

Evaluation of Poly(lactic acid) and Sugar Beet Pulp Green Composites

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Abstract Poly(lactic acid) (PLA) and sugar beet pulp (SBP) were compounded by twin-screw extrusion and injection molded into composite forms. Specific mechanical energy decreased with the addition of SBP during processing. PLA–SBP composites retained more tensile strength than expected based on the Nicolais–Narkis model especially at high levels of SBP suggesting adhesion between SBP and PLA. The thermal characteristics of PLA were not affected by thermo-mechanical processing or by the incorporation of SBP up to 30% weight basis. PLA and PLA–SBP composites had similar tensile properties to other thermoplastic resins and may be used as a cost-competitive replacement.

Keywords Polymer–matrix composites · Polymers · Particle-filled polymers · Extrusion · Injection molding · Poly(lactic acid) · PLA

Disclaimer: Names are necessary to report factually on available data. However, the United States Department of Agriculture neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval to the exclusion of others that may also be suitable.

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Introduction

Composite materials are usually made of two dissimilar materials. Composites are designed for long-term and short-term use and employ non-degradable materials derived from petroleum. Most polymer composites are difficult to recycle or incur substantial cost for disposal. Green composites use agricultural-based polymers and biodegradable plant-based fillers [1]. Green composites can be used in non-durable applications (a few years), products intended for short-term use (a few times), or indoor applications (like wood or automotive parts). Poly(lactic acid) (PLA) is a hydrophobic polymer prepared from renewable agriculture-based feed stocks which are fermented to lactic acid and then polymerized. PLA can be extruded and injection molded [2, 3]. PLA is biodegradable in soil, compost or water, and the degradation products of PLA are non-toxic to the environment. PLA has comparable mechanical properties to petroleum-based plastics, but is more expensive. The use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites. Sugar beet (*Beta vulgaris*) is grown as a commercial crop in many countries such as France, Germany, Turkey, Russia, Poland, the Ukraine and the United States. The fleshy root usually contains 10–15% sucrose. As the source of about one-third of the world supply of sugar, sugar beet is an important agricultural commodity. The U.S. sugar beet industry is estimated at \$1.27 billion annually and over 400 million metric tons of wet pulp is generated each year.¹ Sugar beet pulp (SBP) is usually used as low value animal feed or

¹ Economic Research Service, United States Department of Agriculture, 2003.

disposed of at additional cost. The future profitability of the beet sugar processing industry will be determined by finding new ways to utilize this by-product.

PLA has been blended with fibers [4–6], polymers [7–11], and inorganic fillers [12, 13]. Previous work on PLA–SBP composites cannot be compared to these results due to dissimilar preparation methods [14]. PLA–SBP composites (0–50% w/w SBP) were compression molded at a peak temperature of 200 °C. Our PLA–SBP composites were processed with three separate thermal or mechanical treatments (extrusion, pelletization, and injection molding). The objective of this research is to evaluate SBP as a low-cost filler for PLA to produce polymer composites with suitable mechanical properties for light weight structural materials.

Experimental

Materials

Sugar beet pulp (SBP), provided by Willamette Valley Company (Eugene, Oregon), was ground to a particle size of less than 300 µm. The residual moisture of SBP was 13.4% (w/w) before extrusion processing. The composition of SBP is approximately 75% carbohydrate (pectin, cellulose, and hemicellulose), 9% protein, 6% ash, 9% lignin, and less than 1% oil. Poly(lactic acid), provided by Dow Cargill (Minneapolis, MN), contained over 90% L-lactide. The average molecular weight was 150,000. The glass transition (T_g) and melting temperature (T_m), determined by DSC, was 61 and 151 °C, respectively.

Extrusion Processing

Compounding was performed using a Werner-Pfleiderer ZSK30 co-rotating twin-screw extruder (Coperion Corporation, Ramsey NJ). The barrel was comprised of 14-barrel sections giving a length/diameter ratio of 44:1. The screw configuration is given in Table 1. The screw speed was 130 RPM. PLA was fed into barrel section 1 using a gravimetric feeder (Model 3000, AccuRate Inc., Whitewater, WI). After melting the PLA, SBP was fed into barrel section 7 using a loss-in-weight feeder. The barrel was heated using eight heating zones. The temperature profile was 135 °C (zone 1), 190 °C (zone 2) and 177 °C (zones 3–8). A die plate with two holes (4 mm diameter) was used. The melt temperature of the exudate at the die was approximately 160 °C. Residence time was approximately 2.5 min. Die pressure and torque were allowed

Table 1 ZSK30 screw design for extrusion compounding of PLA–SBP composites

Element type	Cumulative length (mm)
Conveying 42/42 (5×)	210 (PLA)
Conveying 28/28 (4×)	322
Conveying 20/20	342
Kneading block 45/5/42	384
Kneading block 45/5/28	412
Conveying 28/28 (2×)	468
Kneading block 45/5/20	488
Kneading block 45/5/14 (2×)	516
Conveying 28/28	544
Conveying 42/42 (4×)	712 (SBP)
Conveying 28/28	740
Kneading block 45/5/42	782
Kneading block 45/5/28	810
Conveying 42/42	852
Conveying 28/28	880
Kneading block 45/5/28	908
Kneading block 45/5/20	928
Conveying 28/28 (2×)	984
Kneading block 45/5/20	1004
Kneading block 45/5/14	1018
Conveying 28/28 (2×)	1074
Kneading block 45/5/14 (2×)	1102
Conveying 28/28 (2×)	1158
Kneading block 45/5/14	1172
Kneading block 45/5/14 LH ^a	1186
Conveying 20/20 (5×)	1286
Conveying 14/14 (3×)	1328

^a Left-handed screw element

to stabilize between formulations before the sample was collected. Strands were pelletized using a Laboratory (2 in.) Pelletizer (Killion Extruders Inc., Cedar Grove, NJ).

Injection Molding

An ACT75B injection molder (Cincinnati Milacron, Batavia, OH) was used to injection mold ASTM D638-99 Type I tensile bars (Master Precision Mold, Greenville, MI). Conditions for each sample are given in Table 2. Barrel temperature profiles had to be adjusted to help forward material (by cooling the feed section). The cooling time was increased as the samples with high weight fractions of SBP did not extrude as well as native PLA. The shot size had to be increased slightly as the material density decreased with increased pulp content. Packing pressures were inverted for PLA–SBP composites with over 15% SBP due to extreme flashing characteristics. Other conditions included a hot sprue bushing (D-M-E, Madison Heights, MI) temperature of 177 °C, maximum injection pressure of 12,000 PSI, maximum packing velocity of 0.1 IPS, initial velocity of 2.0 IPS (switch point of 1.0 in), secondary velocity of 1.0 IPS (transfer position to

Table 2 Injection molding conditions for compounded PLA–SBP composites

SBP weight fraction	Mold (°C)	Barrel zones 1/2/3/ Nozzle (°C)	Cooling time (s)	Shot size (in.)	1st and 2nd packing pressure and time (KPSI/s)
0.00	80	138/171/193/193	20	3.0	12/12, 4/1
0.07	80	129/171/193/193	24	3.0	12/12, 4/1
0.15	75	116/160/193/193	24	3.2	6/6, 12/7
0.19	75	104/149/193/193	24	3.2	6/6, 12/7
0.30	75	104/149/193/193	24	3.2	6/6, 12/7
0.45	75	93/149/193/193	40	3.2	6/6, 12/7

pressure at 0.45 in.), and a maximum packing velocity of 0.1 IPS.

Characterization

Scanning electron microscopy (SEM) of SBP, PLA–SBP composite surfaces and freeze-fractured surfaces was conducted on a JEOL 6400 V scanning electron microscope (Peabody, MA). Specimens were cryogenically frozen with liquid nitrogen and fractured, mounted and sputter coated with gold. Infrared spectroscopy was performed using a Perkin-Elmer FT-IR in ATR mode.

Tensile properties of PLA–SBP composites were evaluated using an Instron Model 1122 mechanical property testing machine. The thickness of the individual dogbones was measured before testing. The gauge length was 40 mm, and the strain rate was 50 mm/min. Mechanical properties included tensile strength and modulus. Tensile strength is the maximum stress a sample can sustain without fracture. Modulus describes the stiffness of the material and is determined from the slope of the line tangent to the stress–strain curve. All samples were conditioned for more

than 48 h at standard room temperature and humidity (23 °C and 50% RH).

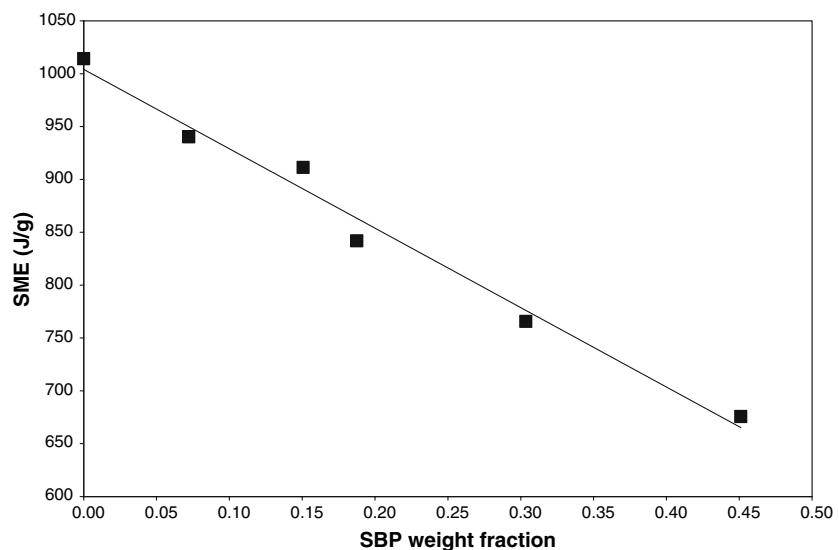
A dual-cell differential scanning calorimeter (Perkin-Elmer DSC 7, Newark, CT) with Pyris Series software was used to determine the thermal transitions of PLA and PLA–SBP composites. Sample size was approximately 20 mg and placed in a stainless steel pan. The scan range was 20–180 °C with a rate of 10 °C/min.

Results and Discussion

Extrusion and Injection Molding

Specific mechanical energy (SME) in extrusion is calculated from the total mechanical energy during processing. SME is known to be an important parameter in extrusion processing of plastics. The SME values obtained for PLA–SBP composites ranged from 675 J/g for 55% PLA to 1014 J/g for 100% PLA (Fig. 1). Increasing SBP content resulted in lower SME values. This result is consistent with the reduction in viscosity as SBP fills the polymer matrix and the water

Fig. 1 Specific mechanical energy of PLA–SBP composites during extrusion as a function of SBP weight fraction



content increases. Usually SME increases as the filler amount increases. At the processing temperature, water is turned to steam, puffing the melt and reducing melt viscosity. It is possible that low molecular weight components of SBP reduced the melt viscosity as well. Reduction in viscosity means that less energy is required to pump the melt through the extruder.

Examination of the surface of the injection molded PLA–SBP composites by SEM (Fig. 2a) and FT-IR (Fig. 3) showed that PLA forms a protective outer layer on the composite. The fracture surface of the PLA–SBP composite shows a highly filled composite with uniform distribution of filler (Fig. 2b).

Thermal Properties

Before processing PLA had a glass transition at 61 °C and a melting temperature of 151 °C (Table 3). After extrusion processing and injection molding, PLA had a T_g of 58 °C and a T_m of 151 °C. Lower T_g indicated

that some degradation of PLA took place during thermo-mechanical processing. The transition temperatures of PLA–SBP composites remained relatively constant as SBP weight fraction increased to 30% w/w. T_g decreased slightly (1–2 °C) as the PLA content was reduced. Hydrolysis could also have caused the reduction but the exposure of PLA to water during extrusion was short (less than 90 s) and the final water content was minimal (less than 1%). The amount of residual moisture increased slightly with increasing content of hydrophilic SBP, but the moisture content of samples up to 30% SBP remained less than 1% (w/w). The incorporation of SBP up to 30% w/w does not significantly alter the thermal properties of PLA. Similar thermal behavior was found for starch-filled PLA with very small endotherms for crystallization at 121 °C [11].

At 45% SBP, the thermal transitions are significantly affected. The T_g is 49.75 °C. A recrystallization peak (T_c) occurred at 108.37 °C and was followed immediately by a melting endotherm at 141.70 °C. The melting endotherm was bimodal, and the second phenomenon occurred at the same temperature (approx. 150 °C) as the other PLA–SBP composites. The degree of crystallinity of PLA with 45% SBP can be calculated by $X_c = 100(\Delta H/93) = 23\%$ where 93 J/g is the melting enthalpy (ΔH) of an infinite PLA crystal [15]. PLA is sensitive to heat and moisture, and it has been shown that repeated heating and cooling cycles degrade PLA [15]. The moisture content of 45% SBP and PLA was 3.4% w/w. Some degradation of PLA was probably due to hydrolysis because PLA was exposed to the hydrophilic SBP at the highest filler content.

Mechanical Properties

Young's modulus increased from 1945 MPa with pure PLA to 2590 MPa as the amount of SBP increased to 45%, consistent with the incorporation of a rigid filler. Tensile strength decreases with increasing SBP content from 69.55 MPa for PLA to 29.55 MPa for 45% SBP. As expected, incorporation of SBP introduces defects into the polymer matrix, reducing the effective cross-sectional area of the continuous PLA phase. SBP is not inert in PLA. According to the Nicolais–Narkis (N-N) model, which is used to identify interactions or adhesion between filler particles and the polymer matrix by relating the filler content in the composite to the ultimate tensile strength, given by [16]:

$$\sigma = \sigma_0[1 - 1.21(V_f^{(2/3)})]$$

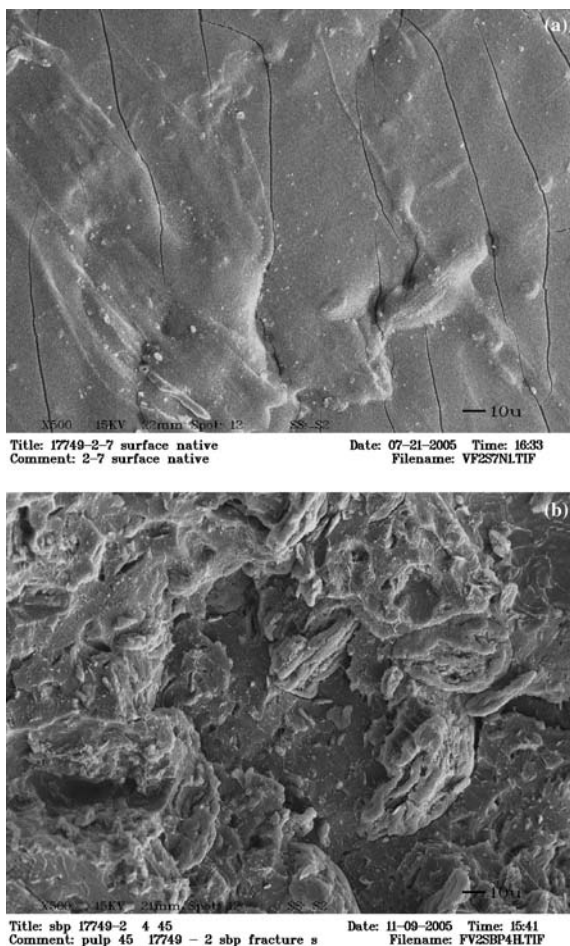
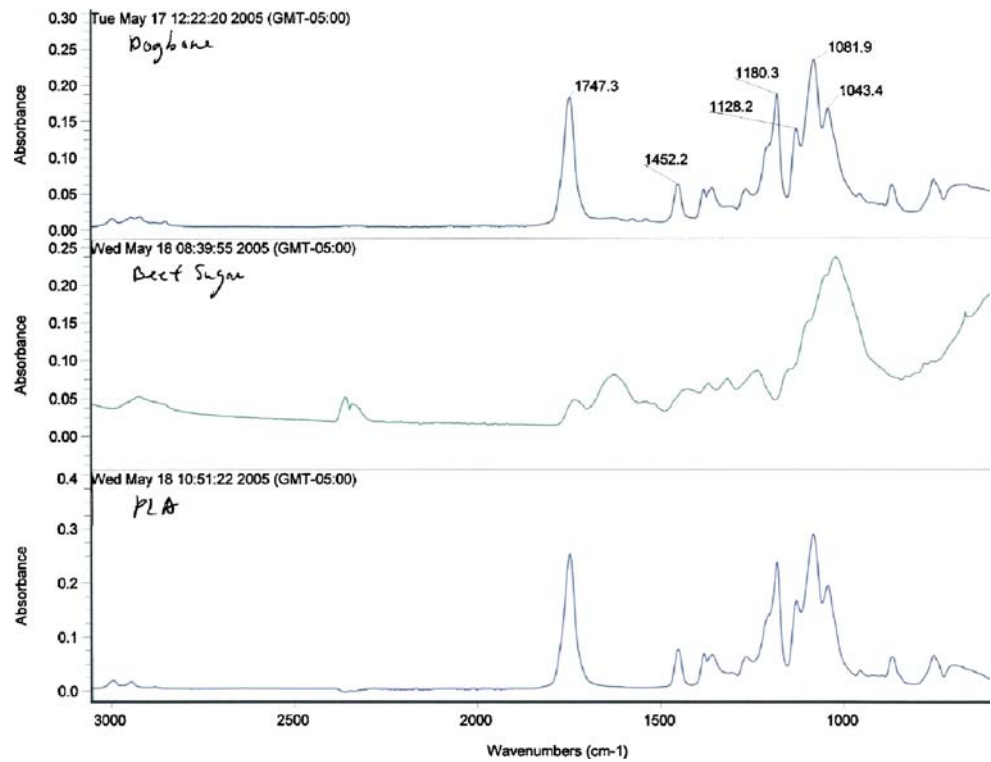


Fig. 2 SEM micrographs of PLA–SBP composites: (a) surface (b) freeze-fractured surface. The magnification is 500× with the scale bar equal to 10 µm

Fig. 3 FT-IR of PLA–SBP composites surfaces after injection molding



where σ_0 is the tensile strength of unfilled PLA, the factor 1.21 is a geometric factor, and V_f is the volume fraction of SBP filler. This model assumes spherical particles, uniform distribution of particles in the polymer matrix, and that the particles do not contribute to the tensile strength. The particle size of SBP was distributed between small particles under 1 μm and larger particles between 10–30 μm (Fig. 4). All particles were irregularly shaped. The Nicolais–Narkis plot is shown in Fig. 5. As SBP volume fraction increases, the tensile strength decreases. However, the reduction in tensile strength is not as large as predicted by the N–N model. As PLA volume fraction increases, the deviation from the model gets larger. At $V_f = 0.14$ the tensile strength is 4% greater than predicted. At

$V_f = 0.44$, the tensile strength is almost 50% greater than predicted by the N–N model. The slope of the line for PLA–SBP (Fig. 5) is less than the slope of the N–N model indicating that SBP is interacting with the PLA in some manner. It also indicates a maximum packing fraction greater than 1; therefore, the retention of tensile strength is probably due to adhesion as well as the fact that SBP contains small particles which may not debond and particles with aspect ratio greater than 1 which may not conform to the N–N model. SBP is a rich source of carbohydrate polymers such as cellulose,

Table 3 Thermal properties of PLA–SBP composites

SBP weight fraction	T_g (°C)	T_c (°C)	T_m (°C)	% Moisture (w/w)
PLA ^a	61.33	–	151.03	0.5
0.00	58.14	–	151.37	0.5
0.07	58.08	129.53	151.87	0.6
0.15	57.68	129.50	151.53	0.8
0.19	57.61	129.03	151.20	0.9
0.30	56.56	128.20	150.37	1.0
0.45	49.75	108.37	141.70,	3.4
			150.00	

^a Before extrusion processing and injection molding

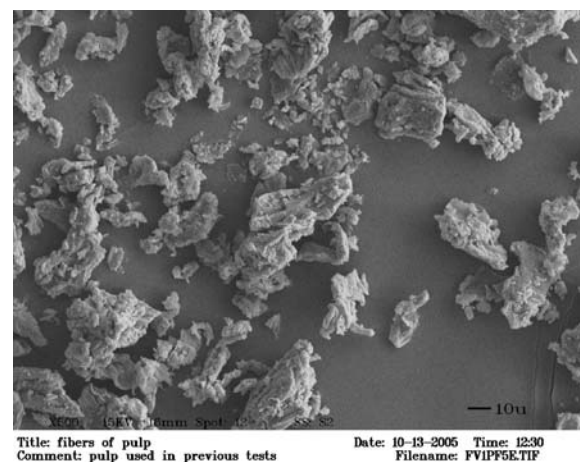
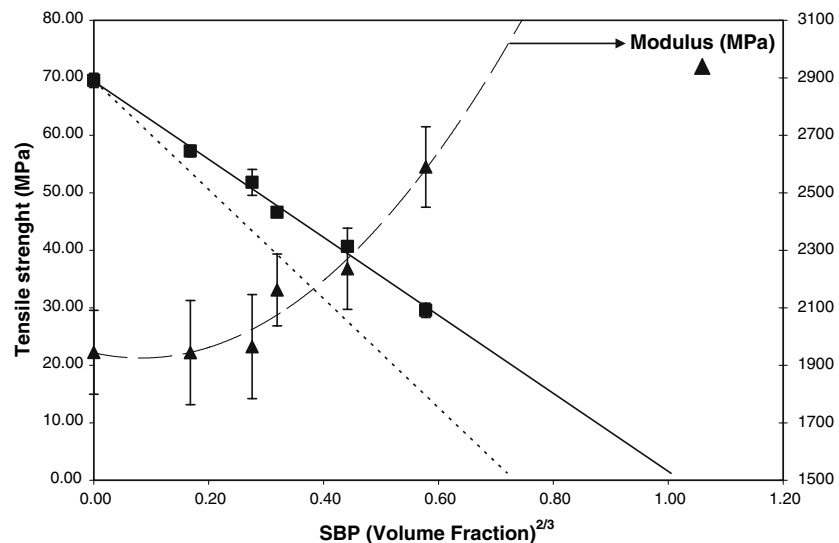


Fig. 4 SEM micrograph of SBP filler. The magnification is 500 \times with the scale bar equal to 10 μm

Fig. 5 Young's modulus (triangles, right axis) and tensile strength (squares, left axis) of PLA–SBP composites. The N-N model for predicted TS is shown with a dotted line



pectin and hemicellulose. SBP is almost 75% carbohydrate and is hydrophilic. PLA is hydrophobic. FT-IR analysis showed that hydrogen bonding could take place between PLA carbonyls and hydroxyl groups of other polymers [15]. It is possible that hydrogen bonding occurred between PLA and the hydroxyl groups on SBP. Similar results were shown for starch-filled PLA where tensile strength decreased from 67 MPa for PLA to 45 MPa for 40% filler [11]. Analyzing the PLA-starch tensile data, it appears that corn starch granules adhere to PLA better than SBP. This is not unexpected since starch granules (essentially 100% carbohydrate) are uniform in size (approximately 10 μm) and shape (relatively spherical) compared to SBP (Fig. 4) which had irregular shapes (particles and fibers) and size distributions. Likewise, the relative increase in Young's modulus for PLA-starch was less than half of the PLA–SBP indicating that SBP is more rigid than starch and has less interaction with PLA.

Conclusions

Addition of SBP up to 30% w/w does not alter the thermal transitions of PLA in PLA–SBP composites. Hydrogen bonding between PLA carbonyls and SBP hydroxyls is a likely explanation for the unexpected retention of tensile strength in PLA–SBP composites as SBP content increases. PLA–SBP composites had similar tensile strengths to composite resins like polypropylene, polystyrene, and poly(ethylene terephthalate) and could be used in place of these resins. PLA–SBP composites are fully biodegradable and fully compostable.

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