

# Biodegradable Polyester Composites Reinforced with Short Abaca Fiber

MITSUHIRO SHIBATA,<sup>1</sup> KEI-ICHIRO TAKACHIYO,<sup>1</sup> KOICHI OZAWA,<sup>1</sup> RYUTOKU YOSOMIYA,<sup>1</sup> HIROYUKU TAKEISHI<sup>2</sup>

<sup>1</sup> Department of Industrial Chemistry, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

<sup>2</sup> Department of Precision Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

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**ABSTRACT:** The mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) composites, reinforced with short abaca fibers prepared by melt mixing and subsequent injection molding, were investigated and compared with PHBV composites reinforced with glass fiber (GF). The influences of fiber length, fiber content, and surface treatment of the natural fiber on the mechanical properties were evaluated. Regarding fiber length, the tensile properties had a maximum at a fiber length of about 5 mm. The flexural properties of the PHBV/abaca composite were improved by the surface treatment of abaca with butyric anhydride and pyridine for 5 h because of the increase of interfacial adhesiveness between the matrix polyester and the surface-esterified fiber, as is obvious from the SEM micrographs. The flexural and tensile properties of PHBV/treated abaca composite were comparable to those of PHBV/GF composite, except for tensile modulus, compared with the same weight fraction of fiber. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 129–138, 2002

**Key words:** biodegradable polyester; natural fiber; abaca; surface treatment; composite

## INTRODUCTION

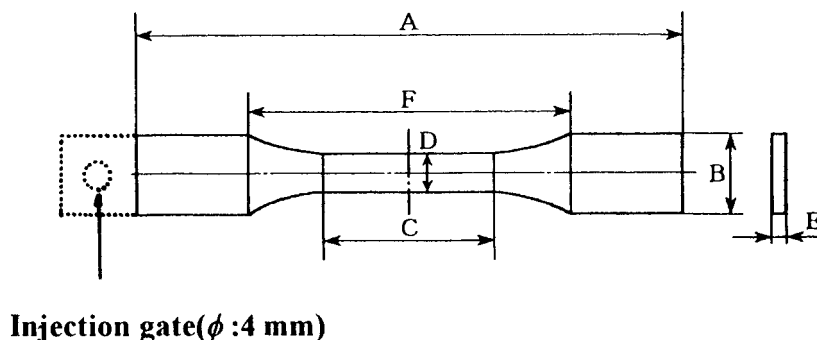
Biodegradable plastics such as aliphatic polyesters, cellulose-based thermoplastics, and other polysaccharide-based plastics have been attracting attention in recent years from the standpoint of protection of the natural environment.<sup>1,2</sup> Among the biodegradable plastics, most of the aliphatic polyesters, for example, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)<sup>3–6</sup> and poly(butylene succinate) (PBS)<sup>7,8</sup> have lower me-

chanical strength and modulus than those of poly(ethylene terephthalate) (PET), which is a popular thermoplastic polyester. Fiber reinforcement is a desirable method to improve the mechanical properties of biodegradable plastics. However, conventional reinforcing materials such as glass fiber (GF), carbon fiber, and aramide fiber are not biodegradable and are also difficult to incinerate. In this respect, natural plant-based lignocellulosic fibers are attractive reinforcing materials.<sup>9,10</sup> The natural fibers may be grouped as follows: (i) leaf (sisal, abaca, pineapple leaf fiber); (ii) bast (flax, hemp, ramie, jute, and kenaf/mesta); (iii) seed (cotton); and (iv) fruit (coconut husk, i.e., coir). Several studies on the biodegradable ther-

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Correspondence to: M. Shibata.

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**A:72 mm, B:10 mm, C:30 mm, D:5 mm, E:2 mm, F:50 mm**

**Figure 1** Dumbbell-shape specimen for tensile and flexural tests (the part shown by dotted line was cut before measurement).

moplastics reinforced with bast-based plant fibers were previously reported.<sup>10–14</sup> However, there is little in the literature on the biodegradable thermoplastics composites reinforced with leaf-based plant fibers. Luo and Netravali<sup>15,16</sup> reported the mechanical and thermal properties of PHBV/pineapple leaf fiber composites. SEM micrographs of the fracture surface of the composites showed fiber pull-out, indicating weak fiber–matrix adhesion. Abaca fiber (i.e., Manila hemp), obtained from the leaf of *Musa Textilis Luig Nee*, is widely used as rope, bag, and paper.

This report describes our investigation of the biodegradable polyester composites reinforced with short abaca fiber, for the purpose of developing completely biodegradable composites with superior mechanical properties. The effects of fiber length, fiber content, and surface treatment of fiber on the mechanical properties are investigated and compared to those of GF composites.

## EXPERIMENTAL

### Materials

PHBV (Biophane, Grade A-1000, 600 × 400 × 0.5 mm sheet) was supplied from Gunze Co. (Shiga, Japan). The abaca fiber, which is native to Ecuador, was imported through Ogura Trading Company (Nagoya, Japan). The abaca fiber (average diameter ~ 0.2 mm) was cleaned and chopped into the desired length, ranging from 3 to 7 mm by use of a ruler. The chopped fibers were washed with water and dried at 70°C in a vacuum oven

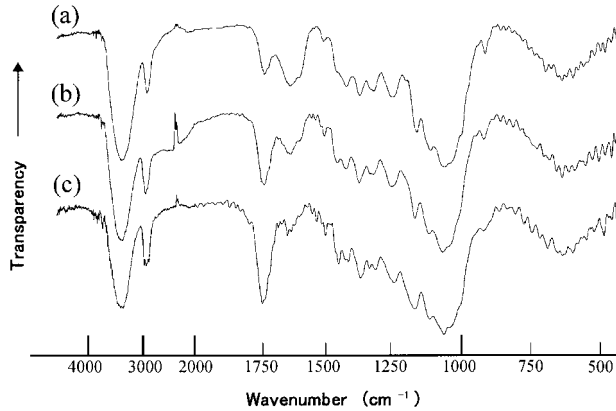
before making the composites. The glass fiber used in this study was chopped silane-treated strand [Grade: RX-CSX (RES06-BM5)] supplied from Nippon Sheet Glass Co. (Japan). The average diameter of the filament was 11 μm and the average fiber length 6 mm. All other chemicals used in this work were reagent grade and used without further purification.

### Surface-Treated Abaca Fiber

The chopped abaca fibers were soaked in butyric anhydride/pyridine (molar ratio 1/1) solution at room temperature for the prescribed time (0.5–24 h). The treated fibers were filtered and washed with water and then with ethanol. Furthermore, the washed fibers were soaked in ethanol at room temperature for 1 h, filtered, washed with ethanol, and then dried at 70°C *in vacuo* before making the composites. The abaca fiber treated with butyric anhydride/pyridine for *x* hours was abbreviated to *x* h-BA abaca.

### Preparation of PHBV/Abaca Composite

The compounds of PHBV and abaca (fiber content: 0–20 wt %) were prepared with a twin rotary mixer (Toyo Seiki Co., Japan). The mixing was carried out at 140°C for 5 min with a rotary speed of 50 rpm. The mixture was crushed to small pieces after immersion in liquid nitrogen, and dried at 70°C *in vacuo* for at least 5 h before injection molding. The dumbbell-shape specimen, as shown in Figure 1, was molded using a desk injection-molding machine (Little-Ace I Type,

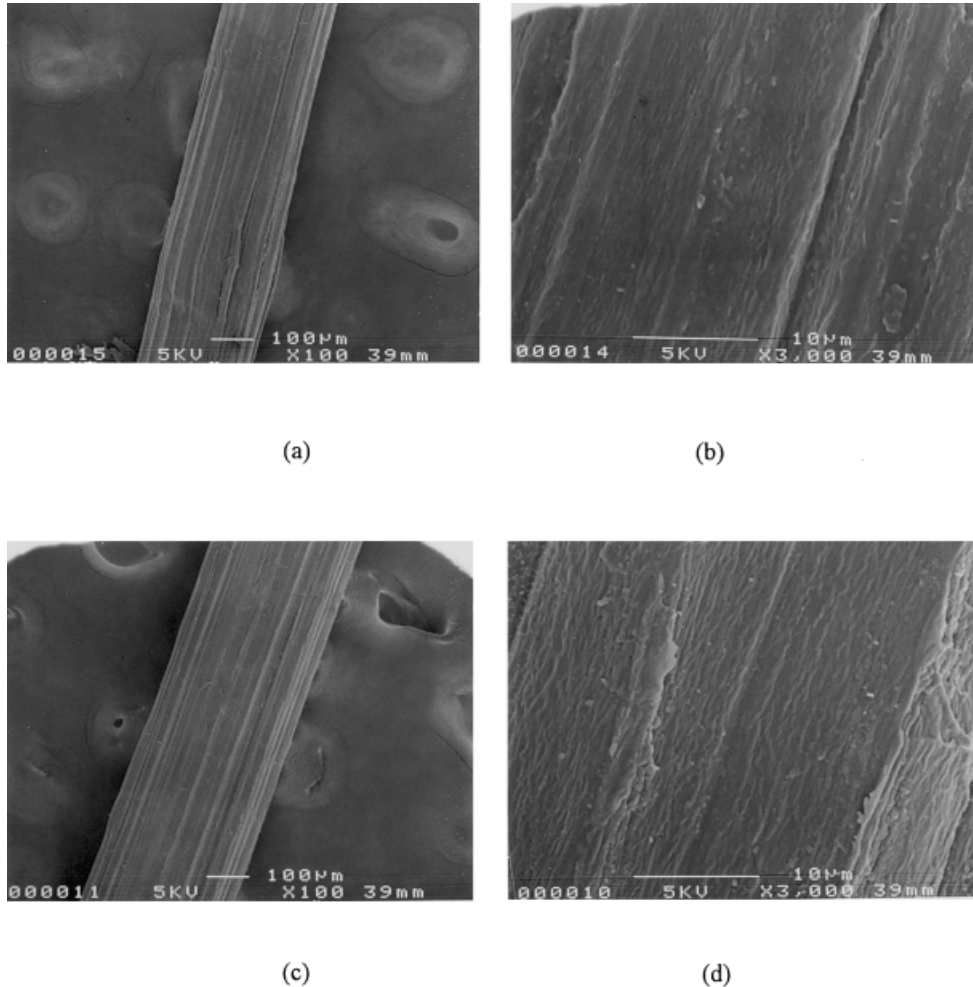


**Figure 2** IR spectra of surface-treated abaca with butyric anhydride and pyridine for (a) 0 h (untreated abaca), (b) 5 h, and (c) 24 h.

Tsubako Co., Japan). An injection-molding gate (diameter: 4 mm) of melted resin and chopped fiber is located at the edge of the dumbbell-shape specimen. The cylinder temperature and the molding temperature during the injection molding were 170 and 80°C, respectively. Although the fiber length after processing was not measured, no apparent damage of fibers appeared in the observation with the naked eye.

**Measurements**

Tensile tests of untreated and treated fibers were performed using an Autograph AGS-500C (Shimazu Co., Japan) based on the standard method for testing the tensile strength of natural fibers [JIS L1069 (1995)]. The tensile strength and moduli of 30 samples per each fiber were



**Figure 3** SEM micrographs of the surface of (a) untreated abaca fiber, (b) untreated abaca fiber (magnified view), (c) 5 h-BA abaca fiber, and (d) 5 h-BA abaca fiber (magnified view).

**Table I Mechanical Properties of Abaca and 5h-BA Abaca Fibers Compared to Those of Conventional Reinforcing Fibers<sup>a</sup>**

Fiber	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Abaca	756	31.1	2.9
5h-BA abaca	842	36.6	2.7
Sisal	511–635	9.4–22.0	2.0–2.5
Jute	393–773	26.5	1.5–1.8
Flax	345–1035	27.6	2.7–3.2
E-glass	2000–3500	70.0	2.5
S-glass	4570	86.0	2.8
Aramide	3000–3150	63.0–67.0	3.3–3.7
Carbon	4000	230–240	1.4–1.8

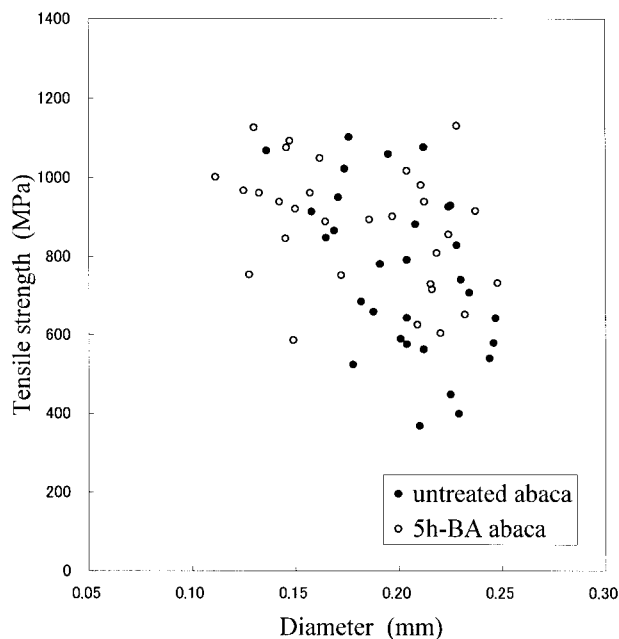
<sup>a</sup> From Bledzki and Gassan, 1999.<sup>9</sup>

measured and averaged. Individual single-fiber specimens were mounted and glued on a paper tab with a drop of cyanoacrylate-based super glue before measurement. The span length was 45 mm and the testing speed was 10 mm/min. The cross section of fiber was calculated from the diameter measured by a micrometer, assuming a cylindrical fiber.

Flexural and tensile tests of the PHBV composites were performed using an Autograph AGS-500C (Shimazu Co.) based on the standard method for testing the flexural and tensile properties of rigid plastics [JIS K7203 (1982) and K7113 (1981), respectively]. The tensile and flexural properties were tested in the longitudinal and transverse directions, respectively. The span length was 30 mm for flexural and 50 mm for tensile tests, and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and standard deviation ( $\sigma$ ) were calculated.

The morphology of the composites was observed by scanning electron microscopy (SEM), using a JSM-840 machine (Japan Electron Co., Japan). All samples were fractured perpendicularly to the flow direction after immersion in liquid nitrogen for about 5 min. The fracture surfaces were sputter-coated with gold to provide enhanced conductivity.

IR spectra were measured by FTIR 8100 spectrometer (Shimazu Co.). Powdered fiber pelletized with potassium bromide was used for recording the spectra. The spectra were used to analyze the changes in the chemical structure of the surface-treated fiber.

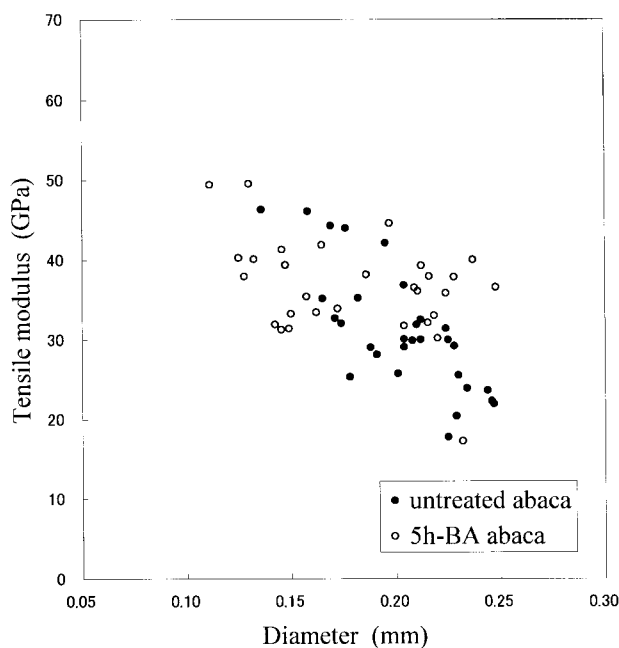


**Figure 4** Tensile strength of abaca and 5 h-BA abaca fibers as a function of fiber diameter.

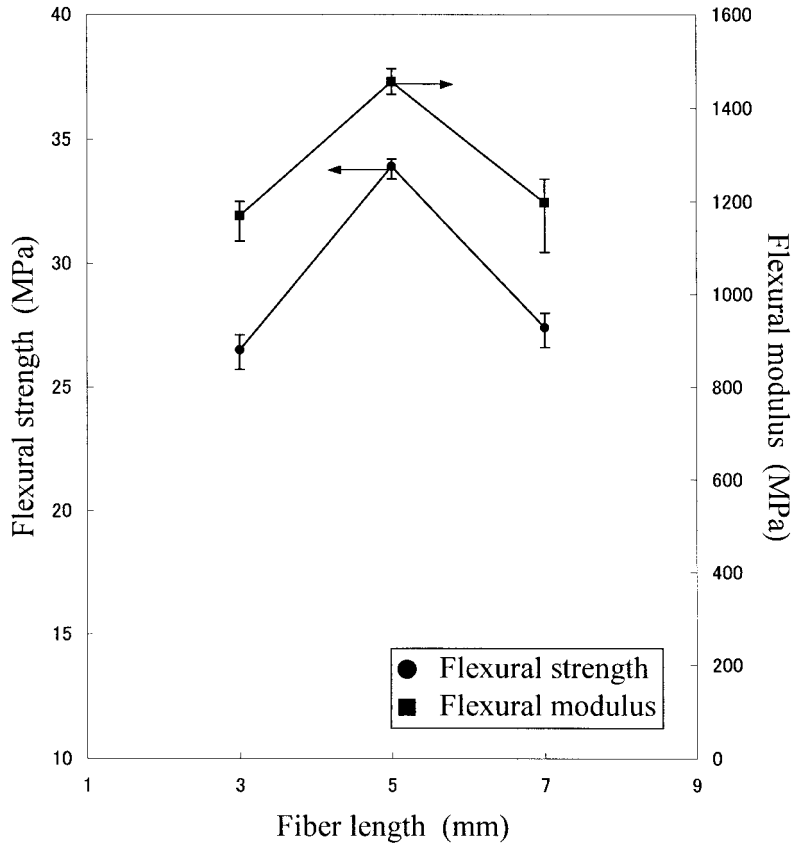
## RESULTS AND DISCUSSION

### Synthesis and Characterization of Surface-Treated Abaca Fiber

Strongly polarized lignocellulosic fibers are inherently incompatible with hydrophobic polymers.<sup>15–18</sup>



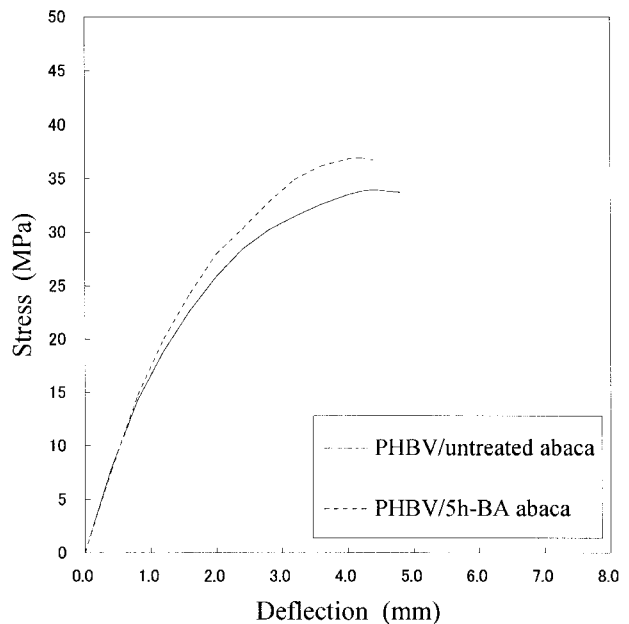
**Figure 5** Tensile moduli of abaca and 5 h-BA abaca fibers as a function of fiber diameter.



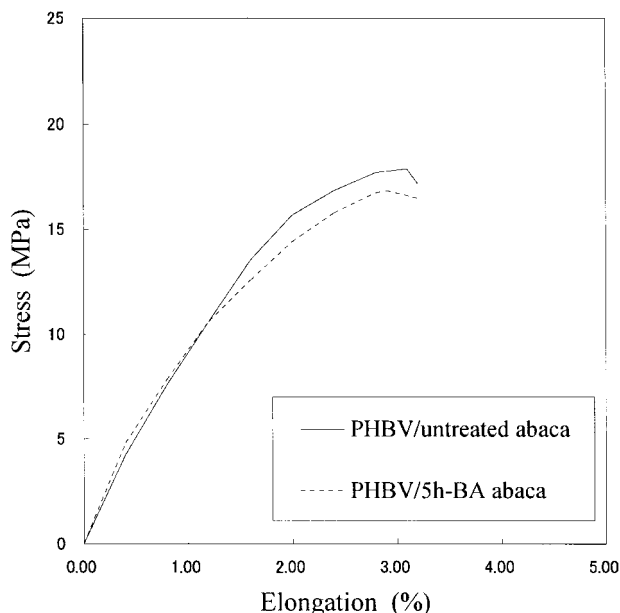
**Figure 6** Flexural properties of the PHBV/abaca composite with 10 wt % fiber content as a function of fiber length.

The benzoyl esterification of sisal fiber was found to enhance the tensile properties of the short sisal fiber-reinforced polystyrene composites because of the improvement of interfacial adhesiveness between matrix polystyrene and lignocellulosic fiber.<sup>19</sup> We investigated the surface esterification of abaca with butyric anhydride/pyridine. Butyric anhydride was selected, given that the carbon number of the acid components in ester groups of PHBV and treated fiber becomes the same. The typical IR spectral changes for the surface treatment of abaca with butyric anhydride/pyridine are shown in Figure 2. The stretching vibration absorption of C=O of the ester group around 1750 cm<sup>-1</sup> increased with the reaction time. In addition, the hydroxyl vibration absorption peak at around 3400 cm<sup>-1</sup> gradually diminished, indicating that the esterification of cellulose hydroxyl group by butyric anhydride proceeds smoothly, to give a surface-esterified abaca fiber.<sup>19</sup>

Although the surface of 5 h-BA abaca fiber was slightly rougher than that of untreated fiber, there was no significant difference, as is obvious



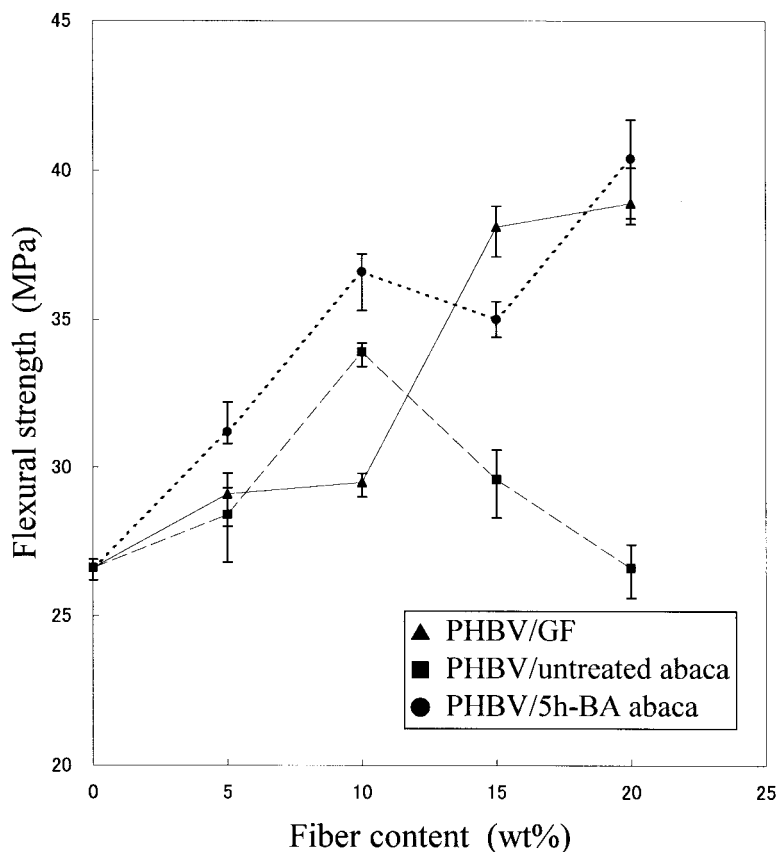
**Figure 7** Stress-strain curves of PHBV/abaca and PHBV/5 h-BA abaca with 10 wt % fiber content in the flexural mode.



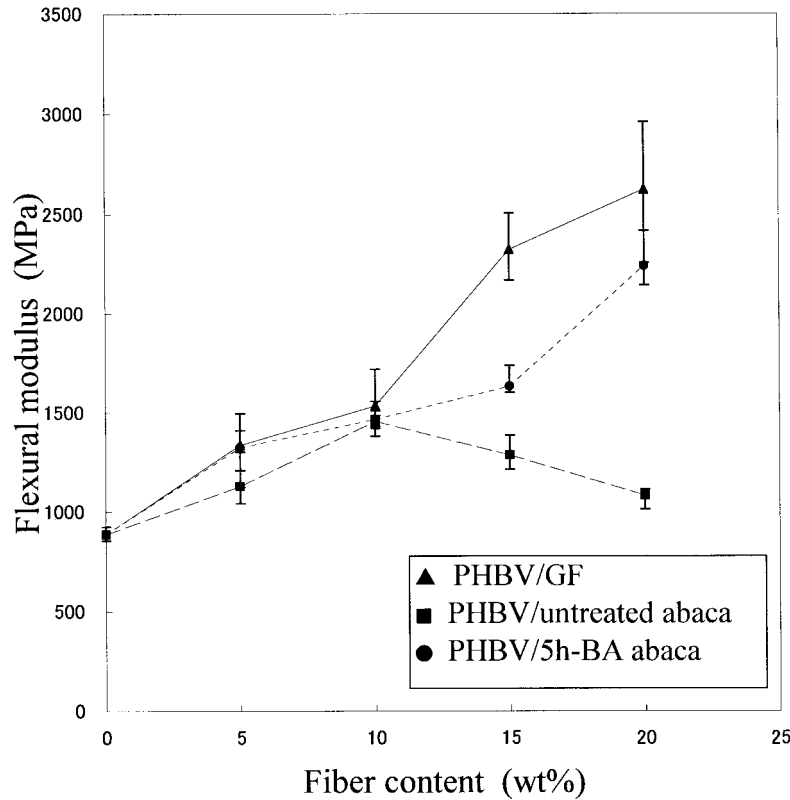
**Figure 8** Stress-strain curves of PHBV/abaca and PHBV/5 h-BA abaca with 10 wt % fiber content in the tensile mode.

from the SEM micrographs (Fig. 3). Thomas et al.<sup>19</sup> reported that the benzylation of sisal fiber, a leaf fiber similar to that of abaca fiber, by aqueous sodium hydroxide treatment and subsequent reaction with benzoyl chloride produces a number of small voids on the surface of the fiber, probably because of the leach-out of alkali-soluble fractions such as waxy layer and lignin, and so forth. In our method using pyridine as a base, no voids were observed, indicating that such a leach-out hardly occurs.

The average diameter of 30 strings of abaca fiber used in this study was  $202 \mu\text{m}$  [ $\sigma$ :  $28 \mu\text{m}$  (14%)]. The abaca fiber used here has higher tensile strength [756 MPa,  $\sigma = 207 \text{ MPa}$  (27%)] and modulus [31.1 GPa,  $\sigma = 7.5 \text{ GPa}$  (24%)] than those of standard sisal and jute fibers (Table I). Abaca fiber ( $1.5 \text{ g/cm}^3$ ) has a considerably lower density than that of *E*-glass ( $2.5 \text{ g/cm}^3$ ). Although specific strength (tensile strength/density) of abaca fiber ( $5.1 \times 10^4 \text{ m}$ ) is lower than that of *E*-glass ( $8\text{--}14 \times 10^4 \text{ m}$ ), the specific modulus (tensile modulus/density) of abaca fiber ( $2.1 \times 10^6 \text{ m}$ )



**Figure 9** Flexural strength of fiber-reinforced PHBV composites as a function of fiber content.



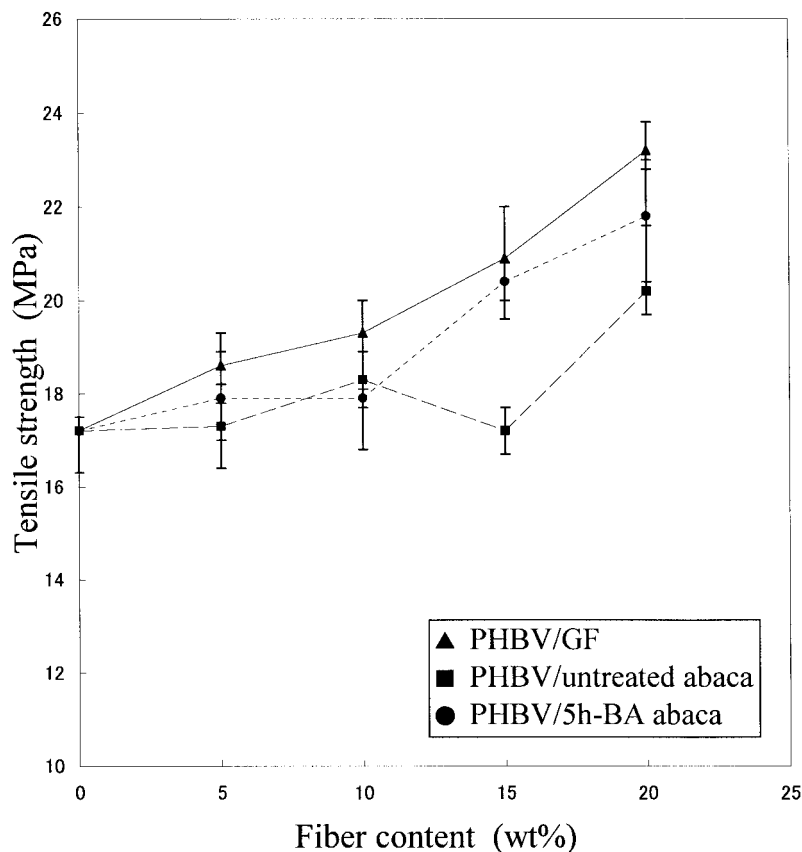
**Figure 10** Flexural moduli of fiber-reinforced PHBV composites as a function of fiber content.

reaches a level close to that of *E*-glass ( $2.8 \times 10^6$  m). Therefore, it is expected that the difference of modulus between abaca-reinforced composite and GF-reinforced composite is not so great, as compared with the same weight fraction of fiber. Figures 4 and 5 show the tensile strength and moduli of untreated abaca and 5 h-BA abaca fibers as a function of fiber diameter, respectively. The strength and moduli increase with decreasing fiber diameter for both the untreated and treated abaca fibers. A similar relationship between tensile properties and diameter is observed in the case of glass fiber. The average tensile strength and modulus of 5 h-BA abaca fiber [average diameter:  $181 \mu\text{m}$  ( $\sigma = 40 \mu\text{m}$ , 22.0%)] is 842 MPa ( $\sigma = 153 \text{ MPa}$ , 18.1%) and 36.6 GPa ( $\sigma = 6.0 \text{ GPa}$ , 16.5%), respectively, which are slightly higher than those of untreated abaca fiber. Considering a slightly lower averaged diameter of the 5 h-BA abaca fiber than that of the untreated abaca used for tensile tests, it is thought that there is no significant difference in tensile properties between untreated and 5 h-treated abaca fibers, as is obvious from the plots of Figures 4 and 5. More-

over, the difference in tensile properties relative to the reaction time (0.5–24 h) of surface treatment was not significant. Because of the serious influence of fiber diameter on the mechanical properties, the short chopped fibers were thoroughly mixed to get an averaged diameter before mixing with PHBV.

#### Mechanical Properties of PHBV/Abaca Composites

The composites of PHBV with untreated and treated abaca fibers (3–5 mm) were prepared by melt mixing and subsequent injection molding. From the observation with the naked eye, abaca fibers were randomly oriented, that is, unidirectional orientation along the flow direction was not observed in the injection-molded dumbbell-shape specimens. The random orientation may be attributed to a low flow speed resulting from the use of a hand-operated ram-type injection-molding machine. A similar orientation was observed for the polystyrene/sisal composite samples prepared by use of a similar hand-operated injection-molding machine.<sup>19</sup> Regarding fiber length, the flex-



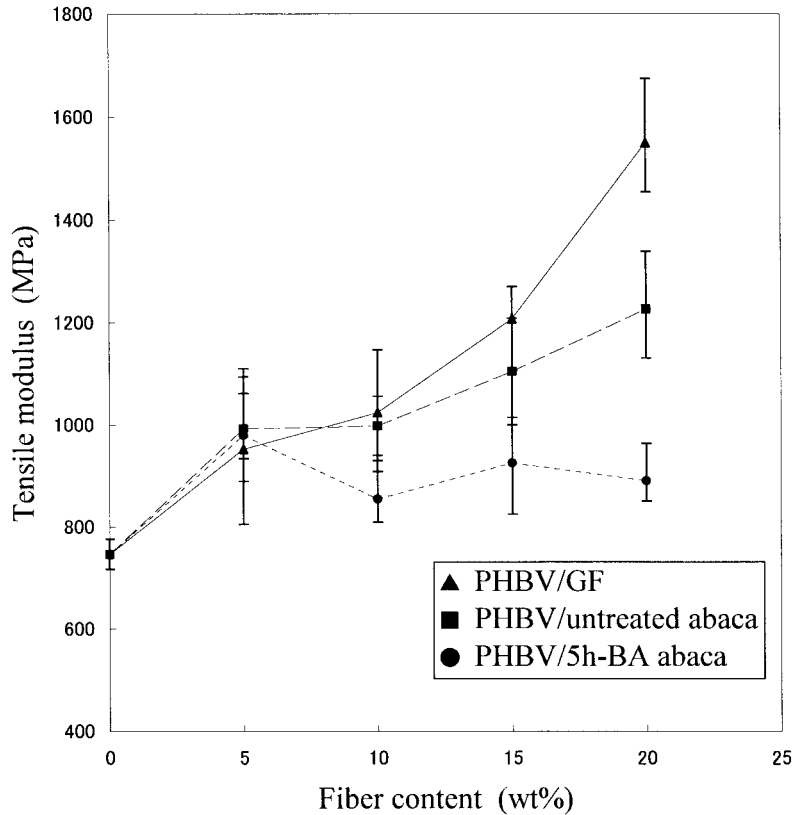
**Figure 11** Tensile strength of fiber-reinforced PHBV composites as a function of fiber content.

ural properties of the PHBV/untreated abaca composite with 10 wt % fiber loading had a maximum at a fiber length of about 5 mm (Fig. 6). As the fiber length increases, there is a chance for better orientation, which may lead to an improvement in mechanical properties of the composite. However, the abaca fiber of 7 mm appears, with the naked eye, to be bending or curling in the composite specimens. Although there is a possibility that another fiber length would afford a maximum in a fiber loading other than 10 wt %, the fiber length was fixed to 5 mm in the following experiments. Regarding the reaction time of surface treatment of abaca with butyric anhydride/pyridine, the PHBV/5 h-BA abaca (weight ratio 90/10) had a slightly higher flexural strength [37 MPa,  $\sigma = 0.73$  MPa (2.0%)] and modulus [1470 MPa,  $\sigma = 28$  MPa (1.9%)] than those of PHBV/12 h-BA abaca (90/10) [35 MPa,  $\sigma = 0.53$  MPa (1.5%); 1420 MPa,  $\sigma = 74.0$  MPa (5.2%)]. In the following experiments regarding fiber content, abaca fiber treated for 5 h was used as the surface-treated abaca.

Figures 7 and 8 show typical stress–strain curves for PHBV/abaca (90/10) and PHBV/5 h-BA abaca (90/10) composites in the flexural mode and tensile mode, respectively. Increase of flexural strength attributed to the surface treatment is obvious from Figure 7; on the other hand, tensile strength does not increase by the surface treatment.

Figure pairs 9–10 and 11–12 show fiber content versus the flexural and tensile properties of the PHBV/abaca or GF composites, respectively. The composite using 5 h-BA abaca had a higher flexural modulus and strength than those of the composite using untreated abaca. For the former composite, flexural strength and moduli increased with increasing fiber content in the range of 0–20 wt % studied in these experiments in contrast to a slightly decreasing trend of these values at around 10–20 wt % fiber content for the latter composite. The reason is not clear, although it may be related to the interfacial adhesion between matrix polymer and fiber, which is more important for the composite with higher fiber





**Figure 12** Tensile moduli of fiber-reinforced PHBV composites as a function of fiber content.

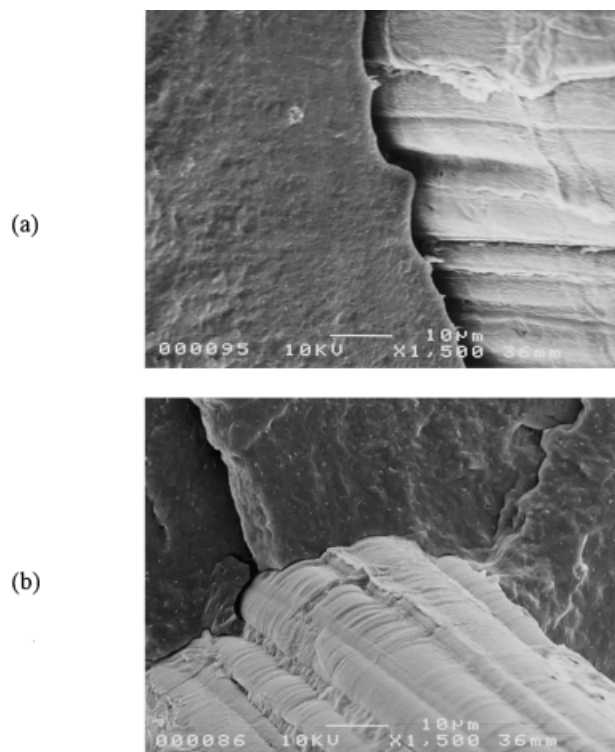
loading. The flexural properties of PHBV/5 h-BA abaca composite were comparable to those of PHBV/GF composite, as compared with the same weight fraction of fiber. An optical photograph shows that glass fiber was unidirectionally oriented, in contrast to the random orientation of abaca fiber along the flow direction. The difference of orientation between GF and abaca fiber should be attributed to the difference of diameter (GF 11  $\mu\text{m}$ , abaca 202  $\mu\text{m}$ ). The effect of fiber reinforcement on the tensile strength and modulus [pure PHBV: 17 MPa ( $\sigma = 0.43$  MPa), 750 MPa ( $\sigma = 20.1$  MPa)] was not very significant for both the abaca composite [20 wt % loading: 20 MPa ( $\sigma = 0.72$  MPa), 1230 MPa ( $\sigma = 66.5$  MPa)] and GF composite [20 wt % loading: 23 MPa ( $\sigma = 0.33$  MPa), 1550 MPa ( $\sigma = 83.2$  MPa)], compared with the improvement of flexural properties. Also, the butyric anhydride treatment of abaca was not effective for the improvement of tensile properties, especially tensile moduli. Although there is a considerable scattering of measured tensile strength and moduli, these values of PHBV/treated or PHBV/untreated abaca slightly

increased with increasing fiber content, as a whole.

Figure 13 shows the SEM micrographs of the fractured surface of both untreated fiber composite and treated fiber composite. It is obvious that the matrix polymer is forced out of the fiber for the untreated fiber composite. On the other hand, it appeared that the interfacial adhesiveness of the treated fiber composite is much better than that of the untreated fiber composite. The improvement of the interfacial adhesiveness by the surface treatment of abaca fiber should result in an improvement of the flexural properties. The biodegradability of these composites is now under investigation.

## CONCLUSIONS

The mechanical properties of randomly oriented PHBV/abaca composites prepared by melt mixing and subsequent injection molding were investigated compared with those of GF-reinforced composite. Regarding fiber length, the flexural prop-



**Figure 13** SEM micrographs of fractured surface of (a) PHBV/untreated abaca fiber (90/10) composite and (b) PHBV/5 h-BA abaca fiber (90/10) composite.

erties had a maximum at a fiber length of about 5 mm. Fiber bending was observed for the composite with the fiber longer than 5 mm. The flexural properties of the PHBV/abaca composite were improved by the surface treatment of abaca with butyric anhydride and pyridine for 5 h because of the increase of interfacial adhesiveness between the matrix polyester and the treated fiber, as SEM micrographs make clear. The flexural modulus and strength of the PHBV/5 h-BA abaca composite increased with increasing fiber content in the studied range of 0–20 wt % [PHBV: strength 27 MPa ( $\sigma = 0.25$  MPa), modulus 900 MPa ( $\sigma = 23.4$  MPa); PHBV/5 h-BA abaca (80/20): strength 40 MPa ( $\sigma = 1.2$  MPa), modulus 2240 MPa ( $\sigma = 110$  MPa)]. The PHBV/5 h-BA abaca

composite had flexural properties comparable to those of PHBV/GF (80/20) composite [strength 39 MPa ( $\sigma = 0.8$  MPa), modulus 2400 MPa ( $\sigma = 150$  MPa)] for the same weight average content. The surface treatment of abaca fiber was not so effective for the improvement of tensile properties.

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