

Kenaf-Fiber-Reinforced Poly(lactic acid) Used for Electronic Products

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ABSTRACT: We have developed high-performance biomass-based plastics that consist of poly(lactic acid) (PLA) and kenaf fiber, which fixates CO₂ efficiently. Adding this fiber to PLA greatly increases its heat resistance (distortion temperature under load) and modulus and also enhances its crystallization, so the ease of molding this material is improved. Eliminating the short particles from the kenaf fiber improves its effect on the impact strength. Kenaf fiber without the particles exhibits effects on these characteristics of PLA practically comparable to the effects of glass fiber. Furthermore, adding a flexibilizer (a copolymer of lactic acid

and aliphatic polyester) to the composites improves their strength. These composites (PLA/kenaf fiber and PLA/kenaf fiber/flexibilizer) show good practical characteristics for housing materials of electronic products in comparison with petroleum-based plastics used in housing such as glass-fiber-reinforced acrylonitrile-butadiene-styrene (ABS) resin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 618–624, 2006

Key words: crystallization; fibers; renewable resources; composites

INTRODUCTION

Recently, interest has been growing in developing biomass-based plastics to reduce greenhouse gas (CO₂) emissions and to conserve petroleum resources. Therefore, attempts are being made to use such plastics in durable products, including electronic products, in addition to nondurable products, including tableware and wrapping. Biomass-based plastics include microbial products such as polyhydroxybutyrate, chemosynthesis products such as poly(lactic acid) (PLA), and chemically modified natural products such as esterified starch and cellulose acetate. Among these, chemosynthesis products have the potential for use in electronic applications because they can be fabricated with desired physical properties, such as heat resistance, mechanical properties, moldability, and recyclability. In addition, chemosynthesis products have relatively good cost performance, particularly PLA, which was first mass-produced among chemosynthesis products. Furthermore, both the fossil energy required and greenhouse gas emitted by PLA production have been confirmed to be quite low in comparison with those of petroleum-based plastics.¹ Consequently, PLA is the most important biomass-based plastic for use in electronic products at present.

However, the physical properties of PLA are insufficient for it to be widely used in electronic products. Specifically, its heat resistance and impact strength are inferior to those of conventional plastics such as acrylonitrile-butadiene-styrene (ABS) and polycarbonate. Moreover, the crystallization rate of PLA is very slow, so its production requires an annealing process that lowers productivity. In addition, the recycling properties of PLA are currently unknown because it has been mainly used for biodegradable products, rather than durable ones. In light of these issues, the impact strength of PLA can be improved by the addition of a petroleum-based flexibilizer.² In addition, its heat resistance can be improved with non-biomass-based technology such as nanocomposite technology³ and by the addition of non-biomass-based fibers such as glass fiber (GF).⁴ GF is a common filler for reinforcing plastics, but it is not an environmentally conscious material because it requires a large amount of production energy. At the same time, GF is insufficiently safe if it is included in the treatment process of crushing waste plastics.

However, little is known about how to improve these PLA properties with biomass-based materials,⁵ and in particular, no remarkable improvements in the housing of electric products have been reported yet.

Given these circumstances, kenaf has recently been gaining a lot of attention as a biomass-based additive. Kenaf has a significantly high ability to fixate CO₂, and its photosynthesis speed is at least three times higher than that of usual plants.⁶ It can absorb 1.4 times its own weight in CO₂, and its carbon content is about

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43%.⁷ Kenaf has been used mainly for textiles, paper, and animal food, but composites of kenaf fiber and PLA^{8,9} or composites of kenaf fiber and petroleum-based plastics¹⁰ have been studied recently. However, these works focused on sheet applications using compression molding for automobile and building materials, whereas housing applications using injection molding for electronic products have not been examined.

In this article, we describe the improvements of the properties of PLA, such as the heat resistance, mechanical properties, and moldability, with the addition of kenaf fiber. We also show the increase in the impact strength of PLA/kenaf fiber composites achieved by the elimination of the short particles (crushed particles) from kenaf fiber and by the addition of a flexibilizer (a copolymer of lactic acid and aliphatic polyester). In addition, it is revealed that these effects of the kenaf fiber are practically the same as those of GF.

EXPERIMENTAL

Materials

PLA (Lacty9030; weight-average molecular weight = 210,000, 94 ± 4 mol % L-isomer, as reported by the manufacturer) was obtained from Shimadzu Co. (Kyoto, Japan).

Two kinds of kenaf fibers were prepared as follows. The bast fiber was crushed to below 5 mm (average length = 3 mm, specific gravity = 1.48). We refer to this crushed kenaf fiber as C-kenaf. Another kenaf fiber was used with the bast fiber cut to prevent the generation of crushed particles (average length = 5 mm, specific gravity = 1.48). We call this long kenaf fiber (or L-kenaf). C-kenaf was obtained from Nature Trust, Inc. (Tokyo, Japan), and L-kenaf was supplied by Toho Tokushu Pulp Co., Ltd. (Tokyo, Japan).

GF (CS3PE; average length = 3 mm, specific gravity = 2.54) was obtained from Nitto Boseki Co., Ltd. (Japan). The flexibilizer (PD-150; a copolymer of lactic acid and aliphatic polyester) was supplied by Dainippon Ink & Chemicals, Inc. (Tokyo, Japan). The ABS resin (GA-501) was obtained from Nippon A&L, Inc. (Tokyo, Japan).

PLA, GF, and the flexibilizer were dried at 100°C for 7–9 h, and the kenaf fiber was dried at 80°C for 7–9 h before they were mixed to produce composites.

Composite preparation

The PLA/kenaf fiber composites (5–30 wt % kenaf fiber) and the PLA/GF composites (20 wt % GF) were prepared through the kneading of these components with a twin-screw extruder ($\phi 25$ mm, length/diameter = 10.2; Kurimoto, Ltd., Osaka, Japan) at $184 \pm 5^\circ\text{C}$. The PLA/L-kenaf composites and PLA/L-kenaf/

flexibilizer composites were also prepared with a single-screw extruder ($\phi 30$ mm, length/diameter = 26; Rikua, Ltd., Kanagawa, Japan) at $184 \pm 5^\circ\text{C}$.

Test pieces of $125 \times 13 \times 3.2$ mm³ were obtained with an injection-molding machine (EC20P, Toshiba Machine, Ltd., Shizuoka, Japan; injection temperature = 180°C, mold temperature = 25°C). All test pieces were annealed at 100°C for 4 h.

Scanning electron microscopy (SEM)

The fractured surfaces of the PLA/kenaf fiber composites were observed with a scanning electron microscope (model JSM-5410, JEOL, Tokyo, Japan). Before analysis, the samples were coated with gold to avoid charging under the electron beam.

Differential scanning calorimetry (DSC)

DSC measurements were performed with a differential scanning calorimeter (Exstar 6000, Seiko Instruments, Inc., Chiba, Japan) in a nitrogen atmosphere. The PLA/C-kenaf composites, PLA, and PLA/GF composites were melted at 200°C, cooled to 100°C at a rate of $-20^\circ\text{C}/\text{min}$, and maintained at 100°C. An exothermic peak caused by crystallization at 100°C was observed.

Viscosity

Viscosity measurements were performed with a capillary rheometer (CFT-500D flowmeter, Shimadzu). The viscosities on the shear rates of the PLA/C-kenaf fiber composites, PLA, and PLA/GF composites were observed at 200°C.

Mechanical properties

The flexural strength and flexural modulus were measured with a strength tester (model 5567 universal tester, Instron) at room temperature. The crosshead speed was 1.6 mm/min.

The notched Izod impact strength was measured with an impact tester (model C1, Toyo Seiki, Karagawa, Japan) at room temperature. The test piece was $62.5 \times 13 \times 3.2$ mm³, and the notch depth was cut to 2.54 mm. The impact resistance was calculated according to ASTM D 256.

Distortion temperature under load (DTUL)

The distortion temperature under a 1.8 MPa load was measured with a distortion temperature tester (TM-4126, Ueshima Seisakusho, Inc., Tokyo, Japan). Test pieces of $125 \times 13 \times 3.2$ mm³ were heated at a rate of $2^\circ\text{C}/\text{min}$ in an oil bath. The temperature was measured when the test piece had deflected 0.25 mm.

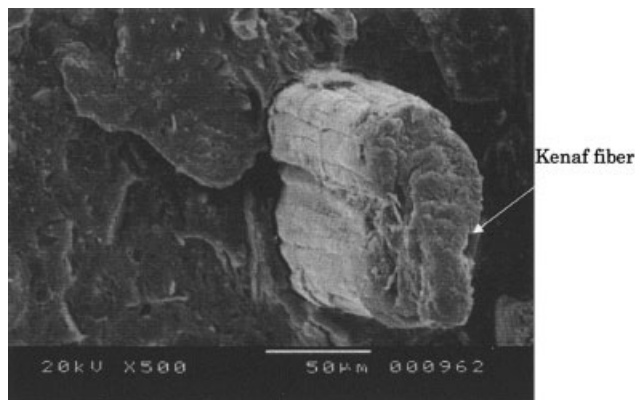


Figure 1 Cross section of a PLA/C-kenaf composite.

Recycling properties

The PLA/C-kenaf fiber composites were kneaded four times with a twin-screw extruder ($\phi 25$ mm, length/diameter = 10.2; Kurimoto). In the melt-kneading method, the fiber (20 wt %) and PLA (80 wt %) were kneaded at $184 \pm 5^\circ\text{C}$. The pellets obtained after 1, 2, and 4 cycles of the recycling process (the recycling numbers were 0, 1, and 3) were dried at 100°C for 7–9 h, and test pieces of $125 \times 13 \times 3.2 \text{ mm}^3$ were obtained by the previously mentioned injection-molding method. These test pieces were annealed at 100°C for 4 h before testing, and then the DTUL, flexural modulus, and molecular weight of PLA were measured.

RESULTS AND DISCUSSION

Effects of kenaf fiber on PLA

As shown in Figure 1, an SEM image of the PLA/C-kenaf composite, the kenaf fiber dispersed in the form of a separated fiber after the melt-kneading and injection-molding processes.

The crystallization rate of PLA was improved by the addition of kenaf fiber. Figure 2 shows the DSC curves of the PLA and PLA/C-kenaf composites. The exothermic peak of the PLA/C-kenaf composite was at 5.6 min, and that of PLA was over 30 min. In general, crystalline PLA has good mechanical properties in comparison with amorphous PLA, but the crystallization of PLA requires an annealing process after the molding.¹¹ We have discovered that the kenaf fiber promotes the crystallization of PLA and provides the possibility of making the annealing process unnecessary by the adjustment of the molding conditions. Normally, cellulose in natural plant fibers acts as a nucleating agent for the crystallization of polymers.¹² The kenaf fiber, which also contains cellulose, probably acts as a nucleating agent for PLA crystallization.

The heat resistance and modulus of PLA were greatly improved by the addition of kenaf fiber (Table I). Figure 3 shows the distortion temperature under a 1.8 MPa load of the PLA/C-kenaf composites. The distortion temperature of the PLA/C-kenaf composite exceeded that of the petroleum-based plastic (ABS) when the composite contained 15% or more kenaf

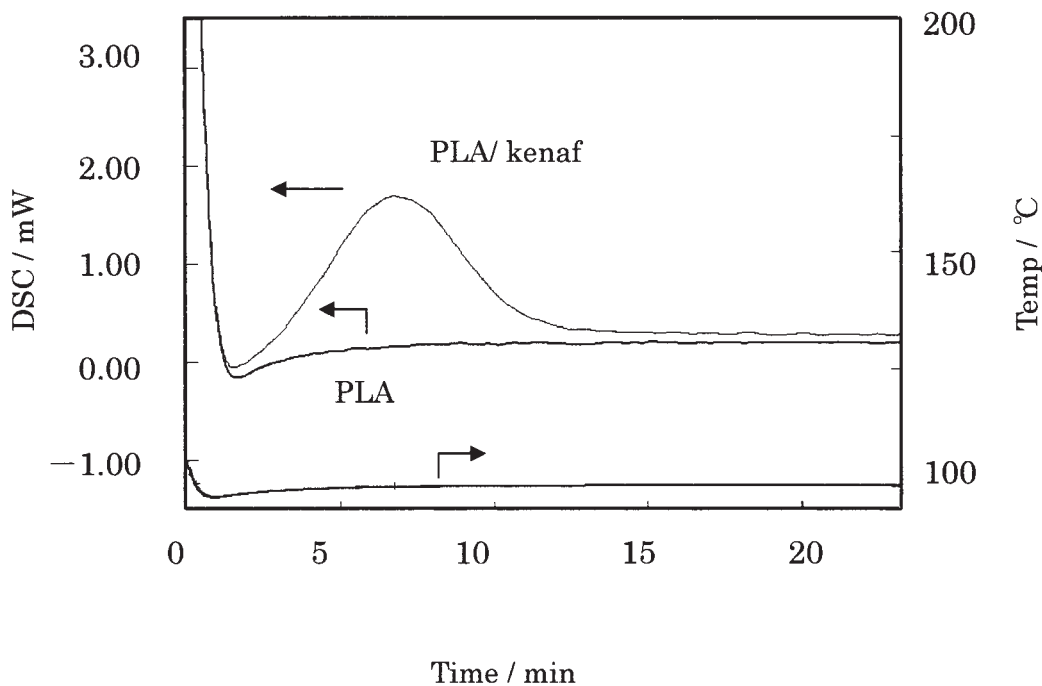


Figure 2 DSC thermograms of PLA with and without kenaf fiber (C-kenaf).

TABLE 1
Mechanical Properties of the Plastic/Fiber Composites

	PLA/C-kenaf (fiber wt%)				ABS/GF (fiber wt%)	
	0	10	15	20	0	20
DTUL (°C)	66	72	107	120	86	100
Flexural modulus (GPa)	4.5	5.4	6.3	7.6	2.1	7.3
Flexural strength (MPa)	132	111	110	93	70	110
Izod impact strength (kJ/m ²)	4.4	3.8	3.2	3.1	19	4.8

fiber. In addition, the modulus of PLA also increased according to the kenaf fiber content. Although its flexural strength was reduced by the addition of the kenaf fiber, its strength still exceeded that of ABS. However, the impact strength of the PLA/C-kenaf composite was still insufficient.

Generally, inorganic fillers, such as GF, improve the heat resistance; this is revealed by the distortion temperature and stiffness of crystalline polymers, including PLA, as mentioned later. The reason is that the inorganic fillers prevent the deformation of molded pieces of these plastics¹³ and promote the crystallization of the plastics on the surface of the fillers. The kenaf fiber probably has the same synergistic effect as inorganic fillers in improving heat resistance and stiffness.

As shown in Figure 4, which presents the viscosities of a PLA/C-kenaf composite, PLA, and ABS, the kenaf fiber at this fiber content hardly increased the viscosity of the PLA composite because of the low viscosity of

PLA itself. In addition, as reported, the fiber has little effect on the viscosity of plastics at relatively high shear rates, such as the rate of 10^{-3} s^{-1} used in this test, which is compared to that of the molding process of the PLA composites because the fiber aligns itself to the flow direction.¹⁴ Therefore, the kenaf fiber can have the same effect on PLA. The viscosity of the PLA/C-kenaf composite is comparable to that of ABS.

The recycling properties of the PLA/kenaf composite are presented in Figure 5. The physical properties and molecular weight were held close to 90% of that of the initial PLA/kenaf composite. The reason for the decrease in the physical properties was mainly the decline in the molecular weight of PLA and the kenaf fiber's length caused by repeated kneading. However, the physical properties of the PLA/kenaf composite probably can be kept constant by the adjustment of the ratio of the initial PLA/kenaf composite and the recycled PLA/kenaf composite.

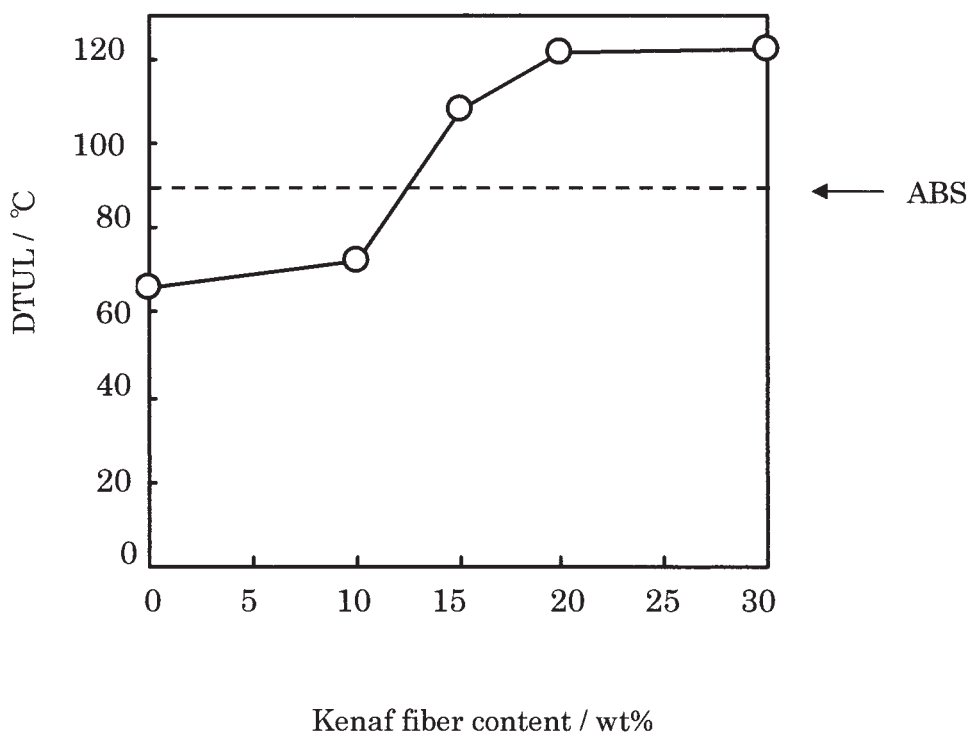


Figure 3 DTUL of a PLA/C-kenaf composite (load = 1.8 MPa).

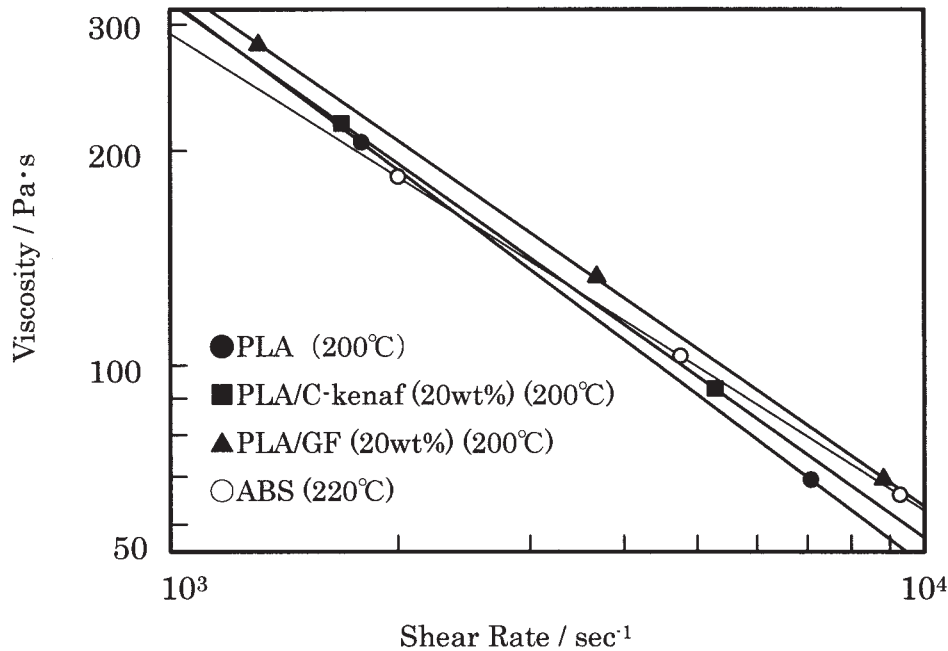


Figure 4 Viscosities of PLA with and without fibers and ABS.

Impact strength improvement of the PLA/kenaf composite

We found that eliminating the crushed particles from kenaf fiber improves the impact strength of kenaf fiber/PLA composites. As shown in Figure 6(A), L-kenaf has a greater effect on the impact strength of kenaf fiber/PLA composites than C-kenaf.

The kenaf fiber was pulled out of the PLA matrix without fracture during the impact test (Fig. 7). Be-

cause L-kenaf can increase the amount of energy required for pulling it out, the impact strength of the PLA composite with L-kenaf without the crushed particles was higher than that of the PLA composite with C-kenaf containing crushed particles. Moreover, as shown in Figure 6(B), instead of using the twin-screw extruder as in the previous test, we further improved the impact strength by preparing the composite with a single-screw extruder, which prevented

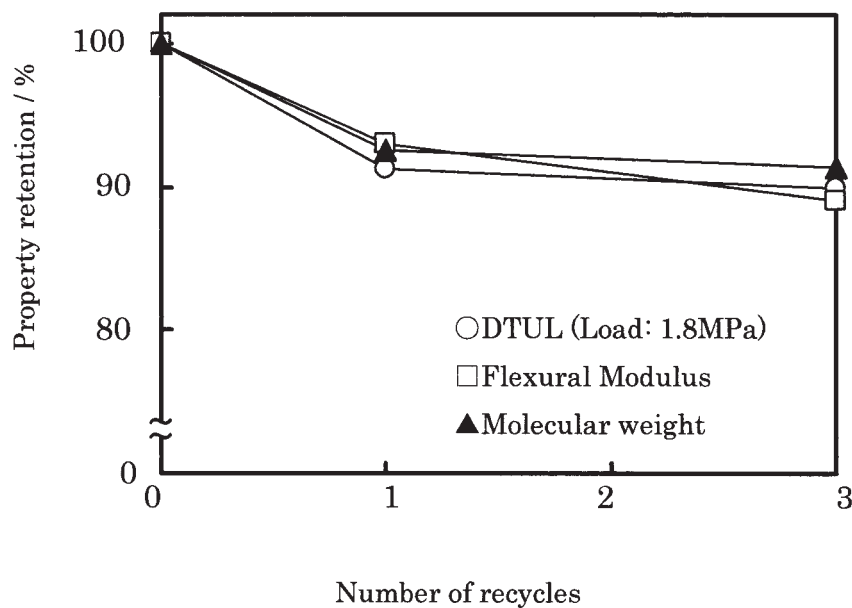


Figure 5 Influence of the recycling process on the properties of PLA/C-kenaf composites.

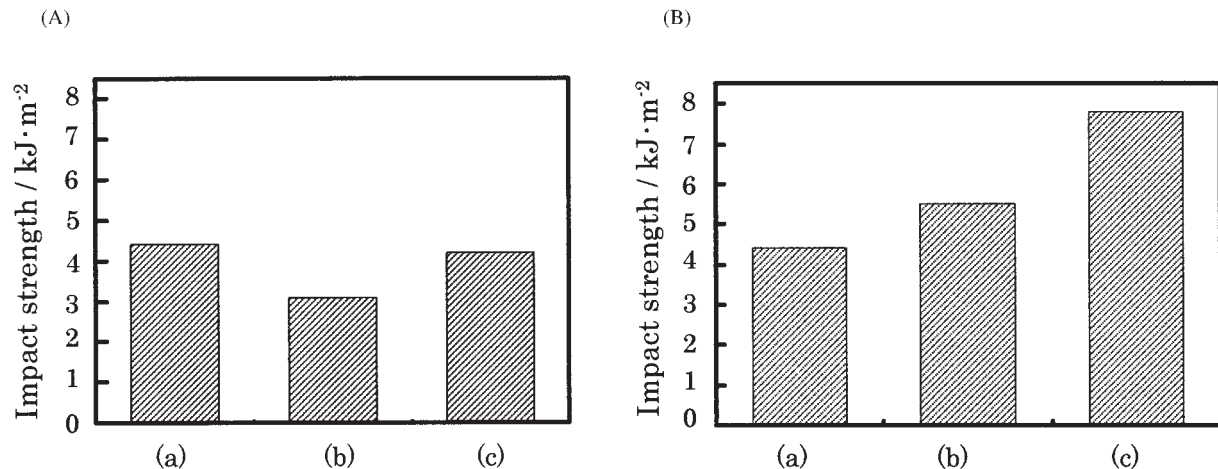


Figure 6 Impact strength of PLA/kenaf composites: (A) production with a twin-screw extruder [(a) PLA, (b) PLA/C-kenaf (<5 mm), and (c) PLA/L-kenaf (5 mm)] and (B) production with a single-screw extruder [(a) PLA, (b) PLA/L-kenaf (5 mm), and (c) PLA/L-kenaf (5 mm)/flexibilizer].

the kenaf fiber from being ground (generation of crushed fiber particles) during the kneading process.

The flexural strength of the PLA/L-kenaf composite was also increased because of the same effect of eliminating the crushed particles.

On the other hand, the heat resistance of PLA/L-kenaf was a little reduced, but it was kept superior to that of ABS with GF. The decrease was mainly due to the diminution of the crystallization degree of PLA caused by a decrease in the surface area of the kenaf fiber from the elimination of the crushed particles. However, the kenaf's effective promotion of the crystallization of PLA was maintained at a good level (exothermic peak time of DSC = 5.9 min).

Adding a flexibilizer (a copolymer of lactic acid and aliphatic polyester) to the composite further improved the impact strength, which exceeded those of the ABS/GF composites (Table II). Generally, flexibilizers reduce the heat resistance of plastics despite an im-

provement in the impact strength. However, by the optimization of the blend ratio of the kenaf fiber to the flexibilizer, the heat resistance and modulus attained a good degree.

As shown by a comparison with ABS with GF, PLA/L-kenaf and PLA/L-kenaf/flexibilizer composites have practical characteristics for use in electronic housing products.

Comparison of kenaf fiber with GF

L-kenaf exhibits effects on the previously mentioned characteristics of PLA practically comparable to those of GF.

GF improved the crystallization rate of PLA, but its ability was inferior to that of the kenaf fiber. The DSC exothermic peak time of the PLA/GF composite was 11 min (for L-kenaf, 5.9 min). Although GF also acts as a nucleating agent,¹³ it has a higher specific gravity, that is, a lower surface area, than kenaf fiber. Consequently, the crystallization rate of the PLA/GF composite was slower than that of the PLA/C-kenaf composite at the same fiber content by weight.

The viscosity of the PLA/C-kenaf composite was comparable to that of the PLA/GF composite, as shown in Figure 4 (the PLA/L-kenaf composite had almost the same viscosity behavior as PLA/C-kenaf).

As listed in Table II, the mechanical properties of the PLA/L-kenaf composite were almost comparable to those of the PLA/GF composite, but the heat resistance of the PLA/L-kenaf composite and its flexural strength were a little inferior to those of the PLA/GF composite. This was mainly because the strength of GF is higher than that of L-kenaf (tensile strength of GF = 3400 MPa,¹⁵ tensile strength of kenaf fiber = 169 MPa¹⁶).

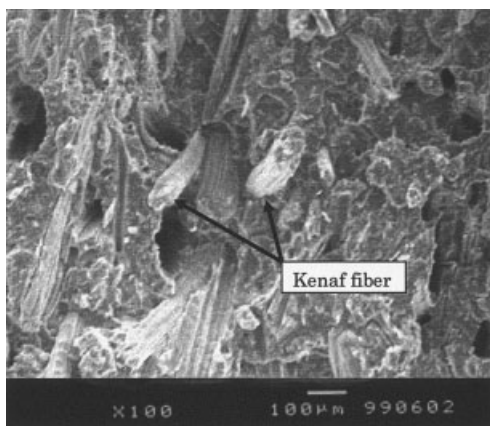


Figure 7 Cross section of a broken PLA/C-kenaf composite.

TABLE II
Properties of PLA/L · Kenaf/Flexibilizer Composites Kneaded by a Single · Screw Extruder

	PLA	PLA/C-kenaf	PLA/L-kenaf	PLA/flexibilizer	PLA/L-kenaf/flexibilizer	PLA/GF	ABS/GF
Fiber (wt %)	0	20	20	0	20	20	20
Flexibilizer (wt %)	0	0	0	20	20	0	0
Izod impact strength (kJ/m ²)	4.4	3.1	5.5	9.1	7.8	5.1	4.8
Flexural modulus (GPa)	4.5	7.6	7.1	4.0	6.8	7.8	7.3
Flexural strength (MPa)	132	93	115	106	72	138	110
DTUL (°C)	66	120	109	66	104	120	100

CONCLUSIONS

A kenaf-fiber-reinforced PLA, which has high heat resistance and strength, has been developed for use in the housing of electronic products. Adding the kenaf fiber greatly increases the heat resistance and modulus of PLA. Moreover, the inclusion of the fiber improves its crystallization rate and ease of molding. The impact strength of the PLA composite has been improved by the removal of the crushed particles from the kenaf fiber and the prevention of their generation through the grinding of the fiber during the kneading process. The kenaf fiber without the particles exhibits effects on these characteristics of PLA practically comparable to those of GF. Furthermore, adding a flexibilizer (a copolymer of lactic acid and aliphatic polyester) to the composites improves their impact strength. The main characteristics of the composites (PLA/kenaf fiber and PLA/kenaf fiber/flexibilizer) are comparable to or superior to those of GF-reinforced ABS, a representative petroleum-based plastic used in housing. These results demonstrate that the developed composites can be applied to the housing of electronic products.

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