Biodegradable Composites from Sugar Beet Pulp and Poly(lactic acid)

4 **AUTHORS**, INCLUDING:

Cheng-Kung Liu
Agricultural Research Service

183 PUBLICATIONS   **1,846** CITATIONS

SEE PROFILE

Marshall L Fishman
Agricultural Research Service

107 PUBLICATIONS   **2,778** CITATIONS

SEE PROFILE

Biodegradable Composites from Sugar Beet Pulp and Poly(lactic acid)

LinShu Liu,*,† Marshall L. Fishman,† Kevin B. Hicks,† and
Cheng-Kung Liu‡

Crop Conversion Science and Engineering (CCSE) and Fats, Oils and Animal Co-products (FOAC),
Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture,
600 East Mermaid Lane, Wyndmoor, Pennsylvania 19038

Sugar beet pulp and poly(lactic acid) (PLA) composites were prepared by compression-heating. The resultant thermoplastics had a lower density, but they had tensile strength similar to that of pure PLA specimens as well as the same geometric properties. Tensile properties depended on the initial water content of sugar beet pulp and the process by which composites were manufactured. In comparison with sugar beet pulp, the composite showed improved water resistance. This can be attributed to the hydrophobic character of PLA and pulp—matrix interactions. The composite thermoplastics showed suitable properties for potential use as lightweight construction materials.

KEYWORDS: Sugar beet pulp; poly(lactic acid); compression-heating; composite

INTRODUCTION

This paper describes research in which sugar beet pulp (SBP) and poly(lactic acid) (PLA) were developed into composites with suitable mechanical properties for lightweight construction materials. The overall objective of this study was to add value to the U.S. sugar beet industry by finding new uses for its processing residues (*1*). Economic activity by the U.S. sugar beet industry is estimated at $260 billion, but this is threatened by increasing world market competition. Enormous quantities of residues, ~400 million tons of wet pulp, are generated from the U.S. beet sugar industry, which are sold as low-value animal feed or must be disposed of in an environmentally acceptable way, which requires additional expense. It is now recognized that finding new ways to profitably utilize the enormous amounts of this low-value byproduct from beet sugar processing is critical for the future profitability of the industry. Beet pulp is a rich source of highly functional cell wall polysaccharides, including pectin, hemicellulose, and cellulose. A diverse range of new products in nonfood areas presents a new strategy to develop a broad market for these polysaccharides. It is absolutely necessary that the finished value-added products have unique functionalities and be competitive in cost with comparable environmentally nonsustainable products currently in the marketplace.

PLA is a hydrophobic polymer prepared from renewable agricultural raw materials, which are fermented to lactic acid followed by polymerization into PLA with desired molecular weights. The polymer erodes mainly by hydrolysis. This mechanism promulgates bulk degradation (*2*). The polymer is randomly chopped into oligomers via the attack of water molecules. The final degradation product, lactic acid, also is a metabolic product of all animals and microorganisms and is believed to be nontoxic. Thus, PLA can be disposed of simply by composting or land-filling. PLA can be used as a hard and tough engineering plastic for a broad variety of applications, for instance, automotive parts, office supplies, and implantable orthopedic devices (*3*, *4*). However, one obstacle to the widespread application of PLA polymers is that they are stiff and brittle in thicker materials. Another obstacle is their present higher price than petroleum-derived thermoplastics. Several studies have suggested the advantages of natural polymers/PLA reinforced thermoplastics (*5*−*8*). Natural polymers usually have low density and low price and are biodegradable. The tensile strength and stiffness of PLA composite can be increased when a portion of jute fibers (*5*) or flax fibers (*6*) is included. On the other hand, moisture adsorption and thermal instability are the drawbacks of most natural polymers, limiting their applications. Commercial production of PLA and natural polymer composites is still a challenge, but these biobased materials have potentially promising markets.

In this study, SBP and PLA composites were prepared by compression-heating. The composites were characterized for structural, physical, and mechanical properties, water resistance, and degradability.

MATERIALS AND METHODS

Composite Preparation. Finely ground dry SBP residue (~300 μm particle size) was obtained as a gift from Tim Ayers of Willamette Valley Co. (Eugene, OR). PLA (M_w 148000, M_n 110000; Cargill Dow, Minnetonka, MN) was milled to small particle size, and fractions of ~300 μm were collected. SBP and PLA particles, containing 0, 10, 20, 40, and 50 wt % of SBP, were mixed for 5 s using a heavy-duty

* Corresponding author [telephone (215) 233-6486; fax (215) 233-6406; e-mail lsliu@errc.ars.usda.gov].
† CCSE.
‡ FOAC.

9018 *J. Agric. Food Chem.,* Vol. 53, No. 23, 2005

Liu et al.

Table 1. Mechanical Properties of SBP/PLA Composites[a]

material	density (g/cm^3)	elongation (%)	fracture energy (J/cm^3)	tensile strength (MPa)	tensile modulus (MPa)
PLA	1.143	6.4 ± 0.4[b]	0.81 ± 0.18	30.5 ± 1.7	1017 ± 69.0
10%[c] SBP/PLA	1.062	6.7 ± 0.5	0.97 ± 0.11	37.5 ± 0.5	1043 ± 39.5
20%[c] SBP/PLA	0.923	7.0 ± 0.3	0.85 ± 0.21	28.9 ± 3.0	869 ± 52.8
40%[c] SBP/PLA	0.804	5.7 ± 0.6	0.70 ± 0.20	11.9 ± 1.6	527 ± 67.3

[a] SBP was pretreated by vacuum-drying. [b] Data expressed as mean ± SD ($n = 3$). [c] Numbers indicate the SBP content in composites (wt %).

Table 2. Mechanical Properties of 50% SBP/PLA from Different SBPs

SBP	tensile strength (MPa)	tensile modulus (MPa)	fracture energy (J/cm^3)	elongation (%)
vacuum-dried	8.5 ± 1.2[a]	460 ± 174	0.64 ± 0.00	4.7 ± 0.3
double-dried	15.4 ± 4.0	583 ± 146	0.52 ± 0.00	4.5 ± 0.4
preheated	23.3 ± 11.2	749 ± 255	0.48 ± 0.12	5.0 ± 0.9

[a] Data expressed as mean ± SD ($n = 3$).

blender at the middle speed. The mixtures were dried for 24 h prior to composite preparation by placing them in a vacuum desiccator. Composite materials were prepared by compression-heating using a Carver Laboratory Press equipped with two heating plates (Fred S. Carver Inc., Summit, NJ). The mixture, ~9 mL, was seeded in an aluminum frame sample mold (75 mm × 20 × 6 mm). The frame holding the mixture was placed between the two pieces of heating plates in the Carver Press, compressed at 100 kg/cm^2 into a rectangle plate with 2.5 mm thickness, and heated at 180 °C for 3 min and then at 200 °C for 1 min. After compression-heating, the samples were removed from the hot plates, placed in an oven at 180 °C, and immediately cooled to 23−25 °C over 120 min.

To evaluate the effect the initial water content and low molecular weight substances, which released from the SBP during the heating process, on the structural and mechanical properties of finished SBP/ PLA composites, SBP particles with three different pretreatments were used for composite preparation. They were (I) vacuum-dried SBP, which was prepared by vacuum-drying (20 μmHg) at ambient temperature for 24 h; (II) double-dried SBP, which was prepared by soaking with anhydrous acetone for 24 h followed by vacuum-drying; and (III) preheated SBP, which was prepared by heating at 180 °C for 3 min and then at 200 °C for 1 min post-vacuum-drying. SBP samples were weighed before and after being dried, and the weight loss due to the different treatments was calculated.

All samples thus prepared were stored in a desiccator at 10% relative humidity over calcium sulfate at 25 °C unless otherwise indicated.

Tensile Tests. Tensile tests were performed on the samples (*9*). Tensile property measurements included tensile strength, tensile modulus, elongation, and fracture energy. These properties were measured with a gauge length (clamp distance) of 40 mm and a strain rate (crosshead speed) set at 50 mm/min. Tensile strength is defined as the maximum stress a sample can sustain without fracture. Tensile modulus is a physical quantity representing the stiffness of a material. It is determined by measuring the slope of a line tangent to the stress−strain curve. The fracture energy indicates the toughness of the materials by integrating the stress−elongation curve. An upgraded Instron mechanical property tester, model 1122 (Instron Corp., Norwood, MA), and Testworks 3.1 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work.

Electron Microscopy. Composite materials were examined for the morphology of their fracture surfaces after tensile testing. Samples were mounted with adhesive to specimen stubs, and the edge was painted with colloidal silver adhesive. The samples were then sputtered with a thin layer of gold and examined in the high-vacuum/secondary electron imaging mode of a Quanta 200 FEG scanning electron microscope (SEM, FEI, Hillsboro, OR). Digital images were collected at 500×, 2500×, and 25000×.

Dynamic Mechanical Thermal Analysis. Small deformation dynamic mechanical analysis (DMA) was performed on a Rheometric
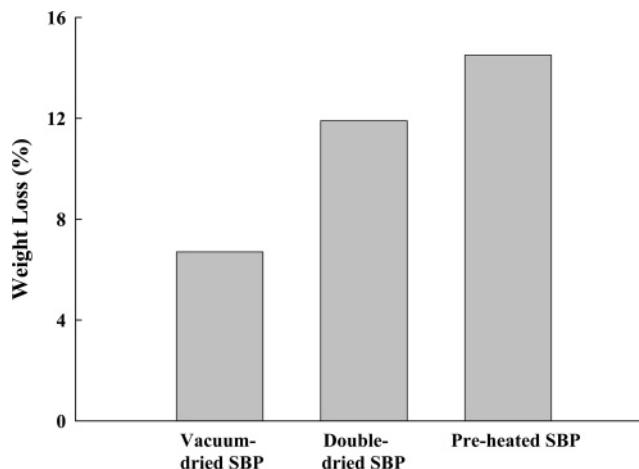

Figure 1. Weight loss of raw SBP particles after vacuum-drying for 24 h or treatment with dried acetone prior to vacuum-drying or heating at 180−200 °C for 4 min post-vacuum-drying. The SBP particles were originally stored in a desiccator over calcium sulfate at room temperature.

Scientific RSA II Solids Analyzer (Rheometric Scientific, Piscataway, NJ) (*10*). The test fixture consists of two 25 mm parallel plates. Typical samples tested had dimensions of about 6.0 mm × 3.0 mm ($d × h$). The samples were placed on the lower plate, and the upper plate was lowered onto the sample to give a slight compressive force (~5 g). The temperature interval was from −100 to 203 °C with the heating rate of 5 °C/min; the temperature was controlled by a liquid nitrogen environmental controller. The samples were tested using a compressive strain of 5% and a frequency of 10.0 rad/s. The data were analyzed using Rheometric Scientific Orchestrator software, version 6.5.7. Storage modulus, loss modulus, and loss tangent were determined.

Water Resistance. Water adsorption by composite materials was determined according to the formula

$$(W_t - W_0)/W_t × 100\%$$

where W_0 was the sample weight prior to water adsorption experiment and W_t was that weighed after the sample was conditioned at 95% relative humidity over water at room temperature until equilibrium (*10*).

Degradation Study. Samples were placed in garden soil (Humus, ACE Hardware Inc., Oak Brook, IL). Each preparation was replicated three times. Soil, 220 g, was stored in a 32 oz screw-neck jar (10.5 mm × 5.5 cm, $h × d$); a sample specimen was vertically inserted in the soils 2 cm from the bottom of the jar, and 75 mL of tap water (pH 6.0) were added to the jar. The water was completely adsorbed by the soils, resulting in a complete contact between the soil and the composite surfaces. The jars were placed in an incubator at 95% relative humidity over water at 40 °C for 4 weeks. At the conclusion of the experiment, the samples were removed from the soils, gently soaked in deionized water to remove surface-adhered soils, vacuum-dried at 20 μmHg at ambient temperature for 24 h, and examined for morphology by SEM. Samples also were placed in a volumetric flask containing tetrahydrofuran (THF; 25 mL for each). The flask was shaken at room temperature for 2−4 h to completely dissolve the PLA. The supernatant was pipetted off and analyzed for amount and molecular weight of PLA as described in the following section. The solid residuals were washed twice with fresh THF and three times with ethanol, dried in a vacuum, and weighed.
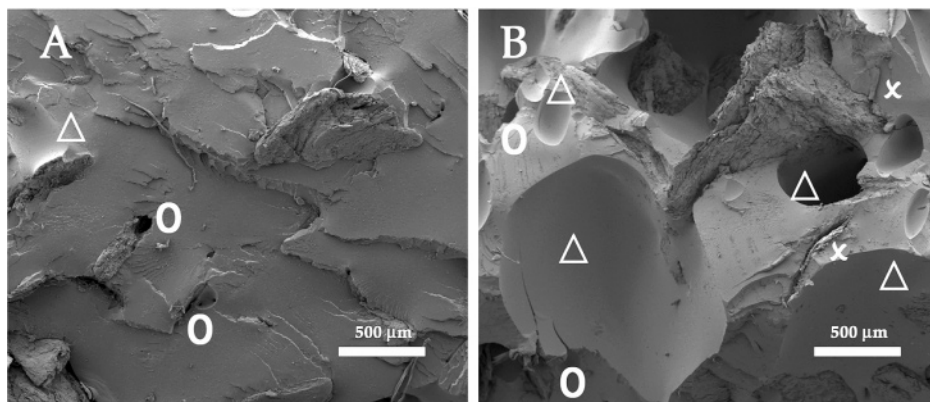
Figure 2. SEM photomicrographs of composite tensile fracture surfaces. The PLA composites contained vacuum-dried SBP at 10% (**A**) or 40% weight (**B**). More void spaces (○), gaps (×), and imprints and holes created by SBP particles that were pulled-out (△) can be clearly seen for the 40% SBP/PLA.
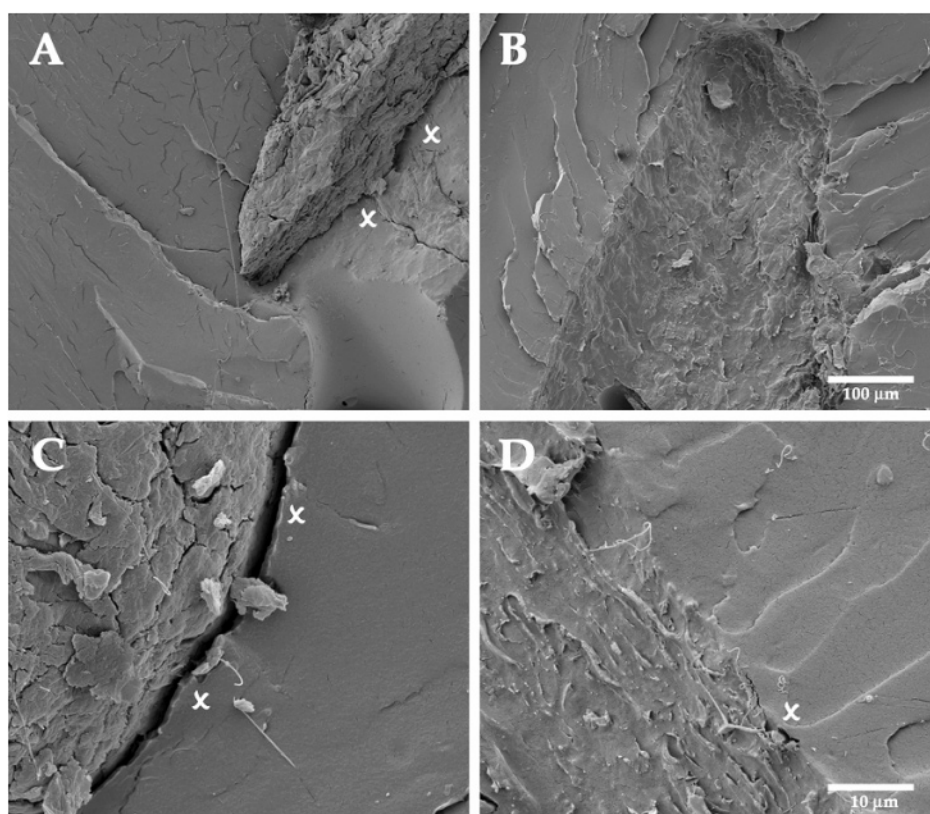

Figure 3. SEM photomicrographs of 50% SBP/PLA tensile fracture surfaces: (**A**, **C**) composites with double-dried SBP; (**B**, **D**) composites with preheated SBP; (×) gap.

Gel Permeation Chromatography (GPC). The molecular weights (MW) of PLA before and after composite fabrication, as well as those after degradation studies, were determined by GPC on a Shimadzu HPLC system (model LC-10AD, Kyoto, Japan) equipped with a Phenogel guard column (model 22824G, 50 mm × 7.8 mm), a Phenogel column (model GP/4446, 300 mm × 7.8 mm, both from Phenomenex, Torrace, CA), a refractive index detector (RID-10A), and an SCL-10A data station. THF was used as effluent at the flow rate of 1.0 mL/min. The analysis was carried out at room temperature as described previously (*11*). A universal calibration curve and the molecular weight of PLA were determined using the Mark−Houwink constant for PLA, $K = 5.45 \times 10^{-3}$ mL/g, and $a = 0.73$, and a set of polystyrene as standards (*11*, *12*). For PLA quantification, THF solutions containing known amounts of PLA were used as standards.

RESULTS AND DISCUSSION

Mechanical Testing. The molecular characteristics of PLA, M_w 148000 and M_w/M_n 1.35, were determined by GPC measurement after composite preparation, indicating the compression-heating treatment did not cause chain scission of the PLA. **Table 1** shows the mechanical properties of PLA and SBP/PLA composites with vacuum-dried fillers. SBP/PLA composites with SBP content of 40% weight were less elastic and less tough and had lower values of tensile strength and modulus than pure PLA samples. Nevertheless, composites with SBP levels equal to or lower than 20% weight were able to retain the mechanical properties of pure PLA. This suggests that at lower SBP content, the particles may have a good

adhesion with the PLA matrix. SBP may bind to PLA in some manner. Good adhesion favors stress transfer from mechanically weaker regions to adjacent stronger phases. This subject will be investigated and discussed in detail somewhere else. **Table 1** also shows that the inclusion of SBP to PLA reduced the composites' density, suggesting the possibility to create light-weight composite materials from SBP and PLA, which have mechanical properties comparable to or stronger than those of PLA alone. Mechanical properties of SBP/PLA are also dependent on the pretreatment of SBP. Pretreatment of SBP by soaking in acetone or heating enhanced the tensile strength and modulus of resulting composites. This was seen even at a higher SBP levels (**Table 2**). The composites with 50% weight of preheated SBP had tensile strength and modulus values similar to those of the composites containing only 20% of vacuum-dried SBP (**Tables 1** and **2**). However, a lower fracture energy was measured for double-dried and preheated SBP/PLA composites, indicating the brittle nature of these composites. The weight loss of SBP particles due to the different drying methods is shown in **Figure 1**. More weight loss was recorded for double-dried SBP than for vacuum-dried. Further weight loss was measured for the preheated SBP. Possibly, the SBP weight loss by drying the particles could be attributed to the removal of adsorbed water. Presumably, vacuum-drying removes only the water that was loosely adsorbed by SBP, whereas double-drying and preheating of SBP removes water both weakly and strongly bound to SBP. Water may be bound to SBP via association with hydrophilic groups and/or interaction with the polymer chains (*13*, *14*). These types of water are characterized as having a phase-transition temperature lower than that of bulk water and thus could not be removed by vacuum-drying. It can be expected that the water carried by SBP will evaporate due to the high temperature during composite formation, but the highly viscous PLA matrix may restrict the escape of water vapor from the closed system. This may result in void spaces and reduce interphase interactions of the particles with the continuous phase. Presumably, the small molecular volatile materials released from SBP at high temperature play the same role as the water molecules. This may explain why preheated SBP/PLA had even better mechanical properties than double-dried SBP/PLA (**Table 2**). The SEM study provided further information from the structural point of view.

SEM Study. The composites were fabricated by compression-heating in the temperature range of 180−200 °C, which is higher than the melting point range of PLA (160−180 °C). Thus, the PLA melted and deposited in the gaps among SBP particles to form a continuous matrix phase (**Figures 2** and **3**). **Figure 2** shows the fracture surfaces of vacuum-dried SBP/PLA samples, which were created by the tensile testing. Void spaces could be clearly seen. Breakage occurred in the PLA phase, leaving platelike fracture surfaces, which are similar in appearance observed with the tensile specimen fracture surfaces of jute/PLA or flax/PLA composites (*5*, *6*). For the composites with lower SBP content, breakage also was observed in the SBP phase (**Figure 2A**), indicating a good adhesion of SBP to PLA. As the portion of SBP in the composite increased, the capability of PLA to form a continuous phase decreased. This may create regions in the composite where less energy is required to initiate a crack. For the composites with higher SBP content (**Figure 2B**), the sizes of the PLA phase were reduced, and many more particles were pulled-out during the tensile test, leaving imprints with clean surfaces on the fracture surfaces. These results suggest poor adhesion between the two polymers. The SEM observations are consistent with the results obtained from the
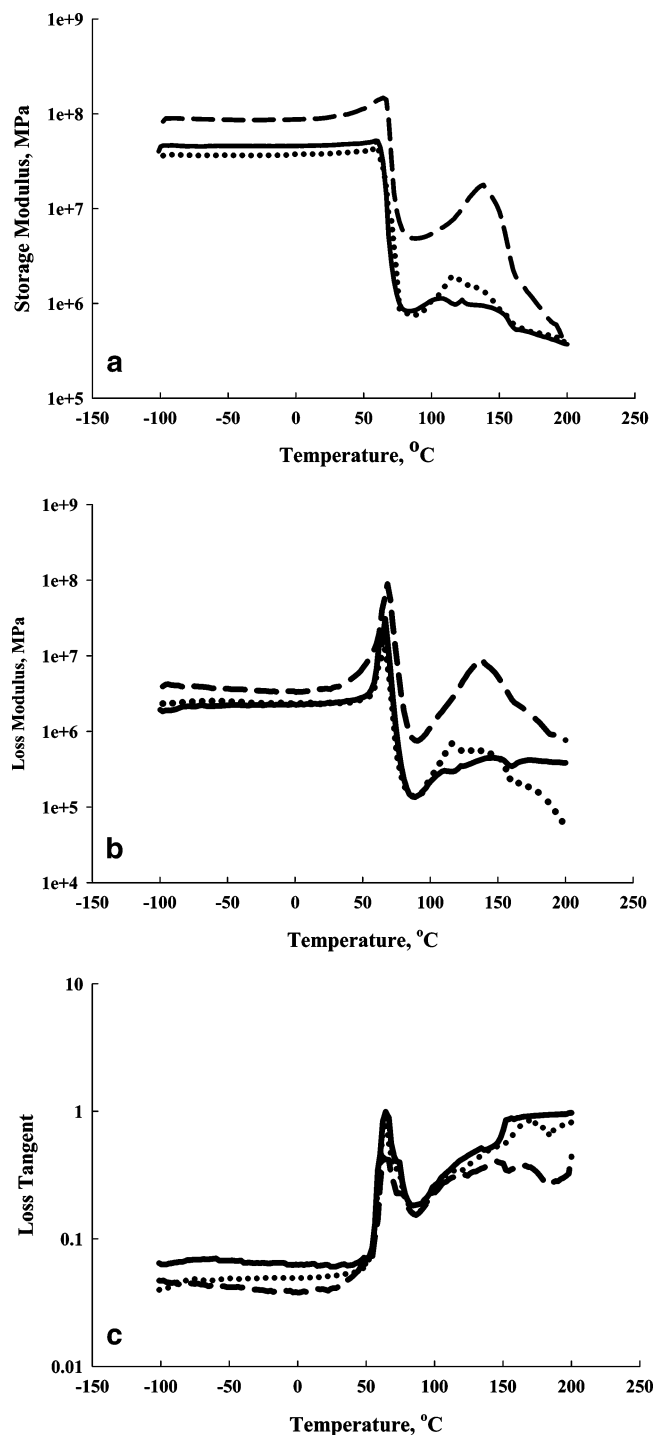

Figure 4. Dynamic mechanical thermal analysis of (**a**) storage modulus, (**b**) loss modulus, and (**c**) loss tangent for PLA (—), 10% SBP/PLA (···), and 20% SBP/PLA (- - -).

tensile tests (**Table 1**), showing SBP content-dependent mechanical properties.

Images of fracture surfaces of double-dried and preheated SBP/PLA are shown in **Figure 3**. In general, the two composites showed many fewer void spaces in the matrix phases and gaps on the intersurfaces than observed with vacuum-dried SBP/PLA. For the 50% SBP/PLA composites with preheated particles, the two phases were well intergrated on the intersurfaces, which is similar to that shown in **Figure 2A** for the composites with a lower SBP content. The differences in structural characteristics
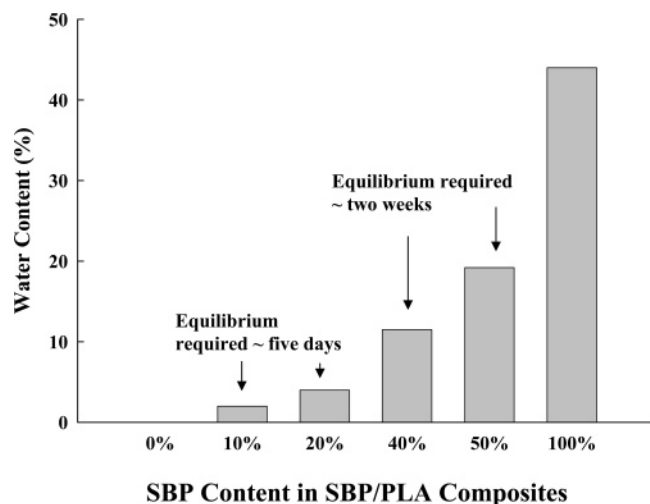
Figure 5. Water content of vacuum-dried SBP/PLA after equilibration at 95% relative humidity at room temperature.

of SBP/PLA composites are responsible for the variation in their mechanical properties.

Dynamic Mechanical Analysis of SBP/PLA Composites. The influence of added SBP on the mechanical properties of PLA composites was confirmed by measuring the temperature-dependent storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) under a small compressive force. Comparisons of typical compressive curves of PLA and SBP/PLA composites are shown in **Figure 4**. The pure PLA samples had a glass transition temperature (T_g) at ~58 °C, which is consistent with the T_g of 55−60 °C specified by the manufacturer. The softening

temperature, T_g, is shifted to a higher temperature when SBP is added. This shift in T_g increases with increasing SBP level. Above T_g, the moduli had a sharp drop for all samples (**Figure 4a**,**b**). However, the moduli started to increase again at ~80 °C, indicating partial crystallization of the samples (*15*). Above this temperature, thermal energy was consumed for dissolution of the amorphous crystalline segments of PLA. An additional energy was required to overcome the resistance to the molecular movements of SBP polysaccharide and protein. The incorporation of SBP seems to enable the composites to maintain a certain level of physical integrity. The loss tangent data of PLA (**Figure 4c**) were similar to that of SBP/PLA composites before the softening temperature, but a big change was seen thereafter. The 20% SBP/PLA samples had much lower tan δ at ~160 °C.

Water Resistance. The water resistance of SBP/PLA and PLA was investigated by measuring the water content after equilibration of the samples at 95% relative humidity over water at room temperature. After 5 days of equilibration, no significant weight changes could be recorded for either 10 or 20% SBP/PLA. For samples with higher SBP content, a longer period, 2 weeks, was required to reach equilibrium. No weight change was measured for PLA (**Figure 5**), whereas weight changes increased as the SBP content increased in composites, indicating that the weight increase of the composites is due to the moisture uptake by SBP. When the weight percent of PLA was much larger than that of SBP, the SBP dispersion phases would be wrapped by a PLA matrix. The hydrophobic PLA layer thus excluded water adsorption on SBP. For the composites with higher SBP content, more SBP particles were on the surface or located at the edge of the sample. These SBP particles were more accessible for moisture uptake.
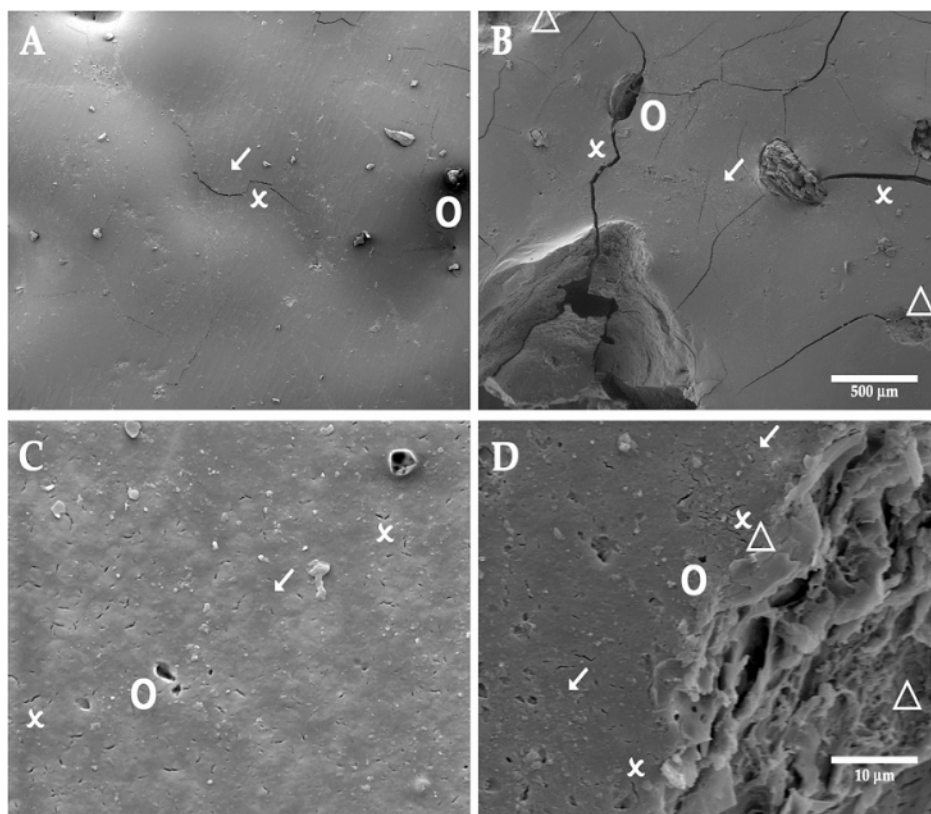

Figure 6. SEM photomicrograph of the cross-section surfaces of PLA (**A**, **C**) and 40% SBP/PLA (**B**, **D**) after being buried in soil for 4 weeks at 40 °C. The PLA matrix showed a rough surface with spreading pockmarks (as indicated by arrows). The vacuum-dried 40% SBP/PLA samples developed the typical surfaces with void spaces (○) and gaps (×) and showed the imprints (△) created by SBP particle loss.

9022 *J. Agric. Food Chem.,* Vol. 53, No. 23, 2005

Liu et al.

Table 3. Degradation of SBP/PLA Composites after Incubation in Soils at 40 °C at 95% Relative Humidity for 4 Weeks

initial SBP/PLA	SBP wt loss (wt %)	M_w of PLA	M_n of PLA	M_w/M_n
0/100[a]	N/A[b]	148000	110200	1.34
0/100	N/A	106000	73100	1.45
10/90	<2	87200	62200	1.40
20/80	<2	79800	49000	1.62
40/60	~7–9	46500	9750	4.76
50/50	<12.5	32700	3680	8.89

[a] Determined before buried. [b] Not applicable.

Biodegradability. After being buried in soil for 4 weeks at 40 °C, specimens of PLA and SBP/PLA composites were mechanically weak and some were broken. SEM images of cross sections of the buried samples revealed the erosion of PLA matrix with a rough and pockmarked surface (**Figure 6A,B**). SEM images also evidenced the SBP particle loss or particle erosion (**Figure 6C,D**). Previously, either scaffolds or thin films fabricated from linear α-hydroxy polyesters have been demonstrated to biodegrade (*16*). Primarily, the mechanism of degradation was by bulk degradation via the hydrolysis of their labile ester linkages. Degradation of PLA or poly(lactic-*co*-glycolic acid) induces an initial decrease in the mechanical properties without a simultaneous decrease in mass or overall dimensions of the samples (*16*). The PLA matrix of the SBP/PLA composites, which also relies on the degradability of the ester bond, also degrades in bulk fashion (**Table 3**). For all buried SBP/PLA composites, PLA weight loss was not detectable. Nevertheless, PLA underwent an obvious decrease in molecular weight and developed a wider molecular weight distribution. SBP weight loss was clearly seen for all samples, but a greater SBP weight loss was measured for composites with higher SBP content. Furthermore, a greater decrease in PLA MW also was seen for the composites with a greater SBP weight loss. The loss of SBP particles, through either erosion or mechanical loss, created a new surface for water penetration. This, in turn, was responsible for degradation of the continuous PLA phase and reducing the mechanical properties of the composite. Furthermore, the organic acids generated by SBP digestion by microbes reduce the pH value in the microenvironments, which accelerates PLA hydrolysis. The role of microbes in SBP/PLA composite biodegradation will be discussed in detail in a subsequent paper. Incorporation of SBP provides a strategy to alter the degradation profile of PLA-based composites.

Conclusions. SBP and PLA can readily form composite materials with lower density and in some cases better mechanical properties than PLA alone. The current study explored conditions under which the composites were prepared. The interaction of dispersed phase and matrix phase seems to be critical for improved mechanical properties of the resultant composites. The removal of absorbed water and an appropriate component ratio will enhance the two-phase interaction. On the basis of this initial study, an extrusion followed by injection-molding method is planned for SBP/PLA composite fabrication.

Furthermore, SBP sells at a price much lower than that of PLA ($0.06/lb as compared to ~$2.00/lb, respectively). Therefore, SBP/PLA composites with mechanical properties similar to those of PLA alone will be more competitive than pure PLA materials in the marketplace.

LITERATURE CITED

(1) Fishman, M. L., et al. Sustainable technologies for polysaccharide-based functional foods and biobased products, [http://www.ars.usda.gov/research/projects/projects.htm?ACCN_NO=404563]. USDA Agricultural Research Service, National Program 306, Quality and Utilization of Agricultural Products, 2001.

(2) Södergård, A.; Stolt, M. Properties of lactic acid based polymers and their correlation with composition. *Prog. Polym. Sci.* **2002**, *27*, 1123−1163.

(3) Mohanty, A. K.; Misra, M.; Hinrichsen, G. Biofibers, biodegradable polymers and biocomposites: an overview. *Macromol. Mater. Eng.* **2000**, *276*, 1−24.

(4) Kaplan, D. L., Ed. *Biopolymers from Renewable Resources*; Springer: Berlin, Germany, 1998; pp 1−412.

(5) Plackett, D.; Andersen, T. L.; Pedersen, W. B.; Nielsen, L. Biodegradable composites based on L-polylactide and jute fibres. *Compos. Sci. Technol.* **2003**, *63*, 1287−1296.

(6) Oksman, K.; Skrifvars, M.; Selin, J.-F. Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos. Sci. Technol.* **2003**, *63*, 1317−1324.

(7) Tharanathan, R. N. Biodegradable films and composite coatings: past, present and future. *Trends Food Sci. Technol.* **2003**, *14*, 71−78.

(8) Liu, L. S.; Onwulata, C.; Fishman, M. L.; Savary, B.; Hicks, K. B. Evaluation of sugar beet pulp and poly(lactic acid) biodegradable composites. *Proceedings of the 33rd United States−Japan Annual Meeting in Natural Resources*; Cherry, J. P., and Pavlath, A. E., Eds.; Honolulu, HI, 2004, pp 80−84.

(9) Liu, C.-K.; Latona, N. P.; DiMaio, G. L. Lubrication of leather with poly(ethylene glycol). *J. Am. Leather Chem. Assoc.* **2002**, *97* (9), 355−368.

(10) Liu, L. S.; Won, Y. J.; Cooke, P. H.; Coffin, D. R.; Fishman, M. L.; Hicks, K. B.; Ma, P. X. Pectin/poly(lactide-*co*-glycolide) composite materials for biomedical applications. *Biomaterials* **2004**, *25*, 3201−3210.

(11) Mikos, A. G.; Thorsen, A. J.; Czewrwonka, L. A.; Bao, Y.; Langer R.; Winslow, D. N.; Vacanti, J. P. Preparation and characterization of poly(lactic acid) foams. *Polymer* **1994**, *35* (5), 1068−1077.

(12) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley-Interscience: New York, 1999; Vol. 4, p VII/23.

(13) Taniguchi, Y.; Horigome, S. The states of water in cellulose acetate membranes. *J. Appl. Polym. Sci.* **1975**, *19*, 2743−2748.

(14) McCrystal, C. B.; Ford, J. L.; Rajabi-Siahboomi, A. R. A study on the interaction of water and cellulose ethers using differential scanning calorimetry. *Thermochim. Acta* **1997**, *294*, 91−98.

(15) Chartoff, R. P. Thermoplastic polymers. In *Thermal Characterization of Polymeric Materials*, 2nd ed.; Turi, E. A., Ed.; Academic Press: New York, 1997; Vol. 1, pp 573−563.

(16) Behravesh, E.; Timmer, M. D.; Lemoine, J. J.; Liebschner, M. A.; Mikos, A. G. Evaluation of the in vitro degradation of macroporous hydrogels using gravimetry, confined compression testing, and microcomputed tomography. *Biomacromolecules* **2002**, *3*, 1263−1270.