

Mechanical Properties and Biodegradability of Green Composites Based on Biodegradable Polyesters and Lyocell Fabric

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ABSTRACT: Green composites composed of regenerated cellulose (lyocell) fabric and biodegradable polyesters [poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(butylene succinate) (PBS), and poly(lactic acid) (PLA)] were prepared by compression-molding method. The tensile moduli and strength of all the biodegradable polyester/lyocell composites increased with increasing fiber content. When the obtained PLA/lyocell composites were annealed at 100°C for 3 h, the tensile strength and moduli were lowered despite the increase of degree of crystallization of the PLA component. The SEM observation of the composites revealed that the surface of the annealed composite has

many cracks caused by the shrinkage of the PLA adhered to lyocell fabric. Multilayered PLA/lyocell laminate composites showed considerably higher Izod impact strength than PLA. As a result of the soil viral test, although the order of higher weight loss for the single substance was lyocell > PHBV > PBS > PLA, the biodegradability of the green composites did not reflect the order of a single substance because of the structural defect of the composite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3857–3863, 2004

Key words: biodegradable; polyesters; fibers; composites; mechanical properties

INTRODUCTION

Biocomposites composed of biodegradable polymer and biofiber (natural fiber) as matrix material and reinforcing element, respectively, have attracted attention from the standpoint of protection of the natural environment in recent years.^{1–3} As biodegradable polymers, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV),^{4–5} poly(butylene succinate) (PBS),^{6–7} and poly(lactic acid) (PLA)^{8–9} are popular. Their biocomposites, using sisal, abaca, pineapple leaf fibers, etc., as cellulosic natural fibers, were already studied by several groups to improve the low mechanical strength and modulus.^{10–14} On the other hand, (viscose-)ryon, cupro, and lyocell are known as cellulosic manmade fiber. Lyocell especially is an environmentally benign manmade fiber, because lyocell is manufactured by cellulose dissolution in *N*-methyl morpholine *N*-oxide, which is used repeatedly in recycling.¹⁵ As compared with flax, lyocell fiber has a comparable strength and longer elongation (3 versus 11–15%). In addition, deviations in the mechanical properties as well as of the shape between different batches of lyocell fibers are lower than for natural fibers. Although lyocell fiber/

biodegradable polymer composites are very interesting eco-friendly composites (green composites) from such viewpoints, little literature is reported.¹⁶ The present study describes an investigation of the green composites composed of biodegradable polyesters (PBS, PHBV, and PLA) and lyocell fabric.

EXPERIMENTAL

Materials

PHBV [Biophane, Grade: A-1000, 600 × 400 × 0.5 mm sheet, glass transition temperature (T_g) 2°C [differential scanning calorimetry (DSC)], melting temperature (T_m) 154°C (DSC)] was supplied from Gunze Co. Ltd. (Kyoto, Japan). PBS [Bionolle 1001, 150- μ m-thickness film, T_g -32°C (DSC), T_m 115°C (DSC)] was supplied by Showa Highpolymer Co. Ltd. (Tokyo, Japan). PLA [LACEA CF-400, 400- μ m-thickness sheet, T_g 60°C (DSC), T_m 172°C (DSC)] was supplied by Mitsui Chemical Co. Ltd. (Tokyo, Japan). Lyocell fabric (SyLPH, 300 dtex, 600 dtex, 2/2 twill, thickness: ca. 0.35 mm) was received from Unitika Textile Co. Ltd. (Osaka, Japan).

Preparation of composites

PHBV/lyocell and PLA/lyocell composites were prepared by sandwiching lyocell fabric between two lay-

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TABLE I
Tensile Properties of PHBV/Lyocell Composites Molded at Various Conditions^a

Exp.no.	Pressure (MPa)	Time (min)	Fiber content (wt %)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
1 ^b	3	5	0	16.3	0.44	30.4
2	0	5	17.6	38.4	0.91	14.8
3	0	10	16.1	39.1	0.77	16.1
4	3	5	29.5	70.8	1.55	14.6
5	3	10	34.6	78.0	1.63	14.7
6	3	30	48.0	85.9	2.23	11.9
7	3	60	53.7	102.4	2.01	10.9
8	5	5	36.7	79.4	1.76	14.5
9	5	10	42.9	86.7	2.31	12.7
10	5	30	49.3	95.2	2.33	11.9
11	5	60	60.0	100.6	2.49	13.7
12	10	5	45.0	93.2	1.99	11.5
13	10	10	50.7	101.9	1.89	11.8
14	10	30	63.2	108.8	2.46	10.6
15	10	60	66.7	97.3	2.93	10.4

^a Molding temperature is 160°C.

^b Only PHBV sheet was used.

TABLE II
Tensile Properties of PBS/Lyocell Composites Molded at Various Conditions^a

Exp.no.	Pressure (MPa)	Time (min)	Fiber content (wt %)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
1 ^b	3	5	0	37.6	0.63	16.5
2	3	5	25.4	80.8	1.49	14.7
3	3	10	26.1	79.5	1.70	14.3
4	3	30	33.6	94.7	2.10	12.2
5	5	5	29.0	86.0	1.60	13.1
6	5	10	30.3	87.9	2.05	13.6
7	5	30	43.9	106.8	2.73	10.7
8	5	60	53.7	117.4	3.16	9.9
9	10	5	34.3	96.4	1.99	12.4
10	10	10	40.0	107.6	2.61	12.6
11	10	30	52.9	114.6	3.23	9.7
12	10	60	60.0	114.4	3.39	9.7

^a Molding temperature is 170°C.

^b Only PBS film was used.

TABLE III
Tensile Properties of PLA/Lyocell Composites Molded at Various Conditions

Exp.no.	Temperature (°C)	Pressure (MPa)	Time (min)	Fiber content (wt %)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
1 ^a	160	3	5	0	45.2	2.82	2.1
2	160	3	5	24.2	46.8	3.15	10.4
3	160	3	10	24.8	48.9	3.49	9.6
4	160	5	5	27.3	53.0	4.21	9.4
5	160	5	10	29.3	58.0	3.96	9.1
6	160	10	5	28.3	57.1	4.05	8.9
7	160	10	10	34.3	65.8	3.87	8.5
8	175	3	5	29.5	60.8	4.48	7.2
9	175	3	10	33.6	64.6	4.07	8.0
10	175	5	5	33.6	67.7	4.26	8.2
11	175	5	10	38.7	76.9	4.67	8.0
12	175	10	5	37.5	80.4	4.74	7.9
13	175	10	10	46.2	89.1	5.31	7.6
14	190	3	5	36.0	67.6	4.16	7.6
15	190	3	10	39.1	73.4	4.27	7.1
16	190	5	5	46.8	87.8	5.17	7.4
17	190	5	10	50.7	91.6	4.76	7.2
18	190	10	5	49.3	91.8	4.98	7.3
19	190	10	10	62.1	100.5	5.55	6.4

^a Only PLA sheet was used.

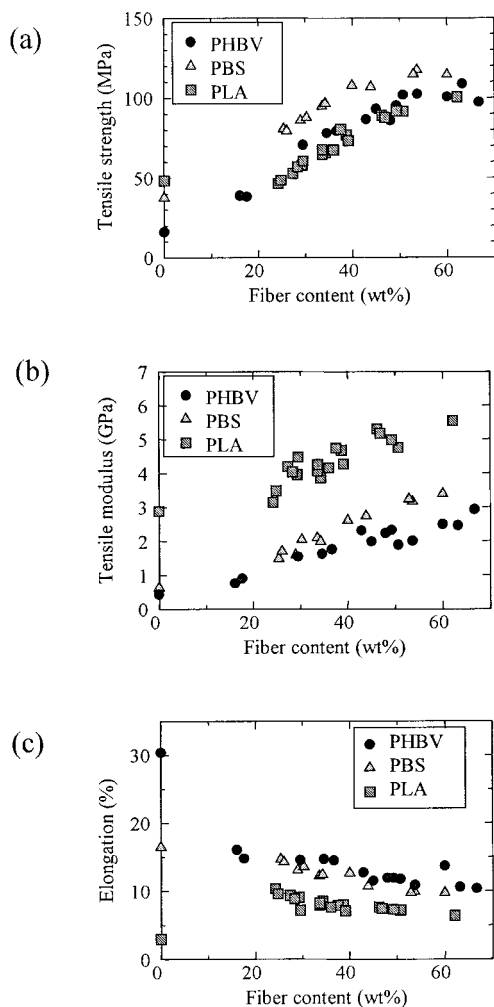


Figure 1 Tensile properties of the green composites as a function of fiber content: (a) tensile strength, (b) tensile modulus, and (c) elongation at break.

ers of the polyester sheet under the prescribed heat (160–190°C) and pressure (3–10 MPa) for 5–60 min. In the case of PBS/lyocell composite, lyocell fabric was sandwiched between two sets of four 150- μ m PBS films. The PLA/lyocell composites were annealed at 100°C for 3 h to enhance the crystallinity. For PLA-based composite, multilayered laminate composites for Izod impact tests were also prepared by sandwiching 6- to 8-ply lyocell fabrics between 7- and 9-ply PLA sheets by turns. A mini test press (Toyo Seiki Co. Ltd., Japan) was used to prepare all the composites. Pressing temperatures are 160, 170, and 160–190°C for PHBV, PBS, and PLA, respectively. After cooling to 100°C under the prescribed pressure, the composites were taken out of the press machine, cooled to room temperature, and then cut to the desired size.

Measurements

Flexural tests of the composites were performed by using an Autograph AGS-500C (Shimadzu Co. Ltd., Kyoto,

Japan) based on the standard method for testing the flexural and tensile properties of rigid plastics [JIS K7203 (1982)]. Span length was 30 mm, and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation were calculated.

Izod impact tests were carried out by using the PLA sheet (65 \times 10 \times 4.2 mm) and multilayer PLA/lyocell composites (65 \times 10 \times 1.75–2.25 mm) at ambient conditions on a Digital Impact Testing Machine DG-I (Toyo Seiki Co. Ltd.) according to JIS K 7110.

The morphology of the composites was observed by scanning electron microscopy (SEM), using a JSM-840 machine (Japan Electron Co. Ltd., Japan). The samples for the observation of matrix/fiber interface were prepared by fracturing the composites after immersion in liquid nitrogen for about 5 min. The surfaces of all the samples were sputter coated with gold to provide enhanced conductivity.

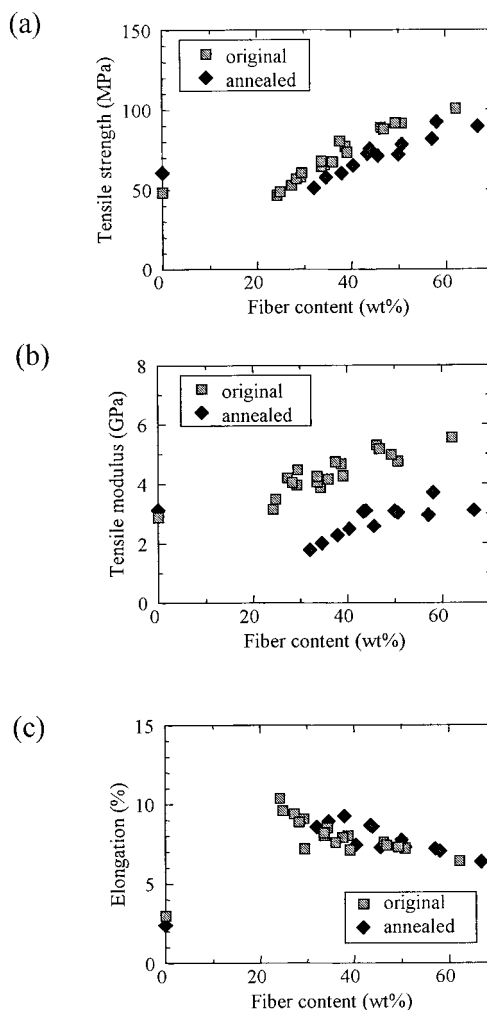


Figure 2 Tensile properties of the original and annealed PLA/lyocell composites as a function of fiber content: (a) tensile strength, (b) tensile modulus, and (c) elongation at break.

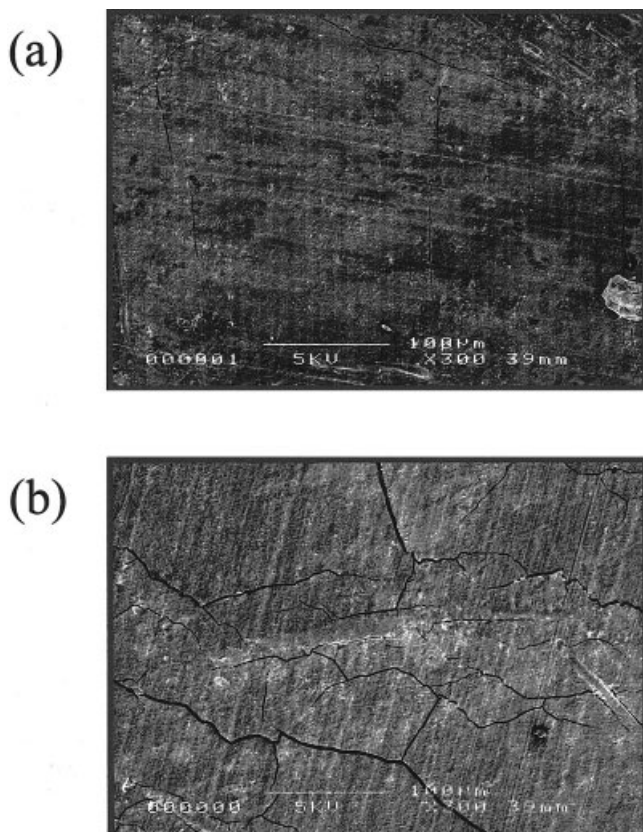


Figure 3 SEM photographs of the surface of the original and annealed PLA/lyocell composites:(a) original sample, and (b) annealed sample.

DSC was performed on a Perkin–Elmer DSC Pyris 1 DSC in a nitrogen atmosphere. The crystallization enthalpy from the glassy state ($\Delta H_{g,c}$) and melting enthalpy (ΔH_m) of the PLA composite were determined from the first heating scan of the composite at a heating rate of $10^\circ\text{C}/\text{min}$.

Biodegradability was evaluated by measuring weight loss of the composite film sample buried in soil. The sample cut into the size of 40×20 mm was buried in a 1 : 1 mixture of leaf mold and black soil for gardening and stored in a room at constant temperature ($25\text{--}30^\circ\text{C}$) and relative humidity (RH; 80%); and water content of the soil was adjusted to the original value (about 40%) by repeated watering. The soil burial test periods were 30, 60, 90, and 120 days. After the soil burial test, the samples were washed with water and dried to their constant weights in a vacuum oven at 40°C . The weight loss averaged for five specimens was employed.

RESULTS AND DISCUSSION

Tensile properties of the green composites

PHBV/lyocell and PBS/lyocell composites were prepared by pressure molding at 160 and 170°C , respec-

tively. In these cases, the increase of molding pressure (0–10 MPa) and molding time (5–60 min) caused the increase of fiber content (16.1–66.7 wt %; Tables I and II). PLA/lyocell composites were also prepared by pressure molding at $160\text{--}190^\circ\text{C}$. In this case, the increase of molding temperature in addition to pressure and time caused the increase of fiber content (24.2–62.1 wt %, Table III). Little difference on tensile properties was observed when the samples of the different molding conditions with the same fiber content were compared. Figure 1 shows the tensile properties of the green composites with various fiber contents. Regarding the values at fiber content 0%, the PHBV, PBS, and PLA sheets prepared by the pressure molding were used for the measurement. Tensile strength and moduli of all the composites increased with increasing fiber content. Tensile moduli of PLA composites had a higher value than those of PBS and PHBV composites when compared at the same fiber content, in accordance with the tensile modulus of pure matrix resin. Similarly, PBS composites had higher tensile strength than PHBV composite at the same fiber content, in accordance with the tensile strength of pure PBS and PHBV. However, the tensile strength of PLA compos-

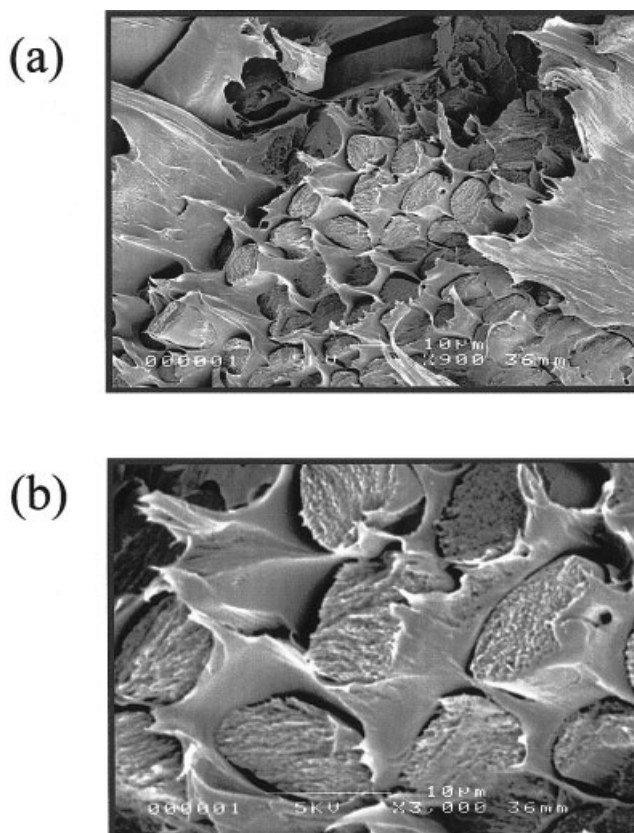
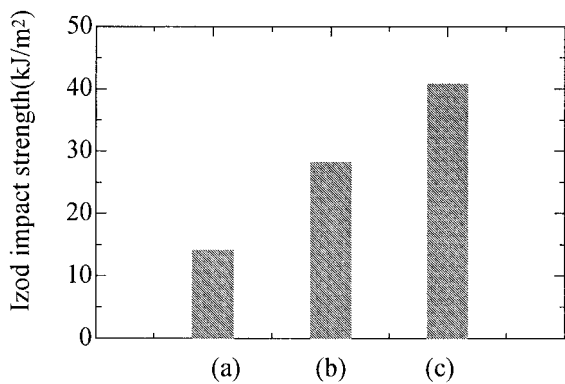


Figure 4 SEM photographs of the fractured surface of the original PLA/lyocell composites: magnification (a) $\times 900$, and (b) $\times 3000$.

ites was comparable to that of PHBV composites, although pure PLA has a higher tensile strength than PHBV. The PLA composites may contain some structural defects. The structure of the PLA composite is discussed in the following section. Regarding elongation at break, PLA composites (6.4–10.4%) showed a higher value than pure PLA sheet (2.1%). On the other hand, the elongation of PBS and PHBV composites decreased with increasing fiber content. These results are attributed to the facts that lyocell fiber has a higher elongation than PLA, and lower elongation than PHBV and PBS. The elongation of original PHBV sheet (4.9%) became 30.4% after pressure molding at 3 MPa, 160°C for 5 min (Table I, Exp. No. 1).

Effect of annealing of PLA/lyocell composites

PBS and PHBV can crystallize at room temperature (20–30°C) because T_g 's of PBS (–32°C) and PHBV (2°C) are considerably lower than the room temperature. However, the crystallization of PLA at the room temperature is very slow because of a high T_g (60°C). Therefore, the effect of annealing at 100°C for 3 h was investigated regarding the PLA/lyocell composites. The original degree of crystallinity (χ_c) of the composite can be evaluated from the value of $(\Delta H_m - \Delta H_{g,c})$, where ΔH_m and $\Delta H_{g,c}$ are the heat of melting and crystallization from the glassy state of the composite in the first heating DSC scan, respectively. By considering the heat of melting of 100% crystalline PLA as 93 J/g,¹⁷ χ_c of PLA component of the original and annealed PLA/lyocell composites (fiber content, ca. 40 wt %) were evaluated to be 15 and 35%. Figure 2 shows the comparison of tensile properties between the original and annealed PLA/lyocell composites. Despite the increase of χ_c by annealing, the annealed



(a)PLA (b)PLA/lyocell 6ply (c)PLA/lyocell 8ply

Figure 5 Izod impact strength of the PLA and multilayered PLA/lyocell composites: (a) PLA, (b) PLA/lyocell (6 ply), and (c) PLA/lyocell (8 ply).

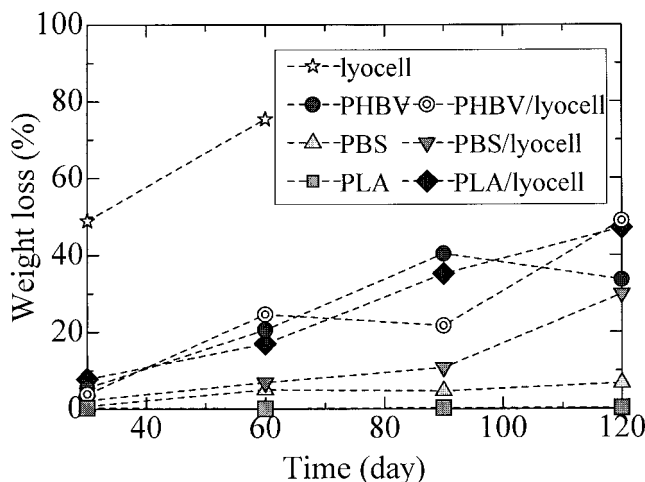


Figure 6 Weight loss of the green composites in the soil burial test.

composites showed significantly lower tensile strength and moduli than the original composites.

Figure 3 shows the SEM photographs of the surface of the original and annealed PLA/lyocell composites. The annealed composite had many more cracks than the original sample. The reason the original PLA composite showed a relatively low tensile strength should be the existence of some cracks in the original composite. Figure 4 shows the magnified SEM photographs of the fractured surface of the original PLA/lyocell composite. It is obvious that PLA permeates among the lyocell fibers in the cloth, indicating that the interfacial delamination between lyocell cloth and PLA is difficult to occur. Therefore, it is thought that the shrinkage of PLA adhered to lyocell cloth caused the cracks after annealing. The occurrence of micro-cracks should be the reason for the lowering of tensile properties.

Izod impact strength of multilayered PLA/lyocell laminate composites

Izod impact tests of multilayered PLA/lyocell laminate composites with fiber content ca. 50 wt % as compared with the PLA sheet prepared by pressure molding was carried out to evaluate the improvement

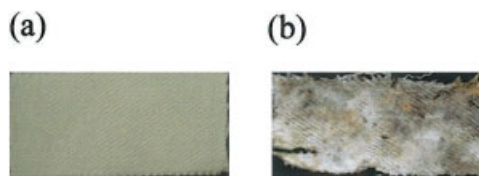


Figure 7 Photographs of lyocell fabric after the soil burial test: (a) before test and (b) at 30 days.

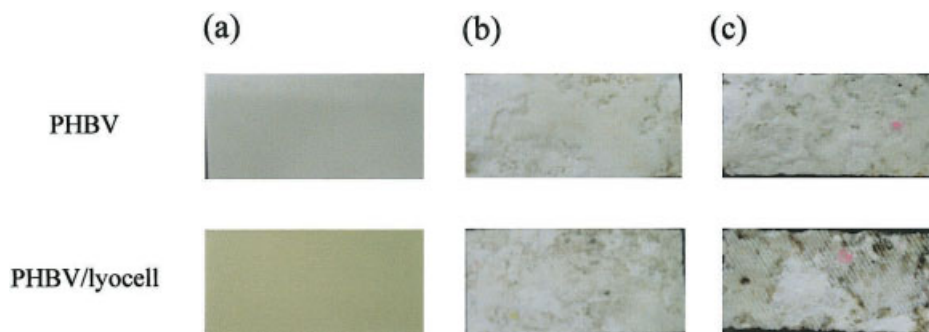


Figure 8 Photographs of PHBV (top) and PHBV/lyocell composite (bottom) after the soil burial test: (a) before test, (b) at 60 days, and (c) at 120 days.

of toughness for the PLA/lyocell composites. The PLA composites with 6-ply (28.2 kJ/m^2) and 8-ply (40.8 kJ/m^2) lyocell fabrics showed approximately two and three times higher impact strength than pure PLA (14.1 kJ/m^2), respectively (Fig. 5). Although the simple comparison between a laminate composite and an injection-molded short-fiber composite may be unsuitable, the short abaca fiber-reinforced PLA composite (fiber length, 5 mm; fiber content, 10 wt %) prepared by injection molding¹⁴ showed a considerably lower Izod impact strength ($10\text{--}12 \text{ kJ/m}^2$). Mieck et al. found that the impact strength of lyocell fiber composites is much higher than of natural fiber composites when the composites prepared by the same fiber length and method were compared.¹⁸ The improvement of impact strength for the PLA/lyocell composite should be attributed to the use of lyocell fabric and the fact that lyocell fiber has a longer elongation than plant-based fibers such as abaca and flax.

Biodegradability of the green composites

Biodegradability of all the green composites with fiber content ca. 40 wt % was evaluated by the soil burial test (Fig. 6). Lyocell fabric showed the highest weight loss (75%) at 60 days, and the recovery of decomposed

fragments was difficult after that (Fig. 7). Regarding the biodegradation of polyester sheet, the order of higher weight loss was $\text{PHBV} > \text{PBS} > \text{PLA}$, as is obvious from Figure 6. PHBV/lyocell composite showed almost the same weight loss as PHBV sheet until 90 days, considering the scattering of the values. This result suggests that the biodegradation of the lyocell in the PHBV/lyocell composite does not so largely proceed until 90 days. It is thought that the surface of lyocell fabric is fully coated by PHBV. The PHBV/lyocell composite shows a higher weight loss than PHBV at 120 days, indicating the lyocell starts to decompose. The change of photographs shown in Figure 8 supports this degradation mode of PHBV/lyocell. PBS/lyocell composite showed a higher weight loss than PBS sheet, indicating that the biodegradation of both the components occurs in the PBS/lyocell composite. Figure 9 supports this degradation mode of PBS/lyocell. Although the PLA sheet showed little weight loss after 120 days, PLA/lyocell composite showed a considerably higher weight loss than PBS/lyocell composite. The lyocell fabric in PLA/lyocell composite obviously degraded, as is shown in Figure 10. Recovery of the PLA matrix delaminated from the lyocell fabric was difficult. Because pure PLA film was almost unchanged after 120 days, the degradation of

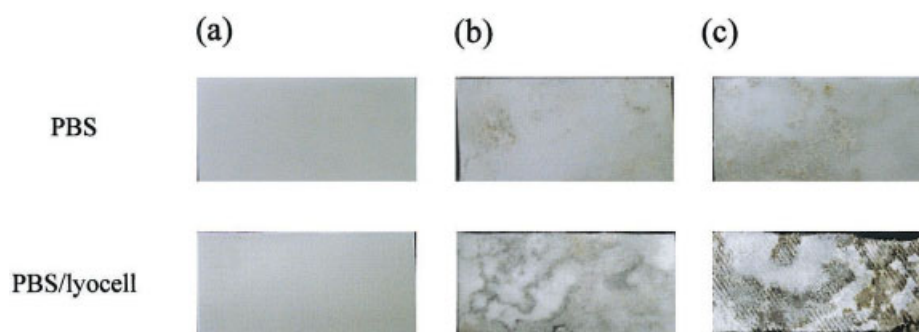


Figure 9 Photographs of PBS (top) and PBS/lyocell composite (bottom) after the soil burial test: (a) before test, (b) at 60 days, and (c) at 120 days.

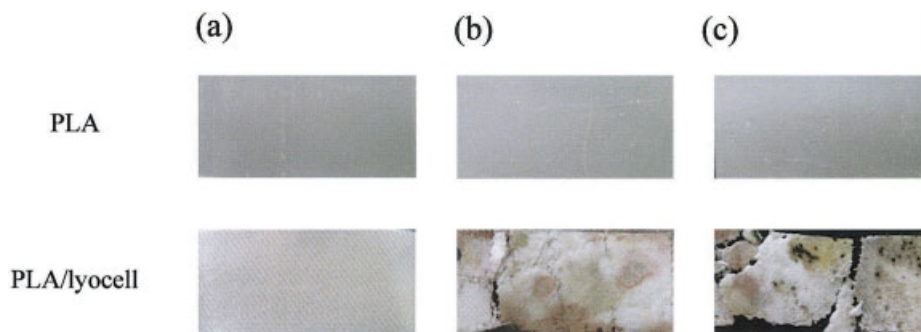


Figure 10 Photographs of PLA (top) and PLA/lyocell composite (bottom) after the soil burial test: (a) before test, (b) at 60 days, and (c) at 120 days.

the PLA in the composite is not thought to proceed. The microcrack or delamination in the PLA/lyocell composite may cause the direct biodegradation of the lyocell fabric in the composite.

CONCLUSION

Green composites composed of lyocell fabric and biodegradable polyesters (PHBV, PBS, and PLA) were prepared by compression-molding method. The tensile moduli and strength of all the biodegradable polyester/lyocell composites increased with increasing fiber content. When the obtained PLA composites were annealed at 100°C for 3 h, the tensile strength and moduli were lowered despite the increase of degree of crystallization of PLA component. The SEM observation of the composites revealed that the surface of the annealed composite has many cracks caused by the shrinkage of PLA adhered to lyocell fabric. As is obvious from the result of the impact test of multilayered PLA/lyocell laminate composites, the toughness of PLA composite was improved by the reinforcement with lyocell fabric. As a result of the soil viral test, the order of higher weight loss of the green composites after 120 day became PHBV/lyocell, PLA/lyocell > PBS/lyocell. The unexpectedly high biodegradability of PLA/lyocell composite is thought to be related

to the direct degradation of the lyocell caused by the microcrack or delamination of the composite.

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