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How to improve mechanical properties of polylactic acid with bamboo fibers

Ryoko Tokoro · Duc Minh Vu · Kazuya Okubo · Tatsuya Tanaka · Toru Fujii · Takayasu Fujiura

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Abstract Bamboo fibers (BF) were mixed in polylactic acid (PLA) to improve its mechanical properties: impact strength and heat resistance. Three different types of BF were extracted from raw bamboo by either sodium hydroxide (NaOH) treatment or steam explosion in conjunction with mechanical processing. They were designated as "short fiber bundle," "alkali-treated filament" and "steam-exploded filament," respectively. Composite samples were fabricated by injection molding using PLA/BF pellets prepared by a twin-screw extruding machine. Among them, the highest bending strength was obtained when steam-exploded filaments were put into PLA matrix. Impact strength of PLA was not greatly improved by addition of short fiber bundles as well as both filaments. In order to improve the impact strength of PLA/BF composites, PLA composite samples were alternatively fabricated by hot pressing using medium length bamboo fiber bundles (MFB) to avoid the decrease in fiber length at fabrication. Impact strength of PLA/MFB composite significantly increased, in which long fiber bundles were pulled out from the matrix. The addition of BF improves thermal properties and heat resistance of PLA/BF composites due to the constraint of deformation of PLA in conjunction with crystallinity promoted by anneal (at 110 °C for 5 h).

R. Tokoro (✉)
Doshisha University, Kyotanabe-city, Kyoto 610-0394, Japan
e-mail: dte0378@mail4.doshisha.ac.jp

D. M. Vu · K. Okubo · T. Tanaka · T. Fujii
Department of Mechanical and Systems Engineering, Doshisha University, Kyoto, Japan

T. Fujiura
Kobe Steel Ltd., 1-5-5, Takazukadai, Nishiku, Hyogo 651-2271, Japan

Introduction

We are consuming lots of fossil resources such as petroleum and coal for modern industries. Public attentions are now being placed on the sustainable natural resources to reduce the global impact due to CO_2 emission. In recent years, bio-plastics having less impact to the environment are of interest, made from biomass [1–5]. Polylactic Acid (PLA) is one of versatile bio-plastics made from corns, potatoes and so on. It is now commercially available. However, applications of PLA are limited as not only structural but also semi-structural materials in the engineering field because PLA is less heat resistance and comparatively brittle. The mechanical properties at elevated temperature are not acceptable to use for automobiles, electrical- and medical appliances. One of ideas is to put some fibers into PLA to solve such problems. Glass fibers can be used, but they are not very gentle from a viewpoint of impact to the environmental. To keep the environment better, natural fibers should be used as reinforcement instead of glass fibers.

People would like to use natural plant fibers having superior mechanical properties as reinforcement if possible. One of benefits using bamboo fibers (BF) is that the bamboo is an abundant natural resource in Asia and Middle & South America. Bamboo is expected as the last sustainable plant resource which has not been massively used [6–11].

However, BF should be processed in practical use, because they often contain useless materials such as

parenchyma cells sticking on with inconvenient shape. Appropriate fiber sizes (length and diameter) should be also revealed to fabricate better PLA/BF composites because of the remarkable scatter in their dimensions. For industrial process, thermal degradation of PLA composites should be discussed because PLA is sensitive to temperature in the process.

In this study, three different types of BF are firstly prepared as reinforcement for PLA composites. PLA/BF composites are fabricated, and their bending and impact properties are examined in order to find which fiber dimensions are appropriate from a viewpoint of mechanical performance of PLA/BF composites. Then, thermal properties of PLA/BF composites are also examined using DSC (Differential Scanning Calorimeter) and DMTA (Dynamical Mechanical Thermal Analysis). Finally, annealing is applied to PLA/BF composites for promoting crystallization of PLA.

Materials

Matrix

Poly-L-lactic acid, a typical biodegradable polymer made from corn was used as matrix. Two types of PLA were prepared in this study. DSC thermograms for PLA resins presently used are shown in Fig. 1.

Polylactic acid in pellet form

LACEA H-100J was supplied by Mitsui Chemicals, Inc. The melt flow index (MFI) for PLA pellets is 8 g/10 min (190 °C, 2.16 kg). T_g and T_m are 55 and 171 °C, respectively. The molecular weight (M_w) of PLA pellets is about 120,000 g/mol.

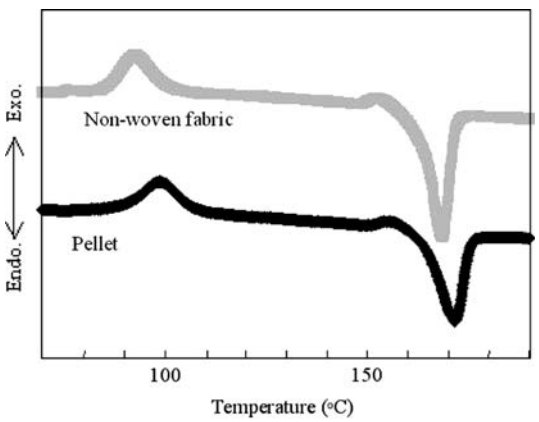

Fig. 1 DSC thermograms of PLA

Polylactic acid in non-woven fabric form

A non-woven fabric of PLA, TERRAMAC span bond, was supplied by Unichika Co., Ltd. The PLA fabric thickness is about 0.04 mm. T_g and T_m for the non-woven PLA fabric are 58 and 165 °C, respectively. No significant differences in their properties are found between two kinds of PLAs.

Bamboo fibers

Three types of BF (fiber bundles and filaments) were prepared as reinforcement of PLA from raw bamboo (see Fig. 2).

Short bamboo fiber bundle (SFB)

Short bamboo fiber bundles consisting of dozens of filaments are mechanically extracted by rolling and cutting machines from Dendrocalams bamboo grown near Hanoi, Vietnam. At first, a bamboo tree is cut into bamboo slabs. Then, bamboo slabs are rolled into bamboo chips by a two-roller machine. Short bamboo fiber bundles are obtained from bamboo chips using a cutting machine. Many parenchyma cells are still sticking on the surface of SFB bundles.

Alkali-treated filament (ATF)

First, thin bamboo strips are put into a sodium hydroxide solution (1.5 N) at 70 °C for 10 h, taken from Moso (Chinese) bamboo grown in Kyoto, Japan. Treated bamboo strips are cyclically compressed by a pressing machine. Then, long bamboo fiber bundles are obtained by scratching with a steel comb. Long bamboo fiber bundles are cut about 30 mm long and separated into filaments (single fibers) by using a mixer. There is a little amount of parenchyma cells sticking on the alkali-treated filament surface. Dimensions of alkali-treated filaments are about 19 μm in diameter and 65 of aspect ratio.

Steam-exploded filament (SEF)

A bamboo tree is first steam-exploded to easily separate fibers (lignin and hemi-cellulose in parenchyma cells are hydrolyzed as well as in fiber bundles). Cut bamboo cylinders are put into a steam chamber. Then, the chamber is filled with over-heated steam at 175 °C and 0.7–0.8 MPa. After keeping this steam condition for 60 min, the steam pressure is suddenly released to make microscopic steam

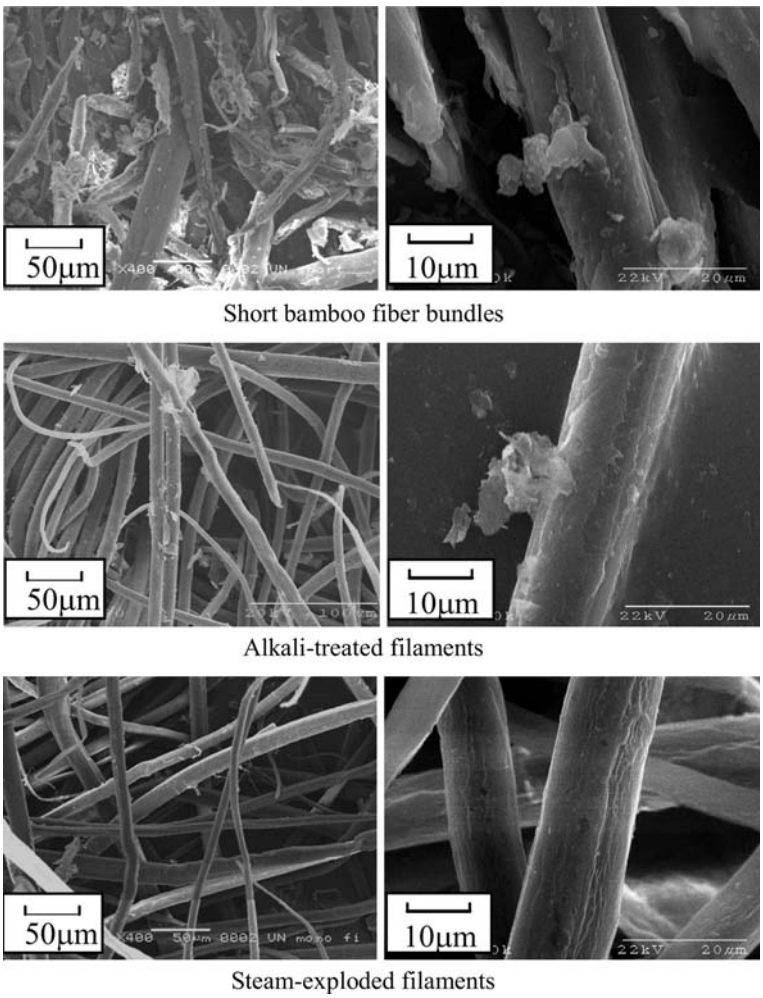

Fig. 2 SEM photographs of bamboo reinforcements

explosions occurring in the cells. The chamber is refilled with steam, and the pressure is successively released. This cycle is repeated for 11 times to assure the sufficient fracture of cell walls. Then, separated fiber bundles are treated with sodium hydroxide solution (1 N) at 100 °C for 15–20 min. Finally, steam-exploded filaments are obtained after mixing with water. Most of parenchyma cells are removed from the surface due to steam-explosion.

Experiments

Fabrication of PLA/Bamboo fiber composite samples

PLA/BF composite pellets (using SFB, ATF and SEF) were fabricated by a twin screw extruder (KTX-30, Kobe Steel Ltd., screw diameter: 30 mm, L/D = 36, L: barrel length) at 180 °C. PLA/SFB compounds were dry-blended and pelletized without water. On the other hand, at first PLA pellets and bamboo filaments were randomly dispersed onto a non-woven PLA fabric strip for PLA/ATF and PLA/SEF compounds. Then, PLA pellets and bamboo filaments were spirally rolled with the strip. Long rolls containing bamboo filaments and some PLA pellets were successively supplied into the extruder from the inlet. The content of bamboo filaments, 40% in weight can be precisely controlled when the rolls are prepared. Test specimens were fabricated by injection molding at 180 °C under 50–60 MPa. The mold temperature was 20 °C. The cooling time was 30 s.

Gel permeation chromatography (GPC) analysis

Number and weight averaged molecular weights of PLA are measured in chloroform by the gel permeation chromatography using polystyrene standards. The analyzer is composed of a Waters GPC system with columns (Shodex, LF-804) and a refractive index detector (SE-71: Showa Denko Co.).

Bending tests

Bending properties of PLA and PLA/Bamboo fiber composites are measured according to ISO 178/1993 standard. The crosshead speed is 1 mm/min. At least seven samples were tested. The fractured surfaces after bending tests are observed by a scanning electron microscope (SEM).

Impact tests

Notched Izod impact tests are performed according to ISO 180. The depth under the notch of the specimen is 8 mm.

Differential scanning calorimetry analysis (DSC)

Crystallinities of PLA specimens are determined by using a DSC analyzer (DSC-60: Shimadzu Co. Ltd.). Samples of about 10 mg are placed in aluminum cells, and heated in nitrogen atmosphere from 40 to 200 °C at a heating rate of 10 °C/min. Crystallinity X_c (%) is then evaluated using the following equation

$$X_c = \frac{\Delta H_c - \Delta H_m}{93} \times 100 \quad (1)$$

here, ΔH_c and ΔH_m denote enthalpies of crystallization and melting, respectively. The constant of 93 J/g is the fusion enthalpy of PLA.

Dynamic mechanical thermal analysis (DMT)

Dynamic mechanical properties of PLA and PLA/Bamboo fiber composites are measured by using a DMT analyzer (DMS6100: Seiko Instruments Co.) in tension. The analyzer is operated at 1 Hz from 23 to 170 °C at a heating rate of 1 °C/min.

Results and discussion

Variation of PLA's molecular weight during fabrication process of composites

The weight averaged molecular weight (M_w) of PLA pellets was 120,000 g/mol. M_w of PLA in the ATF compound made using a twin screw extruder and injection machine, decreased to 70,000 g/mol. M_w of PLA in PLA/BF composites much decreases due to fabrication process. It is known that PLA matrix is easily hydrolyzed in the presence of water [12]. Slight water absorbed in BF should degrade the PLA matrix chemically during the fabricating process.

Variation of bamboo fiber dimensions during fabrication process of composites

Dimensional change of BF is given in Table 1 due to fabrication process. The aspect ratios of alkali-treated and steam-exploded filaments after fabrication process were very low in comparison with those of original filaments before the fabrication process. In the PLA/BF composites using SEF and ATF, filaments should have been broken and become shorter due to large shearing force acting during the extruding process although their aspect ratios were still larger than that of SFB.

Bending strength and fracture behavior

Figure 3 shows the bending strengths of PLA resin and PLA/BF composites. The bending strength of PLA was not greatly improved by putting SFB due to the low aspect ratio around 5–6. The highest bending strength was obtained when steam-exploded filaments were used as reinforcement.

SEM photographs of fractured surface after bending tests are shown in Fig. 4. Fiber pull-outs were found in the fractured surface of PLA/BF composites in all cases. A small quantity of resin sticking onto SFB in comparison with that of ATF and SEF, suggests poor adhesion between SFB and PLA resin. The fractured surface of the SFB composite looks like flat in comparison with those other two composites. In the PLA/ATF and PLA/SEF composites, many fiber pull-outs are found compared to that of the composite using SFB while the strength of PLA/SFB is slightly lower than those of PLA/ATF and PLA/SEF

Table 1 Variation of bamboo fibers' dimension during fabrication process of composites

		Befoere fabrication	After injection
Shoer BF	Diameter (μm)	39.2	21.3
	Length (μm)	215	86.3
	Aspect ratio	7.5	5.7
Alkali-treated pulp	Diameter (μm)	18.8	18.1
	Length (μm)	1,220	189
	Aspect ratio	65.0	11.5
Steam-exploded pulp	Diameter (μm)	24.3	14.9
	Length (μm)	1,740	148
	Aspect ratio	137	11.3

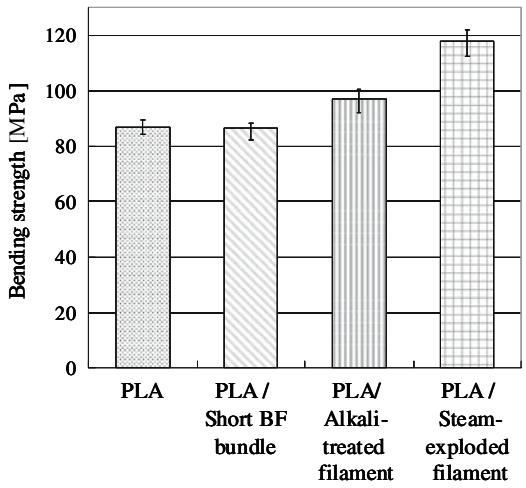

Fig. 3 Bending strength of PLA and PLA/Bamboo fiber composites

composites. The maximum strength was obtained when steam-exploded filaments were used.

To explain the strength variation with respect to reinforcement, the interfacial shear strength between matrix and reinforcement was measured by the micro-droplet test. The interfacial shear strength τ between PLA and BF was estimated by the following equation,

$$\tau = \frac{F_{\max}}{\pi d l} \tag{2}$$

where, $F_{\max}$, d and l denote the maximum load to pull out the fiber from the matrix, fiber diameter and embedded length of the fiber, respectively. The interfacial shear strengths of combinations of PLA/SFB, PLA/ATF and PLA/SEF were 4.3, 9.8 and 12.6 MPa, respectively. When bamboo is not chemically or thermally treated, there is still lignin on the surface of BF. Therefore, hydrophilic PLA weakly sticks on short fiber bundle surface because lignin is not removed. It is known from the results of principal component analysis that alkali treatment after steam explosion process (for extracting steam-exploded filaments) is effective to decrease the ratio of lignin and hemi cellulose [10]. The interfacial strength for SEF was maximum among three reinforcements. The interfacial peeling strength related to fiber debonding may be interrelated with the interfacial shear strength, and it is expected higher if τ is improved. Bending strength of fiber composites directly reflects both interfacial shear and peeling strengths between matrix and reinforcement, where short fibers are randomly dispersed and oriented as long as the reinforcement is strong and stiff in comparison with the matrix. The highest strength of PLA/SEF composite among three composites was attributed to the highest interfacial strengths between PLA and SEF.

Izod impact strength

Figure 5 shows the variation of impact strength of PLA with respect to BF. The impact strength of PLA was not greatly improved by both alkali-treated and steam-exploded filaments. Although the bending strength of PLA/SEF composite is higher than that of PLA/ATF, there is little difference in impact strength between both composites. The effect of fiber reinforcement on the impact strength of composites is more complicated than bending and tensile

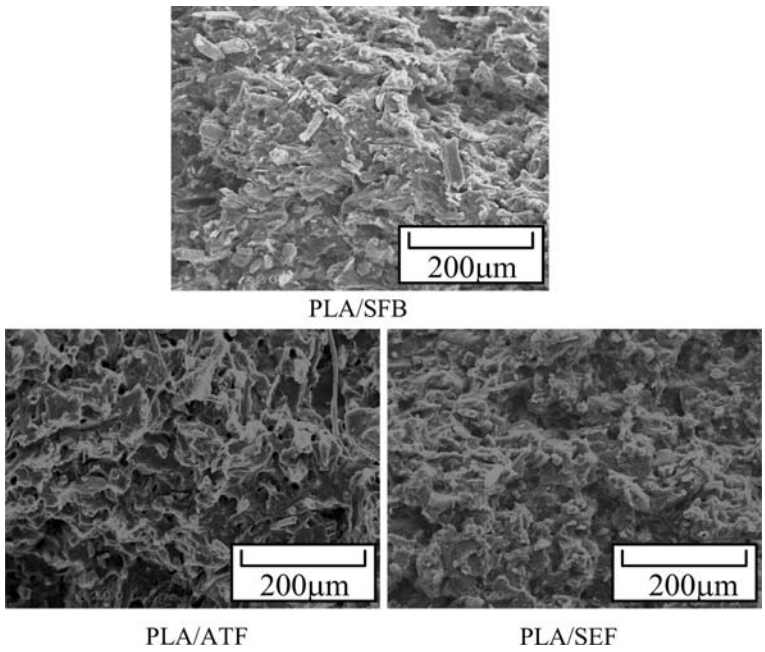

Fig. 4 SEM photographs of fractured surface after bending testing

strengths since the impact strength is attributed to the energy consumption during failure. Higher interfacial strength does not always derive higher impact strength. Medium or lower interfacial strength is sometimes appropriate to increase the dissipating energy during fracture due to fiber pull-out. In this case, longer fibers are preferable. As shown above, the fiber length as well as the aspect ratio for both filaments are not great in comparison with glass fibers in FRTP (fiber reinforced thermo-plastics) fabricated by injection molding. For short fiber reinforced composites, the longer fiber length is, the more energy consumption occurs during fiber pull-out as long as no fiber breakage occurs. It is deduced for BF bundles/filaments that; for SFB, (1) the interfacial strengths (both shear and peeling) are quite low. (2) The aspect ratio is also very low. (3) Therefore, SFB has no function to transfer the stress fiber to fiber via PLA matrix. Sometimes, SFB might be defects to initiate cracks in the material. (4) Then, the bending strength of PLA/SFB is low. (5) Short fiber length does not assure a lot of energy consumption even if fiber pull-out occurs because the force acting between fiber and matrix is low, which is one of components for energy consumption during fiber pull-out.

For ATF and SEF, (1) both interfacial strengths are stronger than those of SFB due to less xylem at the filament surface. (2) The aspect ratios are greater than that of SFB. (3) Therefore, both filaments must reinforce the PLA matrix even if they are randomly oriented. A load applied to the composite is transferred fiber to fiber via PLA matrix. The (interfacial) peeling strength between fiber and matrix is also very important to assure that fibers can transfer internal stress when the fibers are aligned not in the parallel direction to the loading axis. Low peeling strength between fiber and matrix causes fiber debonding easily. Once fiber debonding occurs, no stresses can be transferred through the fiber. No shear stress also acts along the fiber. (4) Then, the bending strengths of PLA/ATF and PLA/SEF composites are higher than that of PLA/SFB composite. (5) However, the aspect ratio for both filaments is not greater than the aspect ratio of glass fibers in FRTP although the diameter of both filaments is as thin as that of glass fibers. In addition, the interfacial shear strength between filament and PLA matrix is not high. Less energy dissipation occurs during failure than for glass fiber reinforced other thermoplastics.

The impact strength of PLA/Bamboo filaments is not as high as expected. In later session, how to improve the impact strength of PLA/Bamboo fiber composites will be discussed.

Differential scanning calorimetry analysis (DSC)

Figure 6 shows DSC thermograms of PLA and PLA/BF composites. The endothermic peak of crystallization should not be clearly appeared in DSC thermogram, if the material was crystallized. However, all diagrams of the PLA and PLA/BF composites have apparent the endothermic peak of crystallization at DSC analysis. It means that PLA was not much crystallized during injection molding with rapid cooling in a metal mold at 20 °C. Table 2 shows crystallinity X_c of PLA. When BF were put into PLA, crystallization of PLA was promoted in comparison with PLA only. Some papers show that natural fibers also could promote the crystallization of polymers on the surface of fillers as well as inorganic fillers [13]. It is found that the surface topography of the fiber is the decisive factor on crystallinity development [14]. In comparison with Table 2 and surface topography in Fig. 2, low crystallinity X_c of PLA was obtained in the composite where smooth surface topography was observed at the BF surface such as PLA/SEF composites. It is considered that the surface roughness

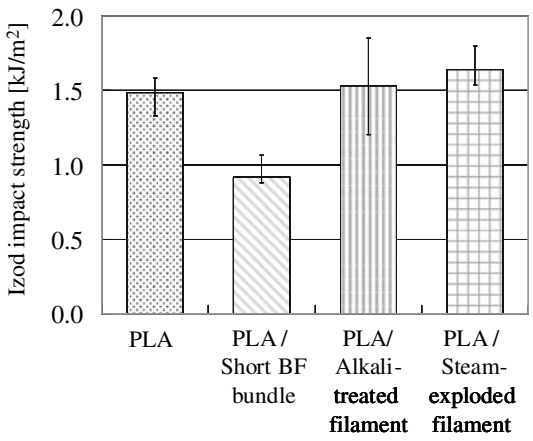

Fig. 5 Impact strength of PLA and PLA/Bamboo fiber composites

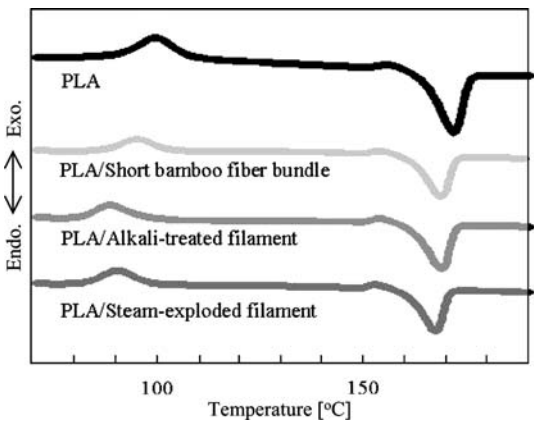

Fig. 6 DSC thermograms of PLA and PLA/BF composites

Table 2 Crystallinity of PLA

	Crystallinity of PLA (%)
PLA	25
PLA/SFB	31
PLA/ATF	29
IPLA/SEF	27

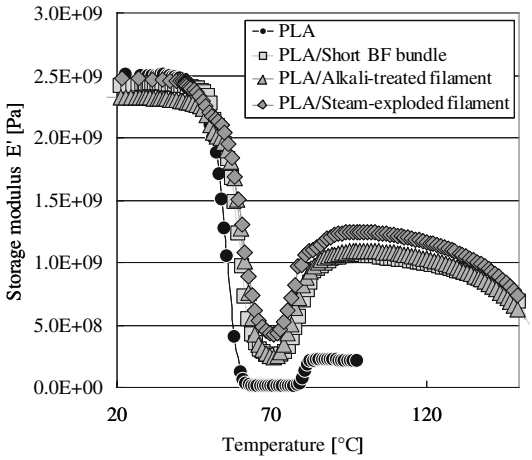

Fig. 7 Storage modulus of PLA and PLA/Bamboo fiber composites respect to temperature

of short bamboo fiber bundles was expected to initiate and growth of crystals in PLA/SFB due to defects and imperfection of SFB surface as well as PLA/ATF. On the other hand, smooth surface of steam-exploded filaments was expected that crystal formation was not initiated on the fiber surface.

Dynamical mechanical thermal analysis (DMTA)

Figures 7 and 8 show the variations of storage modulus and tan(δ) of PLA and PLA/BF composites with respect to temperature. The glass transition temperature of PLA was about 50–55 °C for pure PLA. When bamboo fibers were added into PLA, the glass transition temperature slightly shifted to at 60 °C and the decrease of storage modulus was not significant. The storage modulus of PLA/BF composites increased again at around 70 °C. This could be attributed to the cold crystallization of the semi-crystalline PLA [4]. As shown in Fig. 8, the tan(δ) peak of PLA is very sharp. The tan(δ) peak intensity of PLA/BF composites is very low compared to that of PLA. The temperature at the peak of tan(δ) became also higher when bamboo fibers were put into PLA in comparison with that of neat PLA. These results suggest that the addition of bamboo fibers slightly improves the thermal properties of PLA

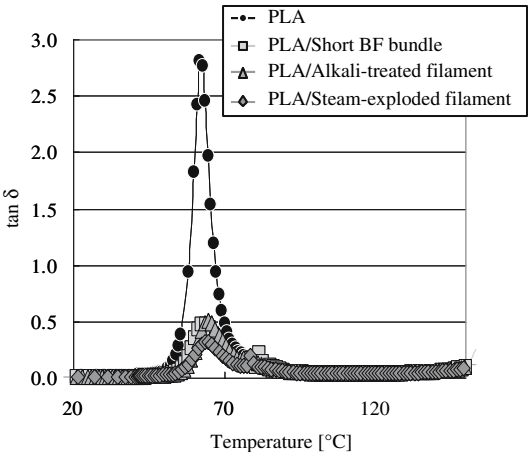

Fig. 8 Tan(δ) delta of PLA and PLA/BF composites respect to temperature

composites at the temperature around the peak of tan(δ) although they are short bundles or filaments. However, its improvement is not so sufficient for practical use of the composite. Remarkable improvement in the thermal properties is discussed later.

How to improve the impact strength of PLA/Bamboo fiber composites

In section "Izod impact strength", impact strengths of PLA and PLA/BF composites were investigated, however the increase in impact strength was not significant due to short length of pull-out fibers in conjunction with weak adhesion between PLA and bamboo fibers. In order to explicitly examine the effect of fiber length on the impact strength of PLA/BF composites, PLA was reinforced with bamboo fiber bundles whose aspect ratio was high in the composite. Samples were prepared by hot-pressing to avoid the decrease in fiber length. Details on the specimen preparation are as follows.

Materials of PLA/Medium length bamboo fiber bundle composites

Polylactic acid in sheet form

PLA sheets, Eco-sheet B441 were supplied by Osaka Jyushi Kakou Co., Ltd. These PLA sheets were fabricated by cast-extrusion (no drawing) using LACEA (pellet form). The thickness of PLA sheets is about 0.2 mm. MFI for PLA sheets is 3 g/10 min (190 °C, 2.16 kg). T_g and T_m for PLA pellets used for the sheets are the same as the previous data while the molecular weight (M_w) of the PLA sheets is

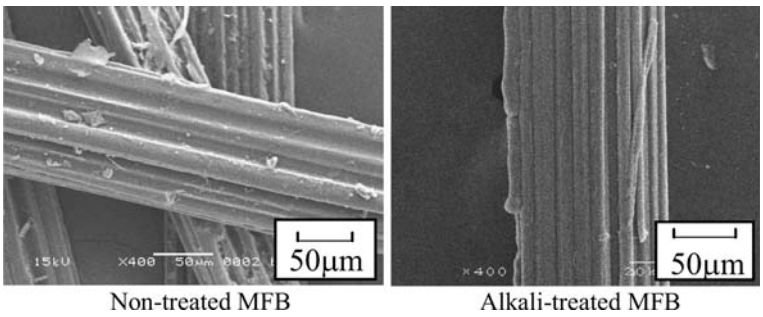

Fig. 9 SEM photographs of medium length bamboo fiber bundles

150,000 g/mol, and it is 20% higher than that of the original PLA pellets. The reason for this increase in molecular weight is not clear. Probably, the original PLA pellets for the sheets were not the same grade as PLA used for fabricating composite pellets. No information was supplied from the company.

Medium length bamboo fiber bundle (MFB)

The following two types of medium length bamboo fiber bundles were prepared as reinforcement of PLA (Fig. 9).

Non-treated MFB Thin strips of Moso bamboo, the waste of commercially available bamboo ceilings were mechanically scratched using a rotating drum on which nails were attached. There are many bundles in the bunch of scratched strips, long and short in length, thin and thick in diameter. Bamboo fiber bundles whose diameter is 45–120 μm are selected by using a sieving machine. Generally, the length of fiber bundle is proportional to the bundle diameter. The bundle length after fabricating samples will be given in the following section.

Alkali-treated MFB First, long bamboo fiber bundles were extracted by alkali treatment for 10 h at 70 °C (refer to section "Alkali-treated filament (ATF)"). Then, they were cut 5 mm. The expected fiber bundles whose nominal diameter was about 190 μm were selected by using the sieving machine.

Fabrication of PLA/Medium length fiber bundle composites

PLA/MFB composites were fabricated by using a hot pressing machine instead of the twin screw extruder in order to avoid the decrease in fiber length. To fabricate samples, PLA sheets on which MFB were randomly dispersed were laminated in the metal mold with each other. Then, they were hot-pressed at 190 °C under 10 MPa for 5 min to form a composite plate.

Impact strength of PLA/MFB

When medium length fiber bundles were put into PLA, the impact strength greatly increased as shown Fig. 10. The length of non-treated MFB was 2.98 mm while the aspect ratio was 23.0. Those of alkali-treated MFB were 6.27 and 40.5 mm, respectively. The residual aspect ratio of bamboo fiber bundles in the PLA matrix is much greater than those for other previous reinforcements. SEM photographs of fractured surface of both new composites after Izod impact testing are shown in Fig. 11. More pull-out fiber bundles whose aspect ratio is longer than those for other cases are found in the fractured surface of PLA/non-treated MFB and alkali-treated MFB composites. Because the adhesion

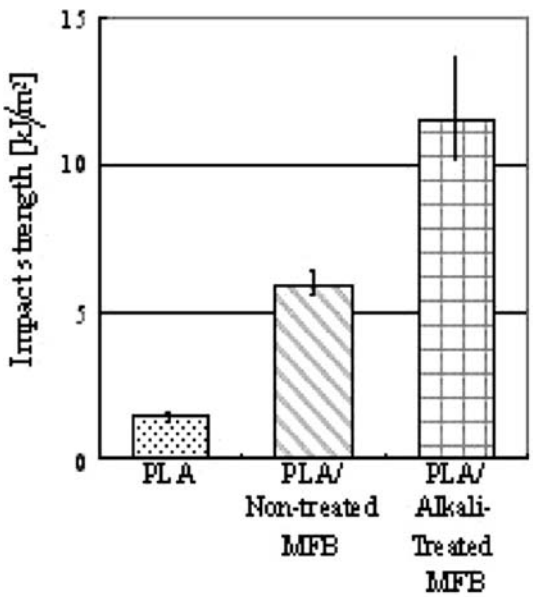

Fig. 10 Izot impact strength of PLA and PLA/Medium length fiber bundle composites

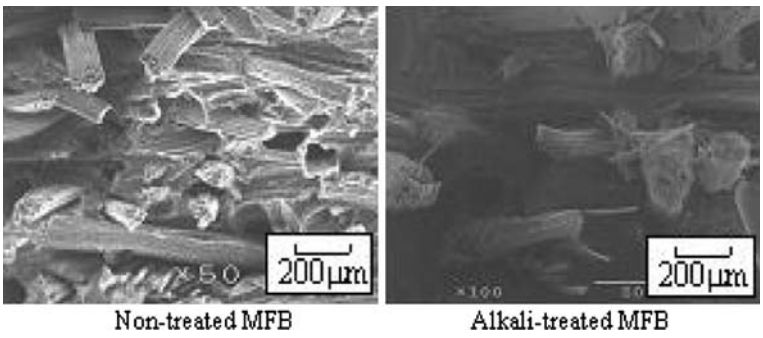

Fig. 11 SEM photographs of fractured surface after impact testing

between bamboo fibers and PLA is not enough even for the alkali-treated case, pull-outs frequently occur with consuming fracture energy resulting high fracture toughness. The impact strength evaluated by the energy dissipated during failure became high in the case of medium length bamboo fiber bundles. Impact strength of PLA/alkali-treated MFB composite was higher than that of MFB composites due to probably higher interfacial strength and higher aspect ratio than PLA/non-treated one.

How to improve thermal properties of PLA/Bamboo fiber composites by annealing

In sections "Differential scanning calorimetry analysis (DSC)" and "Dynamical mechanical thermal analysis (DMTA)", it was found that addition of bamboo fibers was effective to improve the thermal properties of PLA. However, the increase in thermal properties such as modulus was not as high as expected. Since PLA is a crystalline polymer, annealing promotes crystallization of PLA [15–19]. Mechanical properties of PLA depend on the degree of crystallinity and crystalline morphology. Furthermore, the presence of fibers as reinforcement in a crystalline polymer matrix tends to influence the microstructure of crystalline matrix at the interface if the polymeric matrix is inherently crystalline, and thereby the mechanical properties of composites at elevated temperature must also be improved.

Annealing condition for PLA and PLA/BF composites

Since it is found that cold crystallization peak appeared at around 100 °C when PLA was reinforced by kenaf fiber [20], 110 °C was selected as the annealing temperature of PLA and PLA/BF composites. To find the appropriate condition of annealing time, PLA/short bamboo fiber bundle composite whose crystallinity of PLA was the highest in all cases (shown in Table 2) was annealed while the annealing time was altered from 15 min to 5 h. Tensile properties of PLA and PLA/SFB composite after annealing were measured at room temperature (23 °C) and 80 °C. The strengths of non-annealed PLA and PLA/BF composites at 80 °C were not estimated due to large deformation of the specimens. The tensile strength retention was calculated by the following equation,

$$\text{Tensile strength retention} = \frac{\text{Tensile strength at } 80\,^{\circ}\text{C}}{\text{Tensile strength at } 23\,^{\circ}\text{C}}. \quad (3)$$

As shown in Fig. 12, the longer the annealing time is, the heat resistance for PLA is improved as well as the PLA/SFB composite. Based on the present result, both PLA and PLA/BF composite were annealed for 5 h at 110 °C in the following case. Then, the effect of annealing on the thermal and mechanical properties of PLA and PLA/BF composite were examined.

Effect of annealing on the thermal properties of PLA and PLA/BF composite

Figure 13 shows the DSC thermograms of PLA and PLA/SFB, PLA/ATF and PLA/SEF composites after annealing. The endothermic peak of crystallization disappeared in all cases (see DSC thermograms given in Fig. 6 for PLA and

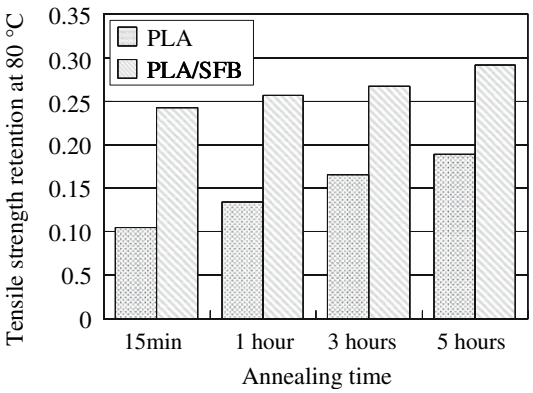

Fig. 12 Tensile strength retention of PLA and PLA/SFB at 80 °C

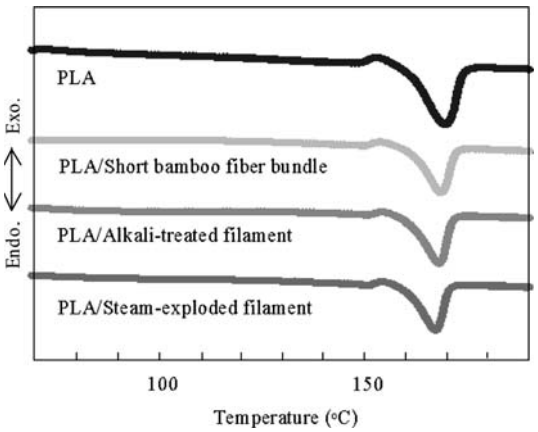

Fig. 13 DSC thermograms of PLA and PLA/BF composites after annealing

Table 3 Crystallinity of PLA after annealing

	Crystallinity of PLA (%)	Increase of crystallinity (%)[a]
PLA	42	69
PLA/SFB	50	104
PLA/ATF	50	102
PLA/SEF	43	74

[a] Increase of crystallinity with respect to non-annealing PLA

PLA/BF composites without annealing.) Table 3 shows the crystallinities (X_c) of PLA and PLA in PLA/BF composites after annealing and the increase in crystallinity X_c of PLA and PLA in PLA/BF composites after annealing with respect to the crystallinity X_c of neat PLA without annealing (24.6%). Bamboo fibers look more effective to improve heat resistance of PLA in the case of annealing. It is known that the crystal formation is not initiated on the smooth surface of reinforcement. If a reinforcing fiber had a smooth surface, bulk crystallization occurred in many locations around the fiber. Moon [21] found that in composites with a high fiber volume fraction, transcrystallinity occurred only in the interface. Spherulites are not formed in the space between fibers because the distance between fibers is too short. PLA/BF composites in the present study had high fiber content so that the bulk crystallization did not occur in small areas between fibers. The low crystallinity of PLA in PLA/SEF composites was attributed to two reasons; smooth surface and high volume fraction of fiber reinforcement. The effect of fiber content on the crystallinity of PLA was also experimentally confirmed by using two kinds of PLA/SEF composites whose fiber fraction were 20% and 50% in weight. The crystallinities of PLA in those composites were 51% and 42%, respectively. On the other hand, the crystallinity of PLA in PLA/SFB and PLA/ATF whose fiber content was 50% in weight was 50% and 47% (Table 4). In comparison with the crystallinity of PLA in PLA/SFB and PLA/ATF composites with 40% in weight of fiber fraction, those containing 50 wt.% fibers became slightly low. It indicates that crystallinity of PLA in PLA/SFB was affected insignificantly by the space of spherulites for crystal formation and growth because surface roughness of short bamboo fiber bundles was expected to initiate and grow crystals in PLA/SFB due to defects and imperfection of SFB surface as well as PLA/ATF.

Table 4 Crystallinity of PLA in PLA/BF composites with respect to fiber weight content

Fiber weight content	Crystallinity of P LA (%)		
	20 wt.%	40 wt.%	50 wt.%
PLA/SFB	–	50	50
PLA/ATF	–	50	47
PLA/SEF	51	43	42

Figures 14 and 15 show the variations of storage modulus and tan(δ) for both pure PLA and PLA/BF composites after annealing with respect to temperature. The temperature of annealed PLA where the observed modulus sharply decreases is about 50 °C, and the decrease in storage modulus is slightly low in comparison with non-annealed PLA (Fig. 7). The storage modulus of PLA/BF composites decrease less insignificant than that of PLA. Furthermore, the tan(δ) intensities of annealed PLA and PLA/BF composites are less than that of non-annealed PLA and PLA/BF composites (compared with Fig. 8), even the peak of tan(δ) still appears in annealed PLA. It is apparent that the thermal properties and heat resistance of PLA and PLA/BF composites are well improved by annealing process (at 110 °C for 5 h) in comparison with non-annealed ones.

Effect of annealing on mechanical properties for PLA and PLA/BF composites

To quantify the effect of annealing on the mechanical properties for all kinds of PLA and PLA/BF composites used in this study, tensile tests were conducted at 80 °C. The tensile strength retentions at 80 °C for annealed PLA and PLA/BF composites with respect to the tensile strength of annealed PLA resin at 23 °C are shown in Fig. 16. The PLA/steam-exploded filament composite has the highest heat resistance among all materials although crystallinity of PLA in the PLA/steam-exploded filament composite is not highest. The present study shows that the addition of bamboo fibers improved the thermal properties and heat resistance of PLA/BF composites by annealing due to deformation constraint of PLA around bamboo fibers as well as promoted crystallinity of PLA.

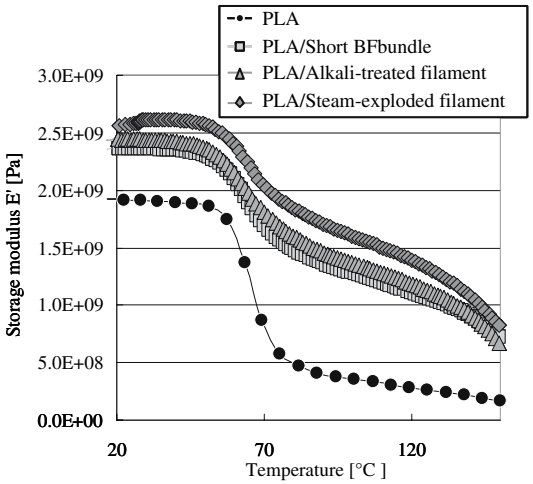

Fig. 14 Storage modulus of PLA and PLA/Bamboo fiber composites after annealing respect to temperature

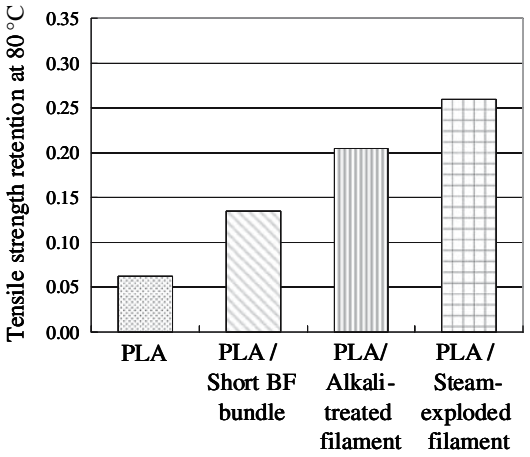

Fig. 16 Tensile strength retention of annealed PLA and PLA/BF composites at 80 °C

The previous literature shows the change in fracture toughness of PLA is due to the crystallinity derived from annealing [22]. It is important to investigate the effect of annealing on the fracture toughness of PLA and PLA/BF composites. Fracture toughness (K_{IC}) (i.e., stress intensity factor K_I at failure) for each sample was measured under Mode I loading, which was given by the following equation

here, "*F, S, B, W*" and "*a*" denote the critical load, span, thickness, width and initial crack length of the specimen, respectively. The initial crack was made by a mini-band saw and razor blade. Variations of fracture toughness and its retention respect to non-annealed PLA are shown in Fig. 17. Here, the fracture toughness retention is defined with respect to that of non-annealed PLA (3.78 MPa$\sqrt{\text{m}}$).

$$K = \frac{FS}{BW^{3/2}} f(a/W)$$
$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \quad (4)$$

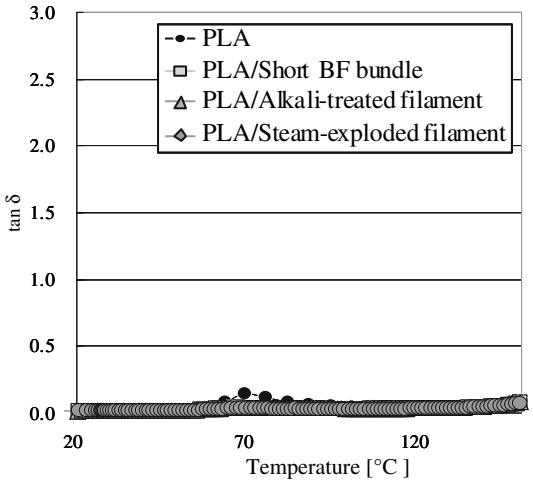

Fig. 15 Tan(δ) delta of PLA and PLA/BF composites respect to temperature

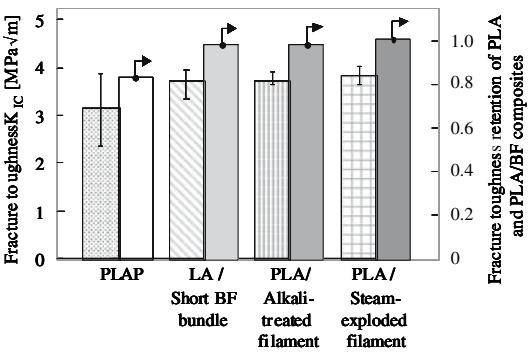

Fig. 17 Fracture toughness and fracture toughness retention of PLA and PLA/BF composites

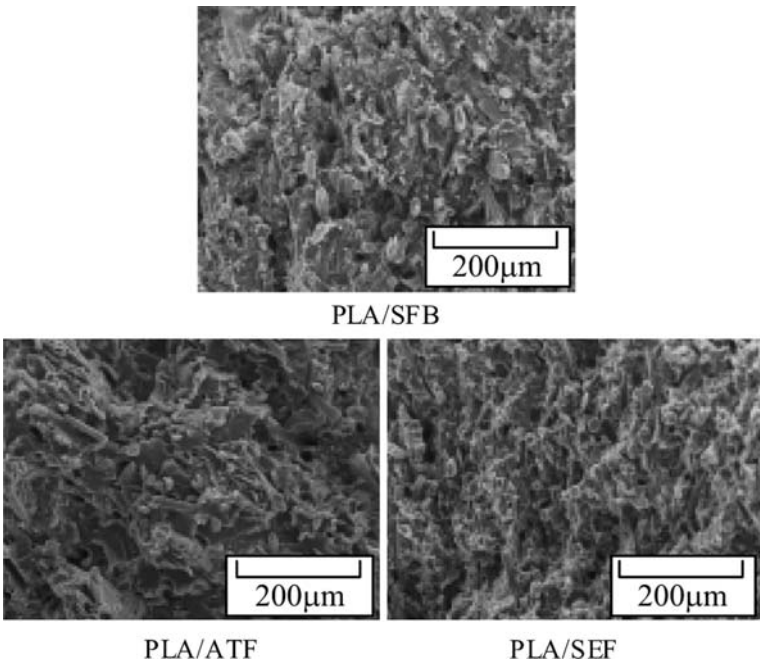

Fig. 18 SEM photographs of fractured surface after fracture toughness testing

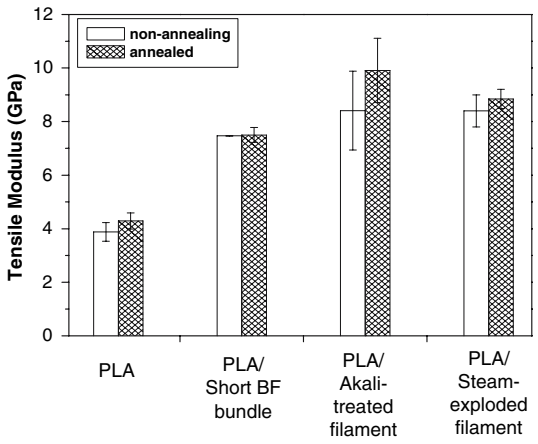

Fig. 19 Tensile modulus of PLA and PLA/BF composites at 23 °C

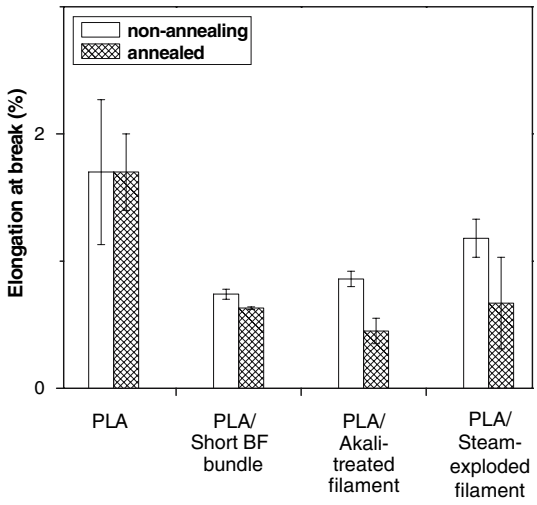

Fig. 20 Elongation at break in tensile test of PLA and PLA/BF composites at 23 °C

The fracture toughness of PLA decreases about 20% due to annealing. However, fracture toughness of PLA/BF composites is slightly improved in comparison with that of non-annealed PLA. Among three reinforcements, SEF draws the highest improvement due to annealing.

Fractured surfaces of PLA/BF composites after fracture toughness testing were observed by a SEM (Fig. 18), showing interfacial fracture between bamboo fibers and PLA resin. The highest fracture toughness retention of PLA/SEF composite was obtained due to probably better adhesion between bamboo fibers and the resin since delamination occurred and cracks propagated along the interphase. More energy was consumed if the failure occurs in the resin region due to plastic deformation of PLA.

The tensile modulus and elongation at break at 23 °C for PLA and PLA/BF composites are shown in Figs. 19 and 20. These study show that annealing makes PLA/BF composites more stiffness due to increasing crystallinity of PLA.

Annealing is effective to improve the thermal properties, heat resistance and stiffness of PLA/BF composites without decreasing the fracture toughness.

Conclusions

In this study, three types of bamboo fibers were prepared as reinforcement to improve the mechanical properties of PLA at not only room but also elevated temperatures. Bending, impact and thermal properties were evaluated for

PLA and PLA/Bamboo fiber composites. Annealing was applied to PLA/BF composites in order to improve the mechanical properties at elevated temperature. The experimental results show that:

(1) Among three bamboo fibers, steam-exploded filament most significantly increases the bending strength of PLA matrix composites due to the highest interfacial strength between PLA and steam-exploded filament.
(2) Addition of bamboo fibers promotes crystallinity of PLA in PLA/BF composites.
(3) When medium length bamboo fiber bundles are put into PLA, the impact strength greatly increases due to frequent occurrence of long fiber pull-outs.
(4) Thermal properties and heat resistance of PLA and PLA/BF composites are well improved by annealing (at 110 °C for 5 h) in comparison with non-annealed ones.
(5) Addition of bamboo fibers improve thermal properties and heat resistance of annealed PLA/BF composites in comparison with annealed PLA due to deformation constraint of PLA around bamboo fibers as well as crystallinity promoting PLA.

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