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Investigation of Jute-Lignin-Poly (3-hydroxybutyrate) Hybrid Biodegradable Composites with Low Water Absorption

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Abstract: This study developed a novel PHB-lignin-jute biodegradable composite with preferable mechanical properties and low water absorption. The appearances of fracture surface of composites were analyzed by scanning electron microscope. The result suggested a Gaussian-like distribution of the size particles supporting the presence of lignin with a radius smaller than 0.5 μm. According to X-ray diffraction, the presence of lignin and jute fibers was decreased the crystallization of PHB. Moreover, the glass transition temperature of PHB increased, and the endotherm during glass transition was decreased. The maximum tensile strength and modulus of composites were obtained with 30 wt% jute fiber contents and 4 wt% lignin contents. The presence of jute fibers was largely increased the water absorption of composites. However, the presence of lignin was effectively decreased the water absorption of composites at saturation levels.

Keywords: Jute fiber, Lignin, Poly (3-hydroxybutyrate), Composites, Water absorption

Introduction

Recently, biodegradable polymers receive an attention as alternative of petroleum based polymer. Polyhydroxyalkanoates (PHAs) are linear polyesters produced in nature by bacterial fermentation of sugar or lipids. More than 150 different monomers can be combined within the family to give materials with extremely different properties [1-3]. Poly(3-hydroxybutyrate) (PHB) is the best characterized PHA. High price is the disadvantage of PHB materials to apply in various fields [4-7]. Meanwhile, the cellulose fibers such as jute, flax, sisal and ramie as a reinforcement material receive same attention, because of low density, light weight and low cost, especially renewable and biodegradable [8-13].

Based on the requirement of biodegradability and low price of composites, cellulose fiber reinforced biodegradable polymer composites (CFBC) were developed by many researchers [14-19]. However, it is an obstacle to widespread use of the CFBC having that high water absorption of CFBC due to the presence of hydroxyl and other polar groups in various constituents of cellulose fibers [20-23]. Thus, the applications of CFBC are limited.

Lignin is generally defined as natural polymeric products arising from an enzyme initiated dehydrogenative polymerization of three primary precursors, i.e. trans-coniferyl, trans-sinapyl, and trans-p-coumaryl [24]. As industrial production, lignin is always prepared by paper making waste. As the report of Canetti and Bertini [25], lignin acted as the reinforcement and nucleating agent largely improved the crystal structure of composites. In addition, the low water absorption of composites with lignin is expected because of the phenyl group with large nonpolarity in lignin structure.

Currently, PHB-jute composites were hindered to apply in many fields due to high water absorption as well as other CFBC materials. Meanwhile, how lignin presence affects water absorption of PHB-jute composites is not examined in previous studies yet.

The purpose of this paper is developing a novel PHB based biodegradable composite. Therefore, jute fibers and lignin reinforced PHB hybrid composites are prepared. In this composite, jute fibers and lignin act as reinforcement. Especially, the lignin acts as nucleating agent is expected to improve the crystallization of PHB. Moreover, we clarify the effect of presence of jute fibers and lignin on the mechanical properties, water absorption and structure of PHB-lignin-jute hybrid composites.

Experimental

Materials and Sample Preparation

The poly(3-hydroxybutyrate) (PHB) used in this study was purchased from Sigma-Aldrich Corp. with a 185 °C of melting temperature, and 42 °C of glass transition temperature. Lignin was purchased from Leechem Corp. (Korea).

Jute fibers were cut into 3 mm with aspect ratio of 32.6. PHB-lignin-jute composites (PLJ) were prepared in chloroform solvent as following steps. (1) PHB was dissolved in chloroform as the ratio of 1:5 (w/v). (2) Jute fibers and lignin were put into PHB solution with different contents. (3) PHB solution was subjected to ultrasonic bath for 24 h. (4) Solvent chloroform was evaporated from the solution. Testing samples were fabricated by compressing molding machine at 185 °C and a pressure of 60 MPa. The sample preparation of PLJ composites was shown in Table 1.

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Table 1. Contents of lignin and jute fibers for making samples

Sample ID	PHB (wt%)	Lignin (wt%)	Jute fibers (wt%)
P	100	0	0
PL	96	4	0
PJ20	80	0	20
PJ30	70	0	30
PJ40	60	0	40
PLJ20	76	4	20
PLJ30	66	4	30
PLJ40	56	4	40

Characterization Methods

Morphological Analysis

The cross-section of tensile test samples was observed using a scanning electron microscope (SEM) (JEOL, JSM-7000F). The instrument was operated at 15 kV, and various sample surfaces were scanned to obtain the appearance of the PHB-jute interface.

Crystal Structure

The extent of crystallization formation of different composites and pure PHB was determined by X-ray diffraction. The datum were obtained at 20 °C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000 W tube (Cu Kα radiation, λ=0.154 nm). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 5 to 40 °.

Thermal Properties

Thermal analysis was performed with differential scanning calorimeter (DSC) under an ultrahigh purity nitrogen atmosphere. The equipment was calibrated with indium and tin standards. Samples were heated from 25 to 230 °C with a 10 °C/min heating rate. Melting point temperature (T_m), glass transition temperature (T_g) and heat of fusing (ΔH_m) were determined from the endothermic curves.

Furthermore, composite samples were cut into 20×13×3 mm, and heating on a thermostatic stage at 80 °C. An electronic thermometer was employed to record the temperature of upper layer in given time as shown in Figure 1.

Mechanical Properties

Tensile tests were carried out using a universal test machine (4467; Instron Corp.) to evaluate the tensile properties of samples according to ASTM D 638-03. Cross-head speed was chosen at 10 mm/min. Flexural tests were carried out using a universal test machine (4467; Instron Corp.) to evaluate the flexural property of samples according to ASTM D790-03. Sample dimension was 60×12.7×3 mm, the span length was chosen at 48 mm.

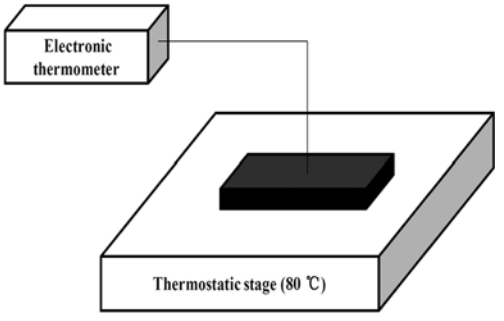

Figure 1. Sketch map of thermal resistance test.

Water Absorption

The sample was immersed in distilled water at room temperature in different glass containers for a long period, after that, wipe the water on composites surface, and weigh the samples on a balance with a precision of 0.1 mg. The moisture absorption at given time (Mt) was calculated by equation (1).

$$Mt = 100\ (Wt - Wd) / Wd \quad (1)$$

Where, Wd and Wt referred to the weight of dry sample and wet sample, respectively.

Results and Discussion

Morphological Analysis

The appearances of fractural structure of composites were shown in Figure 2. A compact bonding between jute fibers and PHB was found in picture (a), (c) and (d). The dispersion degree of lignin in the composites was visualized carrying out a SEM morphological analysis on picture (b). The micrographs showed lignin as a dispersion of particles having a diameter ranging from 0.3 to 1.3 μm. Quantitative analysis of SEM images was used to evaluate the lignin particles dimension and distribution in the composites. In Figure 3, the amount of particles was reported as a function of different radius intervals for sample PL and the particles having a radius ranging from 0.3 to 0.7 μm accounted for

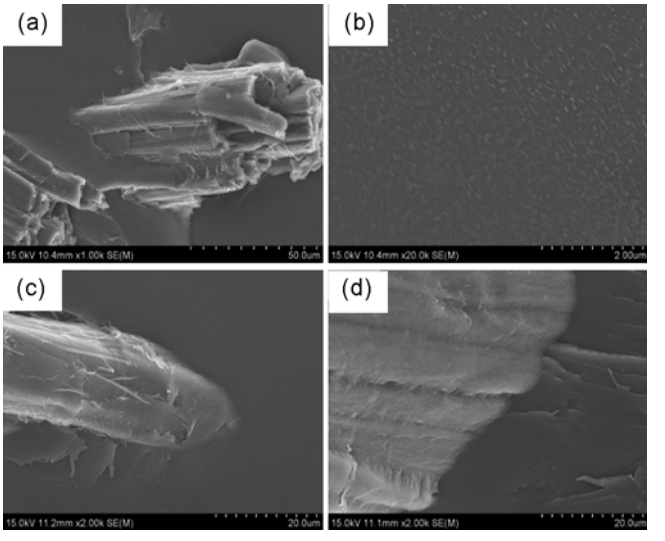

Figure 2. Cross-sections micrographs of PLJ composites; (a) sample PJ20, (b) sample PL, (c) and (d) sample PLJ20.

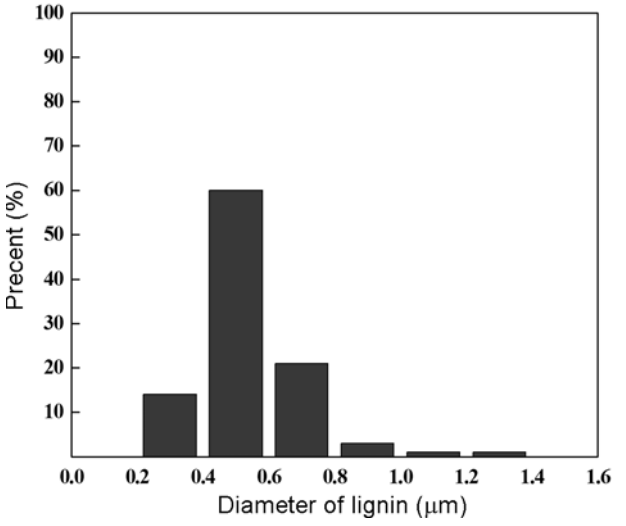

Figure 3. Size distribution of lignin particles in PL composite.

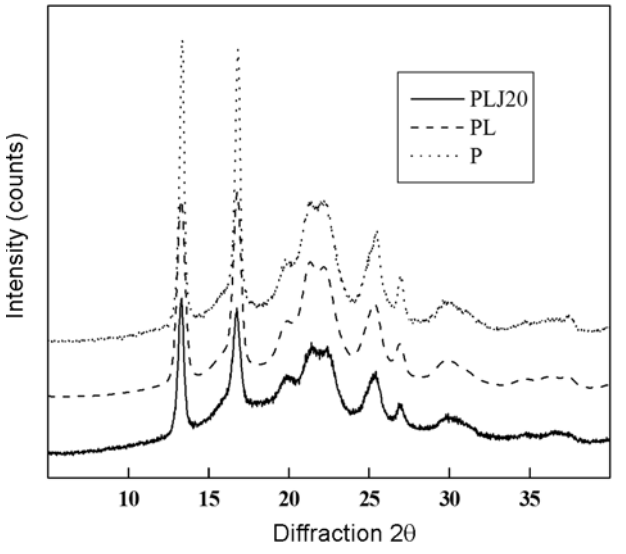

Figure 4. XRD profile of different sample.

more than 90 %. Based on the morphological investigation, it is pointed out that some of large lignin domains consisted of cluster of particles. The trend reported in Figure 3 suggested a Gaussian-like distribution of the size particles supporting the presence of lignin with a radius smaller than 0.5 μm.

Crystal Structure

As shown in Figure 4, the extent of increasing as the sequence of PLJ20, PL and pure PHB reveals that the presence of lignin and jute fibers decreased the crystallization of PHB. Furthermore, the effect of fiber presence on crystallization is more sensitive than that of lignin presence. The similar results were found in Kai's paper [26]. However,

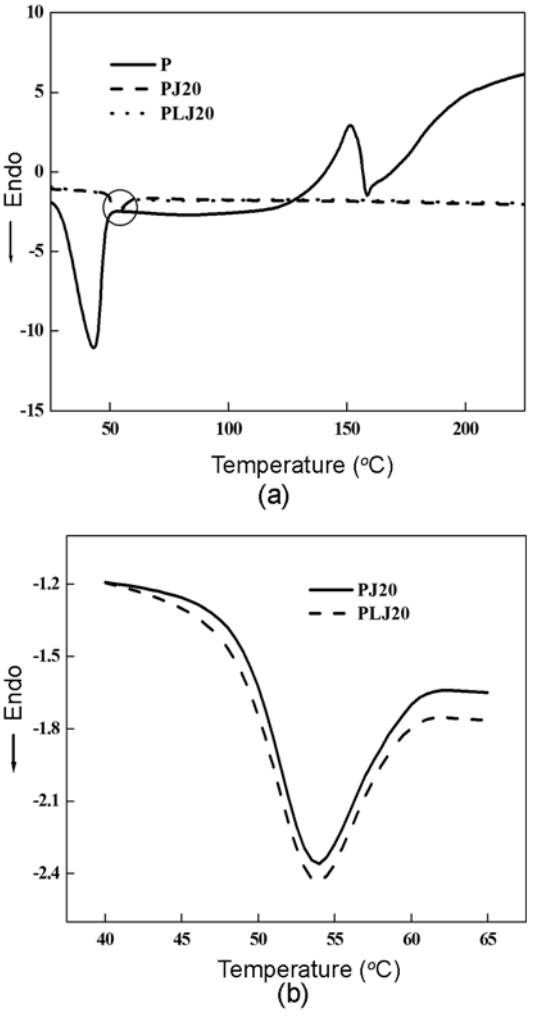

Figure 5. DSC curves of different sample.

there was only a tiny decrease of crystallization in Kai's study, which should due to the small lignin contents (1 %) in composites. The lignin contents (4 %) in this study is higher than that in Kai's paper, thus the decrease of crystallization of PHB in our work is more obvious. Moreover, the improved flowability of PHB was caused by low crystallization could lead to good bonding between jute fibers and PHB.

Thermal Analysis

Figure 5 shows the DSC curves of different samples. Endothermic peaks of three materials around in 42-53 °C were regarded as glass transition temperature. The presence of lignin and jute fibers increased the glass transition temperature of PHB. The area of endothermic peak of sample PLJ20 was less than that of sample PJ20, since the crystallization of sample PLJ20 was less than sample PJ20. And the endotherm during glass transition of sample PLJ20 was less than that of sample PJ20.

Figures 6(a) and (b) show the thermal resistance property

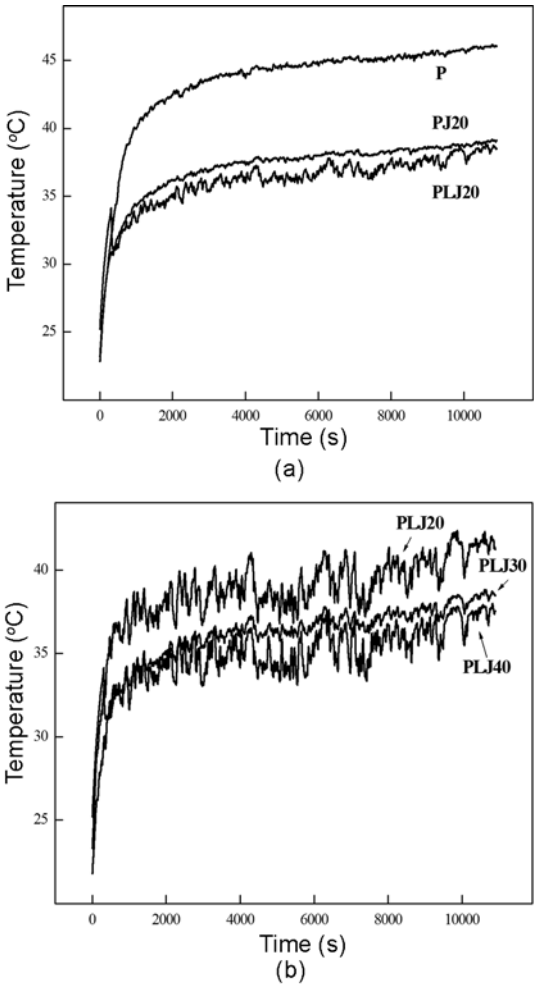

Figure 6. Temperature-time curve of various composites on a thermostatic stage at 80 °C.

of various composites, according to Figure 6(a), in the same heating time, the temperature of PHB material was higher than that of PJ20 and PLJ20 composites. It was attributed to the presence of jute fibers. Jute fibers possessed a higher thermal resistance than PHB material. It could more clearly obtain from Figure 6(b). In the same heating time, there was a lower temperature at higher jute fiber contents. It indicated that the jute fibers contributed a majority of thermal resistance in composites. Moreover, in comparison between sample PJ20 and PLJ20, the temperature of sample PJ20 was higher than sample PLJ20 in the same heating time. It is attributed to the presence of lignin and its high thermal resistance as well.

Tensile Properties

According to Figure 7 and 8, the tensile strength and modulus of PHB were slight increased because of the presence of lignin. Furthermore, the presence of jute fibers largely increased the tensile strength and modulus of PHB.

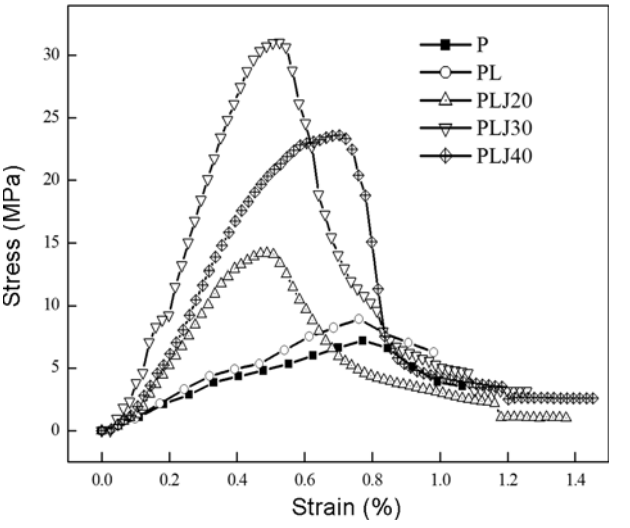

Figure 7. S-S curves of various composites during tensile test.

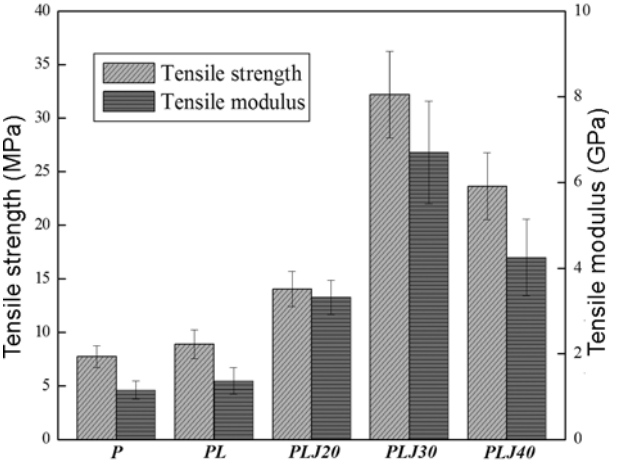

Figure 8. Tensile properties of various samples.

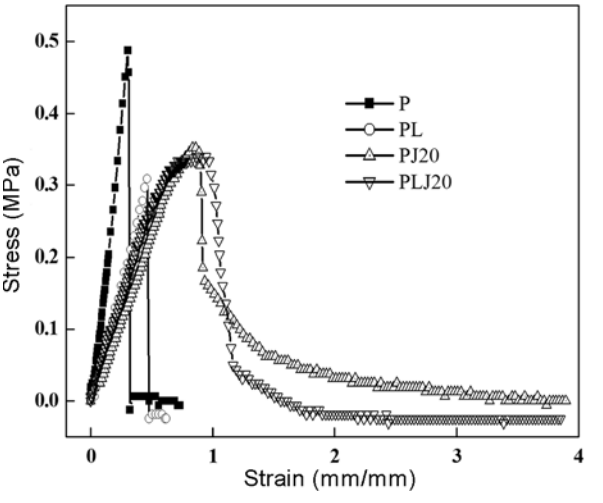

Figure 9. Stress-strain curves of various composites during flexural test.

The sample PLJ30 appeared the largest tensile strength and modulus values. For random distribution of fibers, 40 wt% contents of jute fibers was too much to adequately wetting by PHB matrix, it is casused the poor stress transfer between jute fibers and PHB matrix. Thus, the strength and modulus of sample PLJ40 were lower than those of sample PLJ30.

Flexural Properties

During the flexural test, pure PHB had the highest bending stress and lowest strain at break because of its high crystallization as shown in Figure 9. Contrarily, lower bending stress and higher strain at break were found at sample PL and PLJ20. It was because that the presence of lignin and jute fibers decreased the crystallization and brittleness of PHB, making the composites can withstand higher flexural deformation than pure PHB materials.

Water Absorption

Moisture absorption into composites was conducted by three ways: (1) micro gaps between polymer chains, (2) gaps and flaws at the interfaces between fiber and polymer because of incomplete wet ability and impregnation and (3) micro cracks in the matrix formed during the compounding process. Figure 10 shows the water absorption curves for various jute fiber reinforced PHB composites.

From Figure 10, it was clear that the fiber-reinforced composites rapidly absorbed water at the initial stage and later a saturation level was attained without any further increase. An exponential decay model (see equation (2)) was suggested to fit the behavior of water absorption of PJ20 and PLJ composites.

$$Y = y_0 - A \exp(-x/t_i) \quad (2)$$

Where, y_0 referred to the water absorption in saturation level, A and t_i referred to the speed of closing to limitation.

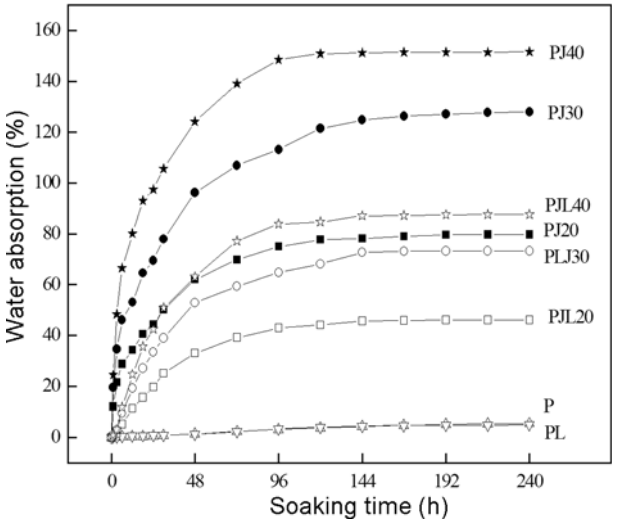

Figure 10. Water absorption of various samples.

Table 2. Parameters in first order exponential function

	y_0	A	t_i
PJ20	79.77	69.42	33.01
PLJ20	46.13	47.38	38.29
PJ30	127.94	109.61	37.15
PLJ30	73.32	74.10	39.43
PJ40	151.49	129.67	24.53
PLJ40	87.61	89.46	34.49

The parameters of different composites were shown in Table 2. The saturated absorption of composites increased with increasing fiber contents. Water absorption of sample PJ20 and PLJ20 were 79 and 46 %, respectively. Contrarily, sample P and PL did not show any water absorption. In PJ20 composite, the water absorption was high due to the presence of hydroxyl and other polar groups in various constituents of jute fibers. The poor compatibility of hydrophilic jute fiber and hydrophobic PHB results in a number of gaps and flaws. In the case of sample PLJ, the presence of lignin with phenyl group made it more hydrophobic in nature. Moreover, the presence of lignin decreased the crystallization of PHB matrix, and causing the better adhesion between matrix and fibers, which decreased the velocity of the diffusing molecules.

Conclusion

A good adhesion between jute fibers and PHB were found at both PJ20 composite and PLJ20 composite. The presence of jute fibers and lignin decreased the crystallization of composites. Thus, the glass transition temperature of PHB increased, and the endotherm during glass transition was decreased. Moreover, the decrease of crystallization and brittleness of PHB leaded to the high displacement at break of sample PLJ in flexural testing. The maximum tensile strength and modulus of composites were found at PLJ30 composite. The presence of jute fibers largely increased the water absorption of composites. However, the presence of lignin effectively decreased the water absorption of composites.

References

1. S. Kusaka, H. Abe, S. Y. Lee, and Y. Doi, *Appl. Microbiol. Biot.*, **47**, 140 (1997).
2. L. L. Madison and G. W. Huisman, *Microbiol. Mol. Biol. R*, **63**, 21 (1999).
3. R. H. Marchessault, *Tre. in Polym. Sci.*, **4**, 163 (1996).
4. H. Preusting, J. Kingma, G. Huisman, A. Steinbüchel, and B. Witholt, *J. Environ. Polym. Degrad.*, **1**, 11 (1993).
5. S. Y. Lee, *Tibtech*, **14**, 431 (1996).
6. S. Y. Lee, K. S. Yim, H. N. Chang, and Y. K. Chang, *J. Biotechnol.*, **32**, 203 (1994).

7. E. Y. Lee, D. Jendrossek, A. Schirmer, Y. Choi, and A. Steinbüchel, *Appl. Microbiol. Biotechnol.*, **42**, 901 (1995).
8. V. Vilay, M. Mariatti, R. M. Taib, and M. Todo, *Compos. Sci. Technol.*, **68**, 631 (2008).
9. M. Z. Pan, D. G. Zhou, J. Deng, and S. Y. Zhang, *J. Appl. Polym. Sci.*, **114**, 3049 (2009).
10. T. Yu, J. Ren, S. Li, H. Yuan, and Y. Li, *Compos. Part A*, **41**, 499 (2010).
11. Y. Seki, *Mater. Sci. Eng., A*, **508**, 247 (2009).
12. J. B. Naik and S. Mishra, *J. Appl. Polym. Sci.*, **106**, 2571 (2007).
13. T. Stuart, Q. Liu, M. Hughes, R. D. McCall, H. S. S. Sharma, and A. Norton, *Compos. Part A*, **37**, 393 (2006).
14. E. Zini, L. M. Focarete, I. Noda, and M. Scandola, *Compos. Sci. Technol.*, **67**, 2085 (2007).
15. S. Shibata, Y. Cao, and I. Fukumoto, *Compos. Part A*, **39**, 640 (2008).
16. S. Ochi, *Mech. Mater.*, **40**, 446 (2008).
17. J. Gironès, M. T. B. Pimenta, F. Vilaseca, A. J. F. Carvalho, P. Mutjé, and A. A. S. Curvelo, *Carbohydr. Polym.*, **74**, 106 (2008).
18. M. A. Dweib, B. Hu, H. W. Shenton III, and R. P. Wool, *Compos. Struct.*, **74**, 379 (2006).
19. H. S. Yang, M. P. Wolcott, H. S. Kim, S. Kim, and H. J. Kim, *Polym. Test.*, **25**, 668 (2006).
20. B. Singh, M. Gupta, and A. Verma, *Polym. Compos.*, **17**, 910 (1996).
21. L. Liu, J. Yu, L. Cheng, and W. Qu, *Compos. Part A*, **40**, 669 (2009).
22. P. A. Sreekumar, S. P. Thomas, J. M. Saiter, K. Joseph, G. Unnikrishnan, and S. Thomas, *Compos. Part A*, **40**, 1777 (2009).
23. S. A. Hashemi, H. Arabi, and N. Mirzaeyan, *Polym. Compos.*, **28**, 713 (2007).
24. K. V. Sarkanen and C. H. Ludwig, "In Lignins: Occurrence, Formation, Structure and Reactions", pp.1-18, Wiley-Interscience, New York, 1971.
25. M. Canetti and F. Bertini, *Compos. Sci. Technol.*, **67**, 3151 (2007).
26. W. Kai, Y. He, N. Asakawa, and Y. Inoue, *J. Appl. Polym. Sci.*, **94**, 2466 (2004).