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EVALUATION OF SUGAR BEET PULP AND POLY(LACTIC ACID) BIODEGRADABLE COMPOSITES

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Abstract

Sugar beet pulp reinforced poly(lactic acid) thermoplastics were prepared by a compression-heating method. With low sugar beet pulp content, the composites were able to retain or even enhance the tensile properties of original poly(lactic acid), while having a lower density. Tensile properties also depend on the initial water content of sugar beet pulp and the temperature at which composites were processed. The improved water resistance (in comparison with pure sugar beet pulp) was attributed to pulp-matrix interactions and to the higher hydrophobic character of the poly(lactic acid). The composites showed suitable properties for the use as lightweight construction materials.

Introduction

This paper describes the research in which sugar beet pulp (SBP) and poly(lactic acid) (pLA) were developed into composites with suitable mechanic properties for lightweight construction materials. The overall objective of our research program is to add value to the U.S. sugar beet industry by finding new uses for their 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, about 400 million tons of wet pulp, are generated from the U.S. beet sugar industry that are sold as low value animal feed or must be disposed with added expense. It is now recognized that finding new ways to profitably utilize the enormous amounts of this low value by-product 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 non-food 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 non-sustainable 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 by the mechanism of "block degradation" – the polymer is randomly chopped into oligomers via the attack of water molecules. The generation of pLA oligomers is faster than the release of the final degradation products, the lactic acid monomer, which occurs in the metabolism of all animals and microorganisms and is absolutely non-toxic at naturally occurring levels. Thus the pLA can be disposed simply by land-filling. However, pLA polymers are stiff and brittle in thicker materials. Another obstacle in the path of wider application of pLA is its present higher price relative to petroleum derived thermoplastics. Several researches have suggested the advantages of natural polymers/pLA reinforced

thermoplastics (2-4). Composite tensile strength and stiffness of pLA could be increased when a portion of jute fibres (2) or flax fibres (3) were included. Natural polymers are usually low weight, low price and biodegradable. On the other hand, moisture adsorption and thermal instability are the drawbacks of most natural polymers. Commercial production of pLA and natural polymer composites is still a challenge but has potentially promising markets.

In this study, SBP and pLA composites were prepared by a compression-heating method. The composites were characterized for mechanical properties and water resistance. The structure of the composites was also analyzed.

Materials and Methods

Finely ground dry SBP residue (300 μm particle size) was provided as a gift from Tim Ayers of Willamette Valley Company (Eugene, OR). PLA (Cargill Dow, MN) was milled to small particles and fractions with the size of about 300 μm . The two particles were mechanically mixed at the ratios of 0, 10, 20, 40 and 50 % weight of SBP in total mass. The mixtures were dried for 24 hrs. in a desiccator connected to a vacuum line, then placed in an aluminum mold (75 x 20 x 6 mm), compressed under 50 psi and heated at two temperature sets: (1) starting at 172°C and increasing to 180°C in 3 min, then holding at 180°C for 20 min.; (2) starting at 190°C and increasing to 200°C in 5 min, then holding at 200°C for 20 min. After heating, the molds were immediately removed from the oven and cooled to room temperature. For the composites with 40% and 50% sugar beet pulp, 10 ml of dichloromethane were used to dissolve the pLA, into which was mixed the SBP, and the resulting slurry was cast in the mold. The compression-heating process was performed following the solvent evaporation. For investigating the effect of adsorbed water on composite fabrication, SBP particles were dried in pre-dried acetone overnight and vacuum-dried for an additional 8 hrs, mixed with pLA, then processed for composite fabrication.

Tensile tests were performed on samples (5). Tensile property measurements included tensile strength, tensile modulus and elongation. 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. An upgraded Instron mechanical property tester, model 1122, and Testworks 3.1 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Water adsorption was measured by measuring the water content after the samples were conditioned at 95% relative humidity over water at 25 °C for 5 days.

Results and Discussion

The composites were fabricated by a compression-heating method at the temperature of 180-200°C, which is higher than the melting point of pLA (160-180°C). Thus, the pLA melted and deposited in the gaps among SBP particles to form a continuous matrix phase. At low SBP content, the particles are dispersed in the pLA phase. Table 1 shows the mechanical properties of SBP/pLA composites and pLA. At the SBP level lower than 20% weight, the composites were able to retain or enhance the mechanical properties of pure pLA. This indicates the good adhesion between SBP particles and pLA, thus the

stress could be transferred from the matrix phase to SBP since the SBP is more rigid than the pLA. Similar results also can be seen for the tensile stress (Figure 1) and the stiffness (Figure 2) of the tested samples. Table 1 also shows that the inclusion of SBP to pLA reduced the composite's density, suggesting the possibility to create lightweight materials with strong mechanical properties from SBP and pLA.

Table 1. Mechanical properties of SBP/PLA composites

Materials	Density (g/cm ³)	Elongation to break (%)	Fracture energy (J/cm ³)
PLA	1.161	6.4(0.4)*	0.58(0.050)
10% SBP/PLA	1.145	6.8(0.5)	0.98(0.005)
20% SBP/PLA	0.927	7.1(0.4)	0.68(0.222)
40% SBP/PLA	0.916	6.3(0.4)	0.10(0.002)
50% SBP/PLA	0.858	5.5(0.4)	0.05(0.001)

* Data expressed as mean \pm SD (n=3).

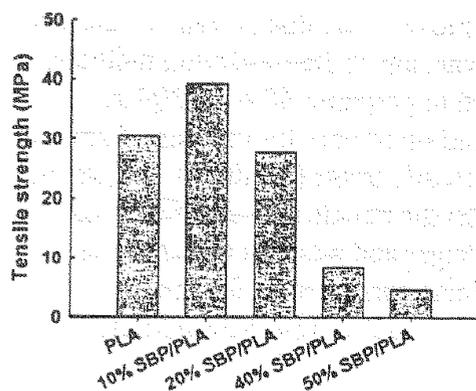


Figure 1. Tensile stress of SBP/pLA

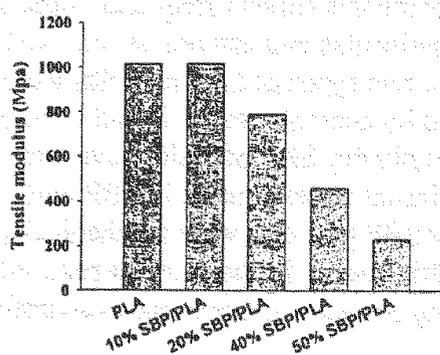


Figure 2. Tensile modulus of SBP/pLA

The weight changes of SBP/pLA and pLA were measured after equilibrating samples for 5 days at 95% relative humidity over water at 25°C. After this period, no further significant weight changes could be recorded. No weight change was measured for pLA (Figure 3a), while 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. Thus, we calculated the water content of SBP in the composites after exposure to moisture, we found that the two composites with SBP content less than 20% weight had similar values, but the values gradually increased (Figure 3b). This could be explained by the interaction of SBP particles with the matrix phase; when pLA had a much larger weight portion than SBP, the SBP dispersion phases will be wrapped by pLA matrix. The hydrophobic pLA layer thus excluded water adsorption on SBP.

Higher SBP contents reduce the mechanical properties of resulting composites (Figure 1 and 2, Table 1). As the portion of SBP in the composite increased, the

capability of pLA to form a continuous phase decreased. In addition, more void volume was created in the composites during processing. These may create regions in the composite where less energy is required to initiate a crack.

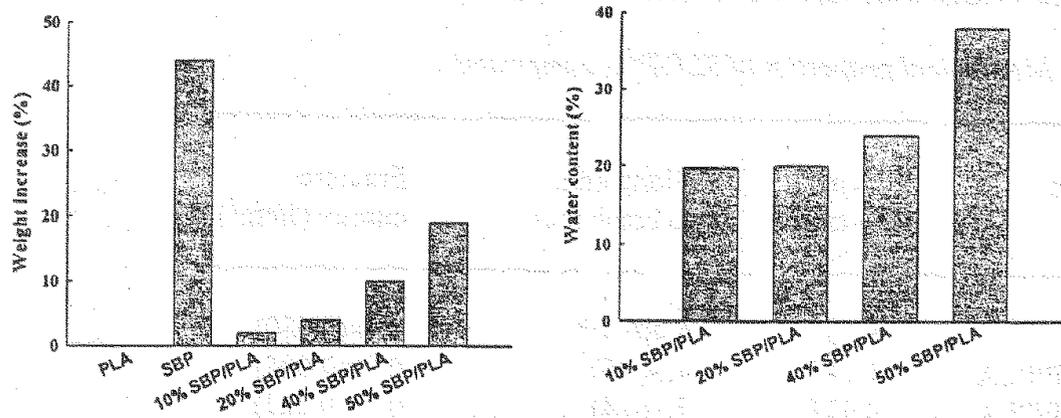


Figure 3 Water content (weight change) in SBP/pLA after equilibrating at 95% relative humidity at 23 °C. (a, left) expressed as % of SBP/pLA, (b, right) expressed as % of dry SBP in each composite sample.

Pre-dried acetone is a solvent frequently used to remove water that is tightly bound to polysaccharide molecules and can not be removed by vacuum or freeze-drying methods (6). In this study, two types of SBP particles were used to prepared 40% SBP/pLA composites: dried by acetone treatment and vacuum, and dried only by vacuum. Samples prepared from highly dry SBP particles have a higher tensile stress (Figure 4), indicating the effect of the initial water content in SBP particles on the tensile stress of SBP/pLA composites. Dry SBP particles were mechanically stronger and adhered easier to the hydrophobic matrix phase; furthermore, it reduced defects generated in finished composites during processing due to the evaporation of moisture from SBP particles.

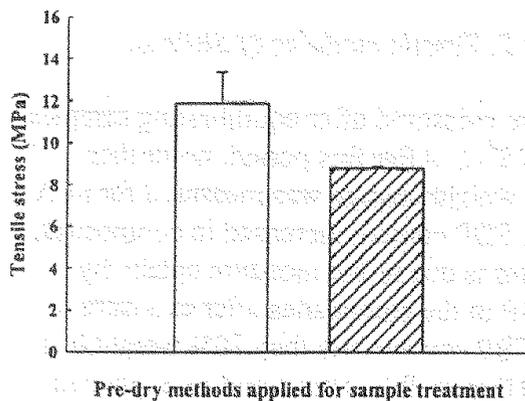


Figure 4 Effect of pre-dried method on tensile stress of 40% SBP/pLA composites. SBP was pre-dried by vacuum (striped bar) or by dry-acetone and vacuum (white bar).

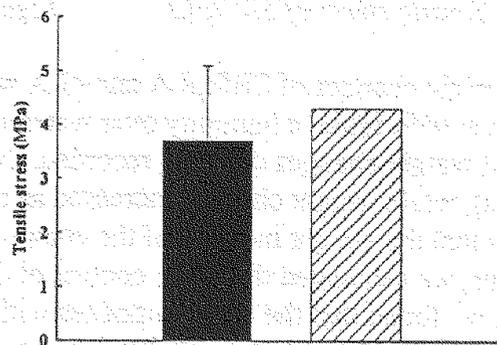


Figure 5. Effect of processing temperature (black bar, 180 °C; striped bar, 200 °C) on tensile stress of 50% SBP/pLA.

Figure 5 shows the effect of processing temperature on the mechanical properties of SBP/pLA composites. Although the difference may not be statistically significant, it shows a trend that samples prepared at 200 °C may have a higher tensile stress value than those obtained at 180 °C. A higher temperature may facilitate the adhesion of pLA with SBP particles since it lowered the viscosity of melting pLA. However, at the temperature above 200 °C, the polysaccharides will be destroyed.

Conclusions

Sugar beet pulp and pLA can form composite materials with lower density and in some cases better mechanical properties. The current study explored conditions under which the composites were prepared. The interaction of dispersion phase and matrix phase seems critical for the mechanical properties of resulting composites. An increase in processing temperature, decrease in the initial water content of SBP and an appropriate component ratio will enhance the two-phase interaction. Based on this primary study, an extrusion followed by injection-molding method is planned for SBP/pLA composites synthesis.

Furthermore, SBP sells at a price much lower than pLA (< \$0.06/lb vs. < ~\$2.00/lb, respectively). SBP/pLA composites with the mechanical properties similar to pLA materials will therefore be more competitive than pure pLA materials in market.

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