: low cost, low density, high toughness, good specific strength properties, renewability, and biodegradability [9,12–15]. In particular, bamboo fiber reinforcement has great potential to improve the thermal and mechanical properties of PLA composites due to its excellent physical properties [16–19]. Additionally, bamboo fiber is easily obtained because of its wide distribution across Asia [20] and fast growth rate in comparison with other plants having fibers [21–23]. Furthermore, bamboo fiber reinforced PLA composites (BFRPCs) would utilize large amounts of bamboo shavings and sawdust, by-products of the bamboo-processing industry. To date, investigations into BFRPCs focused primarily on the effects of various attributes on the thermal and mechanical properties of the composites, such as fiber type, fiber loading, functional additives, and fiber modification to increase the compatibility between the composites. The creep compliance is given by $\frac{\Delta \varepsilon}{\Delta \sigma}$ as a function of elapsed time ($t$), where $\frac{\Delta \varepsilon}{\Delta \sigma}$ is the creep compliance at time $t$, and $t$ is the shift factor. The master curve of creep compliance and the activation energy of the glass transition relaxation were also determined by DMA. Creep and creep recovery cycles were conducted at isothersms between 20 and 50 °C in intervals of 5 °C. A three-point bending mode with a span of 40 mm was used. For each isootherm, 30% of the average flexural strength was applied for 1 h, followed by a 1 h recovery period.

2. Materials and methods

2.1. Preparation of bamboo fibers and recycled poly(lactic acid)

Dried shavings from 3-year-old kei-chiku bamboo (makino bamboo; Phyllostachys makinoi Hayata) were provided by the local bamboo-processing factory. Bamboo fibers were prepared by hammer-milling and sieving fibers between 30 and 60 mesh were investigated. A recycled PLA (rPLA) was purchased from Orbit Polymers Co., Ltd. (Taichung, Taiwan) and had a melting temperature of 145–155 °C.

2.2. Composite panel manufacture

Manufacturing BFRPCs: the flat platen pressing process was applied in our previous papers [2,27]. The weight ratios of the oven-dried bamboo fibers (moisture content <3%) to rPLA powder were 5/95, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, and 80/20 (wt%). The density of the BFRPCs was 1200 ± 30 kg/m$^3$. The dimensions of the BFRPCs were samples 300 mm x 200 mm with a thickness of 4 mm. All BFRPCs were produced in a two-step pressing process as follows: (1) hot pressing (2.9 MPa) at 175 °C for 3 min; and (2) finishing by cold pressing until the temperature of BFRPCs decreased to 30 °C.

2.3. Flexural properties

The modulus of rupture (MOR) and modulus of elasticity (MOE) of the samples were determined by a three-point static bending test with a loading speed of 1.7 mm/min and with a span of 64 mm (ASTM D790-07). The dimensions of the sample were 80 mm x 16 mm with a thickness of 4 mm. Five samples of rPLA composites with various fiber loading were tested at 20 °C. The samples were conditioned at 20 °C and 65% relative humidity for a week before testing.

2.4. Dynamic mechanical analysis (DMA) and short-term accelerated creep test

The dynamic mechanical properties of the BFRPCs were measured in single cantilever bending mode (DMA 8000, PerkinElmer) at a heating rate of 2 °C/min and a frequency of 1 Hz. The storage modulus ($E'$) and loss tangent (tan δ) were recorded in the range of 25–160 °C. The dimensions of the sample were 30 mm x 10 mm with a thickness of 4 mm. Additionally, according to TTSP, a dynamic mechanical analysis (DMA) was carried out to determine the glass transition temperature ($T_g$) and active energy ($E_a$). These experiments were conducted in dual cantilever mode under isochronal conditions at frequencies of 4, 8, 12, 16, 20, 24, 28, and 32 Hz. The dimensions of the sample were 50 mm x 10 mm with a thickness of 4 mm. Tests were conducted in the range of 25–120 °C at a scanning rate of 1 °C/min.

TTSP, using a real-time short-term creep response at elevated temperatures, is used to predict the long-term creep performance of the composites. The creep compliance is given by $S(t) = S(t) + (t/t_s)$, where $S(t)$ is the creep compliance as a function of temperature and time, $T$ is the reference temperature, $T_s$ is the elevated temperature, and $t_s$ is the shift factor. The master curve of creep compliance and the activation energy of the glass transition relaxation were also determined by DMA. Creep and creep recovery cycles were conducted at isotherms between 20 and 50 °C in intervals of 5 °C. A three-point bending mode with a span of 40 mm was used. For each isootherm, 30% of the average flexural strength was applied for 1 h, followed by a 1 h recovery period.

2.5. Static analysis

All results are expressed as the mean ± SD. The statistical analysis was performed with one-way ANOVA and Scheffe’s post hoc test. The results with $P < 0.05$ were considered to be statistically significant.

3. Results and discussion

3.1. Density, moisture content, and static flexural properties of the samples

The density, moisture content, and flexural properties of the BFRPCs are summarized in Table 1. In general, density and moisture content may directly affect the flexural properties of a polymer composite. Except for the density of BFRP80 (999 kg/m$^3$), there was no statistical significance ($P > 0.05$) in density among all composites (1200 kg/m$^3$). The decrease in the density of BFRP80 is attributed to the observable thickness swelling that occurred after compression molding. It can be seen that moisture content increased with increasing fiber loading. With the addition of 80 wt% fiber to PLA, the moisture content increased significantly from 0.4% (BFRPC0) to 3.9% ($P < 0.05$). As expected, the addition of more fiber to a matrix leads to higher moisture content because...
the hydrophilic fiber easily absorbs water from the atmosphere. The water in composites can be stored in the fiber cell walls, the cell lumens, and/or the voids between the lignocellulose and the polymer matrix [28,29]. As shown in Table 1, the moisture content of all the BFRPCs is far below fiber saturation point. Accordingly, in the present study, it seems that the water was located primarily in the cell walls of the bamboo fibers.

On the other hand, Table 1 shows that both the modulus of rupture (MOR) and modulus of elasticity (MOE) of BFRPCs increased with increasing fiber loading up to 60 wt%, at which point a drastic decrease in the flexural properties was observed when the fiber loading was more than 60 wt%. Thus, the BFRPC with 60 wt% fiber exhibited the best flexural properties, with MOR and MOE values of 56.1 MPa and 7.28 GPa, respectively. Stiffer bamboo fiber plays a role in stress transition in a composite, leading to improvement of the flexural properties. However, when the fiber loading reached 80 wt%, the MOR and MOE decreased to 21.8 MPa and 3.18 GPa, respectively. The mechanical properties of the composites are negatively affected by various factors, including poor fiber dispersion caused by intermolecular hydrogen bonding and the wide polarity differences of the surfaces that retard the polymer/fiber bonding interaction [30]. The decline in flexural properties may be attributable to the aggregation of the woody materials. Poor interfacial adhesion leads to composites with poor mechanical properties [27,31–33]. Reports by Lee et al. [2,34] demonstrated that adhesion leads to composites with poor mechanical properties, and that the addition of the appropriate bamboo fiber can significantly improve the thermal resistance of rPLA composites. The latter peak is the maximum tan δ peak due to the annealing crystallization of the PLA matrix. A similar result was also reported by Suryanegara et al. [37]. However, when bamboo fibers were added into the rPLA matrix, the E' of BFRPCs increased with increasing fiber loading up to 60 wt% at temperatures above Tg. Among all the BFRPCs, it can be seen that BFRPC60 exhibited the highest thermal resistance: the E' increased dramatically from the original 1.73 × 10^3 to 1.27 GPa at 98 °C. This result indicated that the addition of the appropriate bamboo fiber can significantly improve the thermal resistance of rPLA composites.

Table 1. Density, moisture content, and flexural properties of various BFRPCs.

<table>
<thead>
<tr>
<th>Code</th>
<th>Fiber loading (wt%)</th>
<th>Density (kg/m^3)</th>
<th>Moisture content (%)</th>
<th>Flexural properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFRPC0</td>
<td>0</td>
<td>1176 ± 32 ♦</td>
<td>3.5 ± 0.3 ♦</td>
<td>49.7 ± 5.1 ♦</td>
</tr>
<tr>
<td>BFRPC5</td>
<td>5</td>
<td>1193 ± 36 ♦</td>
<td>0.9 ± 0.2 ♦</td>
<td>14.6 ± 1.0 ♦</td>
</tr>
<tr>
<td>BFRPC10</td>
<td>10</td>
<td>1176 ± 32 ♦</td>
<td>1.4 ± 0.1 ♦</td>
<td>29.1 ± 1.1 ♦</td>
</tr>
<tr>
<td>BFRPC20</td>
<td>20</td>
<td>1195 ± 12 ♦</td>
<td>2.3 ± 0.3 ♦</td>
<td>38.8 ± 2.2 ♦</td>
</tr>
<tr>
<td>BFRPC30</td>
<td>30</td>
<td>1247 ± 15 ♦</td>
<td>2.7 ± 0.2 ♦</td>
<td>46.5 ± 1.2 ♦</td>
</tr>
<tr>
<td>BFRPC40</td>
<td>40</td>
<td>1228 ± 12 ♦</td>
<td>2.9 ± 0.2 ♦</td>
<td>56.1 ± 2.6 ♦</td>
</tr>
<tr>
<td>BFRPC50</td>
<td>50</td>
<td>1155 ± 19 ♦</td>
<td>3.5 ± 0.3 ♦</td>
<td>47.9 ± 5.1 ♦</td>
</tr>
<tr>
<td>BFRPC60</td>
<td>60</td>
<td>1179 ± 19 ♦</td>
<td>0.7 ± 0.1 ♦</td>
<td>14.6 ± 1.0 ♦</td>
</tr>
<tr>
<td>BFRPC70</td>
<td>70</td>
<td>1133 ± 46 ♦</td>
<td>1.3 ± 0.1 ♦</td>
<td>29.1 ± 1.1 ♦</td>
</tr>
<tr>
<td>BFRPC80</td>
<td>80</td>
<td>1193 ± 36 ♦</td>
<td>1.4 ± 0.1 ♦</td>
<td>29.1 ± 1.1 ♦</td>
</tr>
</tbody>
</table>

Values are means ± SD (n = 5). Different letters within a column indicate significant difference at P < 0.05.

Hong et al. [35] noted that dynamic mechanical flexural properties exhibit sensitivity to the interfacial adhesion between the lignocellulose and the polymer matrix. Fig. 1 shows the plots of the storage modulus (E') and loss tangent (tan δ) as a function of fiber loading level. As illustrated in Fig. 1a, a noticeable drop in E' of all the composites was observed near the Tg (ca. 98 °C) of the PLA due to the increase in chain mobility of the PLA matrix [36]. For BFRPC0 (neat rPLA), the E' dropped dramatically to 1.73 × 10^3 GPa at 98 °C and then increased to 3.83 × 10^3 GPa at 120 °C. The latter increase in E' can be attributed to the annealing crystallization of the rPLA matrix. A similar result was also reported by Suryanegara et al. [37]. However, when bamboo fibers were added into the rPLA matrix, the E' of BFRPCs increased with increasing fiber loading up to 60 wt% at temperatures above Tg. Among all the BFRPCs, it can be seen that BFRPC60 exhibited the highest thermal resistance: the E' increased dramatically from 1.73 × 10^3 to 1.27 GPa at 98 °C. This result indicated that the addition of the appropriate bamboo fiber can significantly improve the thermal resistance of rPLA composites.

This section will outline the use of TTSP to predict the long-term creep behavior of the composites from short-term accelerated creep tests at a range of elevated temperatures. DMA is appropriate for this test because it is capable of testing at a wide range of temperatures. Using BFRPC60 as an example, Fig. 2a shows the creep compliance with elevated temperature in the actual time for the entire duration, and Fig. 2b shows the unshifted and shifted short-term creep compliance curves of BFRPC60 at all the temperatures tested plotted against the test time in a log scale. According to the reduced time using a shift factor (β) calculated from TTSP, the creep curves at elevated temperatures were shifted along the time axis to the right.

3.3. Extended creep behavior of BFRPCs using TTSP

Regarding the shift factor, there are two methods that are being used for WPCs: the William–Landel–Ferry (WLF) equation and the Arrhenius equation. For the WLF equation, the material is tested at working temperatures in the range from Tg to Tg + 100 °C [38].
However, PLA is not appropriate for this method because it exhibits a rubbery state or melting state in this working temperature range (60–160 °C). Therefore, the Arrhenius equation was used for BFRPC in this study. The shift factor, \( \log \alpha_T \), can be related to temperature and activation energy using the following equation:

\[
\log \alpha_T = \frac{E_a / R}{(T - T_{ref})} \times \log e
\]

where \( \alpha_T \) is the horizontal shift factor, \( E_a \) is the activation energy of the glass transition relaxation (kJ/mol), \( T_{ref} \) is the reference temperature (K), and \( R \) is the universal gas constant (8.314 J/K/mol) [5,39]. \( E_a \) was estimated from the frequency dependence of the \( T_g \) of BFRPC measured from DMA and must be overcome for the occurrence of molecular motion causing the transition [40].

Fig. 2c shows tan \( \delta \) curves for a range of frequencies at a heating rate of 1 °C/min. The \( T_g \) at different frequencies was determined from the peak of the tan \( \delta \) curves and the \( E_a \) is calculated from the slope of the plot of \( \ln(f) \) versus \( 1/T_g \) using the following equation:

\[
E_a = -\frac{R}{f} \frac{d(\ln(f))}{d(1/T_g)}
\]

where \( f \) is frequency (Hz) and \( T_g \) is the glass transition temperature. As shown in Fig. 2d, frequency on a log scale versus the inverse of \( T_g \) was plotted.

A linear regression was performed on the slope and \( E_a \) was calculated. According to this calculation, the effect of bamboo fiber loading level on the \( E_g \) of BFRPCs is shown in Table 2. The result indicated that the \( E_a \) values of BFRPCs with various amount of bamboo fiber were in the range of 428.5–493.2 kJ/mol. Consequently, the creep compliance master curves of the various BFRPCs generated using shift factors are estimated from a constant activation energy assumption. The master curves were modeled with the Findley power law [41], which is presented in following equation: \( S(t) = S_0 + \alpha t^g \), where \( S(t) \) is the time-dependent compliance, \( S_0 \) is the instantaneous elastic compliance, \( \alpha \) and \( b \) are constant numbers, and \( t \) is the elapsed time. The creep curves of the various BFRPCs in a log time scale are shown in Fig. 3a, and the result revealed that the compliance decreased with increasing fiber loading up to 60 wt%. Among all the BFRPCs, the compliance of BFRPC60 was the lowest during the creep duration. When 80 wt% fiber was added in the rPLA matrix, however, the compliance increased dramatically. Fig. 3b shows the creep master curves in a normal time scale; the instantaneous elastic compliances (\( S_0 \)) and the predicted reductions in the modulus levels of all the BFRPCs over 1–30 year periods are tabulated in Table 2. The \( S_0 \) of BFRPC60 was the lowest (0.23 GPa) among all the BFRPCs. For the predicted compliance, BFRPC30 showed 0.42, 0.44, 0.46, and 0.47 GPa \(^{-1} \) at 1, 5, 15, and 30 years, respectively. Once the fiber loading increased to 60 wt%, the predicted compliance declined to 0.33, 0.36, 0.37, and 0.39 GPa \(^{-1} \) at 1, 5, 15, and 30 years, respectively. These results implied that the increase in bamboo fiber loading significantly improved the creep resistance of BFRPCs due to the better stiffness and heat conduction of the bamboo fiber. These findings are similar to the flexural properties data. However, when the fiber loading reached 80 wt%, like BFRPC80, the predicted compliance of BFRPC80 was not detectable because the composite was fractured at less than 1-year period. Furthermore, in order to estimate the creep resistance of a sample under long-term conditions, the reduction in modulus was calculated by the following equation: modulus reduction (%) = \( 1 - S_0/S(t) \) \times 100 [6]. As shown in Table 2, the modulus of all BFRPCs reduced in the range of 27–40% over a 30-year period. However, according to the increase

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**Fig. 2.** The creep compliance of BFRPC60 at elevated temperatures in the actual test (a). Unshifted and shifted creep compliance of BFRPC60 using a reference temperature of 20 °C against the test time in a log scale (b). Tan \( \delta \) curves for a range of frequencies at a heating rate of 1 °C/min (c). Frequency in a log scale versus the inverse of \( T_g \) (d).
Table 2

<table>
<thead>
<tr>
<th>Code</th>
<th>$S_0$ (GPa$^{-1}$)</th>
<th>$a$ (GPa$^{-1}$)</th>
<th>$b$ (GPa$^{-1}$)</th>
<th>Reduction in modulus (%)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>BFRPC20</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BFRPC50</td>
<td>0.54</td>
<td>3.47 x 10$^{-4}$</td>
<td>0.32</td>
<td>0.63</td>
<td>0.69</td>
</tr>
<tr>
<td>BFRPC70</td>
<td>0.34</td>
<td>7.21 x 10$^{-3}$</td>
<td>0.14</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>BFRPC90</td>
<td>0.23</td>
<td>9.68 x 10$^{-3}$</td>
<td>0.13</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>BFRPC110</td>
<td>0.25</td>
<td>7.83 x 10$^{-3}$</td>
<td>0.14</td>
<td>0.34</td>
<td>0.36</td>
</tr>
<tr>
<td>BFRPC150</td>
<td>1.77</td>
<td>1.01 x 10$^{-3}$</td>
<td>0.18</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

$S(t) = S_0 e^{at}$, where $S(t)$ is the time-dependent compliance, $S_0$ is the instantaneous elastic compliance, $a$ and $b$ are constant numbers. ND: not detectable.

Fig. 3. Creep master curves of various BFRPCs in a log time scale (a) and in a normal time scale (b) using a reference temperature of 20°C.

rate of the compliance (b value of the Findley power law). The BFRPC60 showed the smallest b value (0.13) among all the BFRPCs. Taken together, the results indicated that the 60 wt% fiber-loaded BFRPC exhibited the best creep resistance.

4. Conclusions

Bamboo fibers exhibit excellent reinforcing effects on the thermal resistance, flexural properties, and creep resistance of recycled poly(lactic acid) (rPLA) composites. Although moisture content increased with increasing bamboo fiber loading, the modulus of rupture (MOR) and modulus of elasticity (MOE) of bamboo fiber reinforced rPLA composites (BFRPCs) were enhanced with increasing fiber loading up to 60 wt%. Stiffer bamboo fiber plays a role in stress transition to improve the flexural properties of a composite. Regarding viscoelastic properties, the storage modulus ($E'$) of all the BFRPCs decreased at temperatures above $T_g$, but $E'$ increased with increasing fiber loading up to 60 wt%. In addition, the BFRPC with 60 wt% fiber exhibited the best creep resistance among all the BFRPCs according to instantaneous elastic compliance and the increase rate of the compliance of the Findley power law. These results indicate that the addition of bamboo fiber to BFRPCs significantly improved creep resistance due to the better stiffness and heat conduction of bamboo fiber. Accordingly, the addition of bamboo fibers into an rPLA matrix can improve its thermal resistance, flexural properties, and creep resistance, especially with 60 wt% fiber.

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References


