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ORIGINAL PAPER

Mechanical Property Characterization of Plasticized Sugar Beet Pulp and Poly(Lactic Acid) Green Composites Using Acoustic Emission and Confocal Microscopy

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Abstract Sorbitol and glycerol were used to plasticize sugar beet pulp-poly(lactic acid) green composites. The plasticizer was incorporated into sugar beet pulp (SBP) at 0%, 10%, 20%, 30% and 40% w/w at low temperature and shear and then compounded with poly(lactic acid) (PLA) using twin-screw extrusion and injection molding. The SBP:PLA ratio was maintained at 30:70. As expected, tensile strength decreased by 25% and the elongation increased. Acoustic emission (AE) showed correlated debonding and fracture mechanisms for up to 20% w/w plasticizer and uncorrelated debonding and fracture for 30–40% sorbitol and 30% glycerol content in SBP–PLA composites. All samples had a well dispersed SBP phase with some aggregation in the PLA matrix. However, at 40% glycerol plasticized SBP–PLA composites exhibited unique AE behavior and confocal microscopy revealed the plasticized SBP and PLA formed a co-continuous two phase system.

Keywords Sugar beet pulp · Poly(lactic acid) · Composite · Extrusion · Injection-molding · Acoustic emission

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

The use of plastics world-wide is causing serious environmental issues associated with its disposal. For example, in the United States, plastics account for over 20% (w/v) of landfill space [1]. The development of environmentally friendly plastics for many different products is essential. Polymer composites may be used as packaging material, food containers, utensils, or light weight construction materials. Green polymer composites use agricultural-based polymers and biodegradable plant-based fillers [2, 3].

Poly(lactic acid) (PLA), is a compostable plastic from agricultural feedstocks produced by the fermentation of starch-rich crops. PLA has similar mechanical and chemical properties to many petroleum-based polymers and has been blended with fibers [4–6], polymers including starch [7–12], and inorganic fillers [13, 14]. Composites of PLA reinforced with biodegradable fillers have been shown to have similar mechanical properties and are cost competitive to some conventional thermoplastic composites [5, 11,

15, 16]. PLA is classified as generally recognized as safe (GRAS) by the Food and Drug Administration of the United States. Due to increased manufacturing capability, the cost for PLA is currently around $1/lb.[1]

Sugar beet (*Beta vulgaris*) is grown as a commercial crop in many countries including the United States. The United States is the fourth largest producer of sugar in the world with approximately 60% coming from sugar beets. The United States harvested over 30 million metric tons of sugar beets and exported over 500,000 metric tons of sugar beet pulp (SBP) in 2006.[2] SBP is a byproduct of sugar recovery from sugar beets and is used as a low cost, low value animal feed. Developing value-added products from SBP enhances the economic value of the sugar industry.

We have compounded PLA composite materials using SBP [17, 18] as well as oilseed coproducts [19] by twin-screw extrusion and injection molding methods. In previous work, it was determined that SBP acts as a particulate filler and has little adhesion to the PLA matrix. This work reports on the characterization of green composites using plasticized SBP and PLA.

Experimental

Materials

SBP, provided by Williamette Valley Company (Eugene, OR), was ground and sifted 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. PLA, provided by Dow Cargill (Minneapolis, MN), contained over 90% L-lactide. The molecular weight average was 150,000. The glass transition (T_g) and melting temperature (T_m), determined by DSC, were 61 and 151 °C, respectively. Glycerol and sorbitol were obtained from Sigma Chemicals and used without alteration.

Extrusion Processing and Injection Molding

SBP and plasticizer (glycerol or sorbitol) were mixed using a commercial mixer (Kitchen Aid) and then extruded using a Brabender single screw extruder with a temperature profile of 50-80-90-100 and a screw rotation of 40 rpm. Samples were ground and stored overnight in a refrigerator. Residual moisture was 5–7% w/w. PLA–SBP composites (70% PLA and 30% plasticized SBP) were compounded using a Werner-Pfleiderer ZSK30 co-rotating twin-screw extruder (Coperion Corporation, Ramsey NJ). Feed rates (78–90 g/min total) were adjusted to maintain the PLA:SBP 70:30 ratio while increasing the plasticizer content. The barrel was comprised of 14 barrel sections giving a length/diameter ratio of 44:1. 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 manual feeder. The barrel was heated using eight heating zones. The temperature profile was 135 °C (zone 1), 190 °C (zone 2) and 177 °C (zone 3–8). A die plate with two holes (4 mm diameter) was used. The melt temperature of the exudate at the die was approximately 150 °C for neat PLA and decreased to 140 °C with increasing plasticizer content. Residence time was approximately 2.5 min. Die pressure, torque, and feed rate were allowed to stabilize between formulations before the sample was collected. Strands were pelletized using a Laboratory Pelletizer (Killion Extruders, Inc, Cedar Grove NJ).

An ACT75B injection molder (Cincinatti 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 1. Barrel temperature profiles had to be adjusted to help forward high plasticized material by cooling the feed section. The cooling time was 24 s, and the maximum injection pressure was 14,000 PSI except for the PLA control (20,000 PSI).

Mechanical Properties

Mechanical property measurements were performed including tensile strength, Young's modulus, elongation and toughness. Tensile strength is the maximum stress a material can sustain under a tensile force without fracture. Young's 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. Toughness is defined as the energy needed to fracture the composites and is defined by the area under the stress–strain curve from 0% strain to fracture (J/cm^3). These properties were measured with a gauge length (the distance between two grips) of 102 mm. Test samples were stored for at least 2 days in a conditioned room at 21 °C and 65% RH before testing. An Instron mechanical property tester (Model 1122) and Testworks 4 data acquisition software (MTS Systems Corporation, Minneapolis, MN) were used throughout this work. The strain rate (crosshead speed) was set at 50 mm/min. Each mechanical property test was repeated at least 5 times to obtain an average value.

[1] Plastics Technology, http://www.ptonline.com/articles/200203fa2.html, 2007.

[2] Economic Research Service, United States Department of Agriculture, 2006.

Table 1 Injection molding conditions for plasticized SBP–PLA composites

Sample	Plasticizer (%)	Mold (°C)	Barrel zones 1/2/3/nozzle (°C)	Hot sprue (°C)	Shot size (in.)	1st and 2nd packing pressure/time (KPSI/s)
PLA	0	80	138/171/193/193	171	3.0	6/6, 12/7
PLA:SBP:sorbitol	0	75	96/148/193/193	160	3.0	6/6, 12/7
	10	65	96/154/182/182	154	3.1	2/6, 9/7
	20	65	96/154/182/182	154	3.1	2/6, 9/7
	30	65	101/160/182/182	154	3.1	2/6, 9/7
	40	65	115/160/182/182	165	3.0	4/10, 8/2
PLA:SBP:glycerol	0	71	127/171/182/182	160	3.0	4/10, 12/1
	10	65	127/160/182/182	160	3.0	4/10, 12/1
	20	65	127/160/182/182	160	3.0	4/10, 12/1
	30	63	115/148/171/171	160	3.0	4/10, 12/2
	40	63	115/148/171/171	160	3.0	4/10, 12/2

Acoustic Emission

Acoustic emission (AE) was used to study plasticized SBP and PLA interfaces. The deformation of composites (as composites are squeezed, torn or stretched) caused by an external force is accompanied by a rapid movement, relocation, or breaking of structural elements such as the polymer matrix or particles. As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals. This basic phenomenon may be defined as an AE event, which is translated by an AE analyzer as a "hit". AE measurements were performed simultaneously during tensile stress–strain tests. A small piezoelectric transducer was clipped against the specimen. This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corporation, Princeton, NJ) and is 10 mm in diameter. AE signals emanating from this transducer during sample deformation were processed with a Model 1220A preamplifier and an upgraded LOCAN-AT AE analyzer (Physical Acoustics Corporation, Princeton, NJ). The analyzer records the energy of each hit, its amplitude, and its duration. Only hits giving maximum amplitudes greater than 35 dB (threshold) from the transducer were counted. The upgraded LOCAN AT, which exceeds the 20 MB limit of old LOCAN's, is connected to a PC base with enhanced graphing and data collection software.

Scanning Electron Microscopy

After tensile testing, fracture surfaces of composite specimens were sputter coated with a thin layer of gold and examined with a Quanta 200 FEG scanning electron microscope (FEI Company, Inc., Hillsboro, OR) operated in the high vacuum/secondary electron imaging mode. Digital images were collected at 500×.

Confocal Microscopy

Confocal laser scanning microscopy was used for the structural study because SBP has strong intrinsic fluorescence at 500–530 nm when excited at 488 nm and PLA can be detected by confocal reflection. Images were made by confocal fluorescence and reflection in two separate channels, then displayed in extended focus, overlaid images. Specimens of PLA–SBP composites were examined 10× lens mounted in an IRBE optical microscope integrated with a model TCS-SP laser scanning confocal scanner head (Leica Microsystems, Exton, PA). The distribution of SBP and PLA was visualized in sets of optical sections extending from the surface to deep within the specimen. Matching optical sections from different PLA–SBP composites were compared.

Results and Discussion

Processing

Specific mechanical energy (SME) during the compounding of plasticized SBP and PLA decreased with increasing the amount of plasticizer in the melt (Fig. 1). The SME of 100% PLA was around 1,400 J/g. As expected, the addition of 30% SBP reduced the SME to around 1,000 J/g. In earlier work, the SME for 100% PLA and 30% SBP–PLA was around 1,025 and 775 J/g, respectively [17]. The difference is attributed to the grade of PLA and the feed rates.

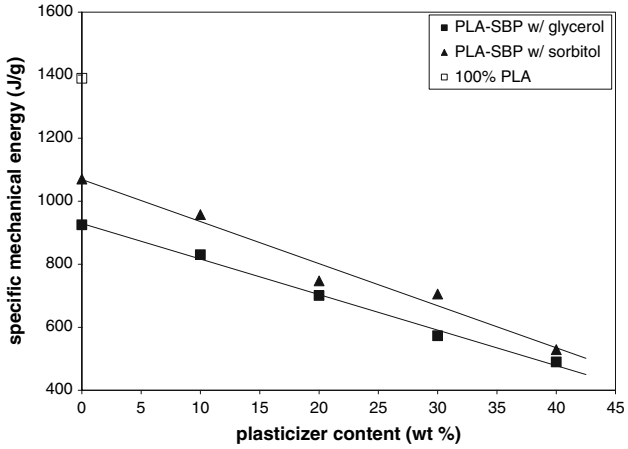

Fig. 1 Specific mechanical energy of plasticized SBP–PLA composites during twin-screw extrusion

In the first experiment the PLA was ground while in this experiment the PLA was in pellet form. The difference in SME between 100% PLA and 30% SBP–PLA for both experiments is approximately 300 J/g. At temperatures high enough to melt the PLA, the plasticizer was encapsulated by SBP which prevented phase separation of glycerol or liquefied sorbitol. When the moisture content (water) of SBP was greater than 30% (w/w), negative pseudoplastic behavior was observed during extrusion processing of 100% SBP [20, 21]. At SMEs above 500 J/g, wet SBP parenchymal cells are partially destructured and soluble pectic substances are released forming a thermoplastic [20]. In all cases, the SME remained above 500 J/g for SBP–PLA composites during compounding.

Mechanical Properties

PLA control samples exhibited a tensile strength of approximately 72 MPa. The addition of 30% SBP to PLA caused a reduction in tensile strength for the composite to approximately 50 MPa. The tensile strength of plasticized SBP–PLA composites (with 30% SBP) decreased with increasing amounts of plasticizer; eventually losing about 25% of its initial strength with 40% plasticizer (Fig. 2a). There is very little difference between using glycerol or sorbitol as a plasticizer. The quantitative assessment of stiffness can be based on measurements of the resistance to a small deformation by tensile force. The common method of determining the stiffness is based on measuring the slope of the stress–strain curve, i.e., Young's modulus measurements. PLA exhibited a Young's modulus value of 1,900 MPa, and the addition of 30% SBP increased Young's modulus to approximately 2,300 MPa as expected when filling a polymer with a stiff particulate. It was evident that the plasticizer significantly decreases the stiffness

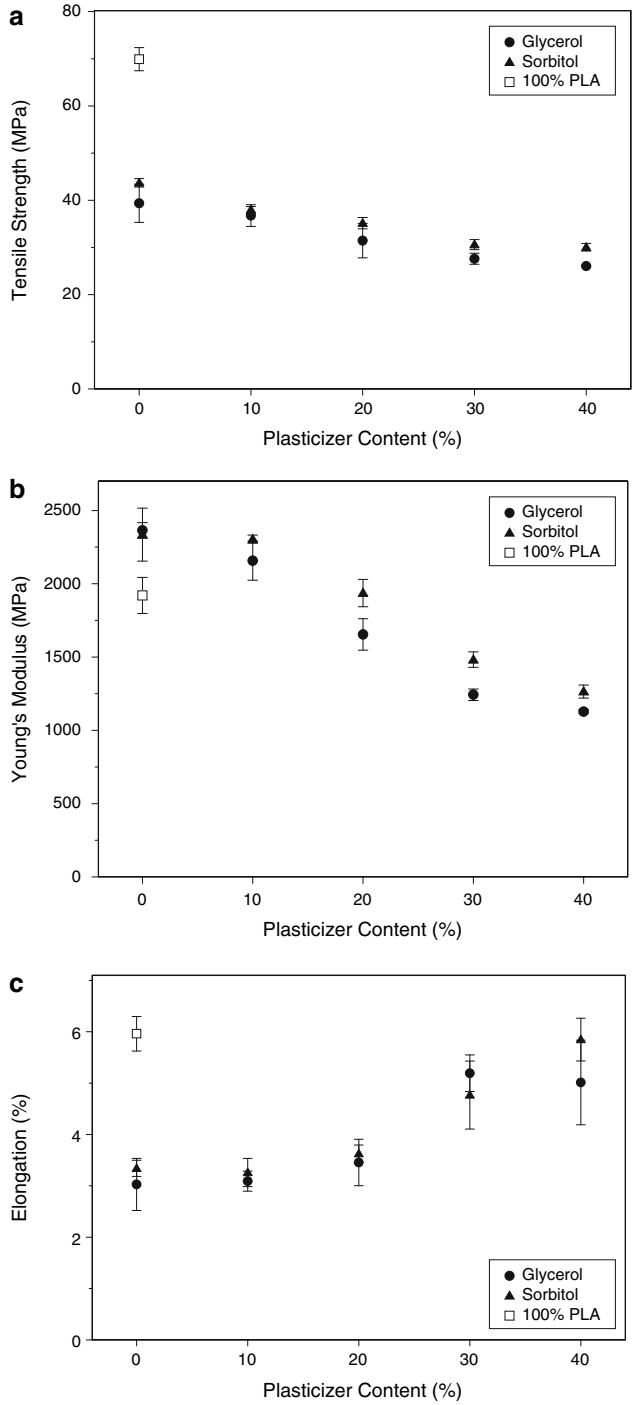

Fig. 2 Mechanical properties of plasticized SBP–PLA composites: (**a**) tensile strength, (**b**) Young's modulus, and (**c**) elongation

of the SBP–PLA composites (Fig. 2b). The elongation of 30% SBP–PLA was less than half that of 100% PLA (Fig. 2c). The elongation of SBP–PLA composites increases with the addition of plasticizer. In preliminary work, neat PLA was extruded with sorbitol or glycerol and was found to be immiscible. Other researchers also found that glycerol did not plasticize PLA [8]. Thus, the increase

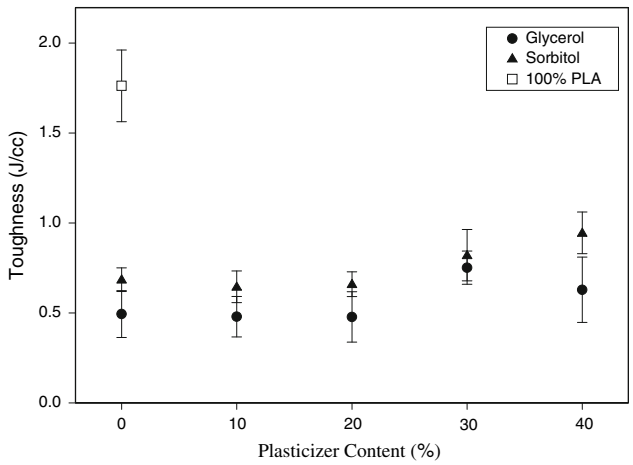

Fig. 3 Material toughness of plasticized SBP–PLA composites

in elongation was probably due to the plasticization of SBP and the formation of a network between the two phases (plasticized SBP and PLA). Figure 3 shows that toughness increased slightly with increasing amounts of plasticizer and seems to be correlated to the increase in elongation.

Acoustic Emission

AE events are plotted using hit rate as a function of time (or strain) during tensile testing. Overlaying AE plots with stress–strain curves provided an interesting perspective on the mechanical properties of plasticized SBP–PLA composites. The AE plot and stress–strain curve for 100% PLA is shown in Fig. 4a (and repeated for clarity in Fig. 5a). It shows that the samples emit very little sound in the first few seconds of extension, followed by a steep increase in the hit rate to a peak point at around 4% strain then a sudden decrease thereafter indicating a major fracture of the sample. The modulus for 100% PLA remains constant until fracture. As the sample undergoes strain, the stress steadily increases until fracture at approximately 72 MPa. In contrast, unplasticized SBP-PLA exhibits two distinct AE peaks (Figs. 4b and 5b). The first peak at 1–2% strain reflected the debonding between SBP and the PLA matrix whereas the second smaller peak at 3% strain indicated the fracture of the PLA phase. The debonding of the SBP occurred before fracture of the PLA matrix and appears to be correlated since debonding peak has significantly greater intensity than the

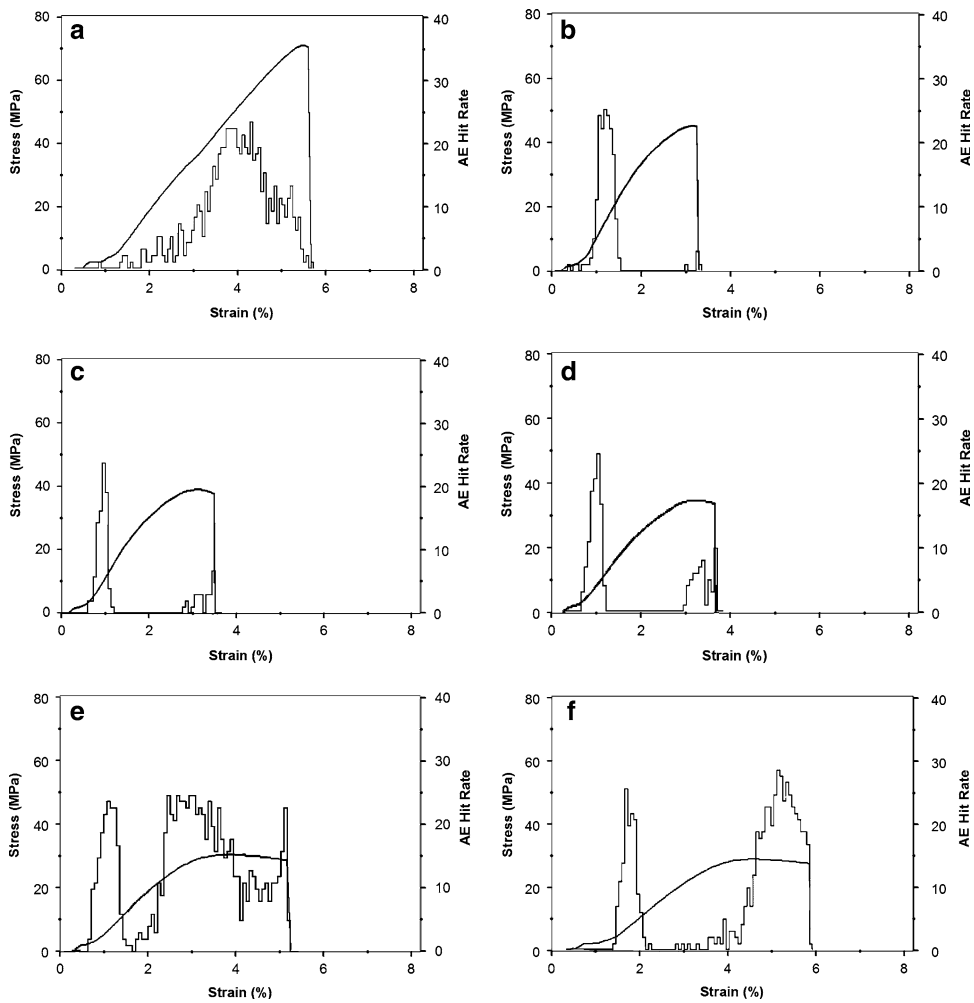

Fig. 4 Acoustic emission and stress–strain curves for sorbitol-plasticized SBP–PLA composites (**a**) 100% PLA, (**b**) 0% sorbitol, (**c**) 10% sorbitol, (**d**) 20% sorbitol, (**e**) 30% sorbitol, and (**f**) 40% sorbitol

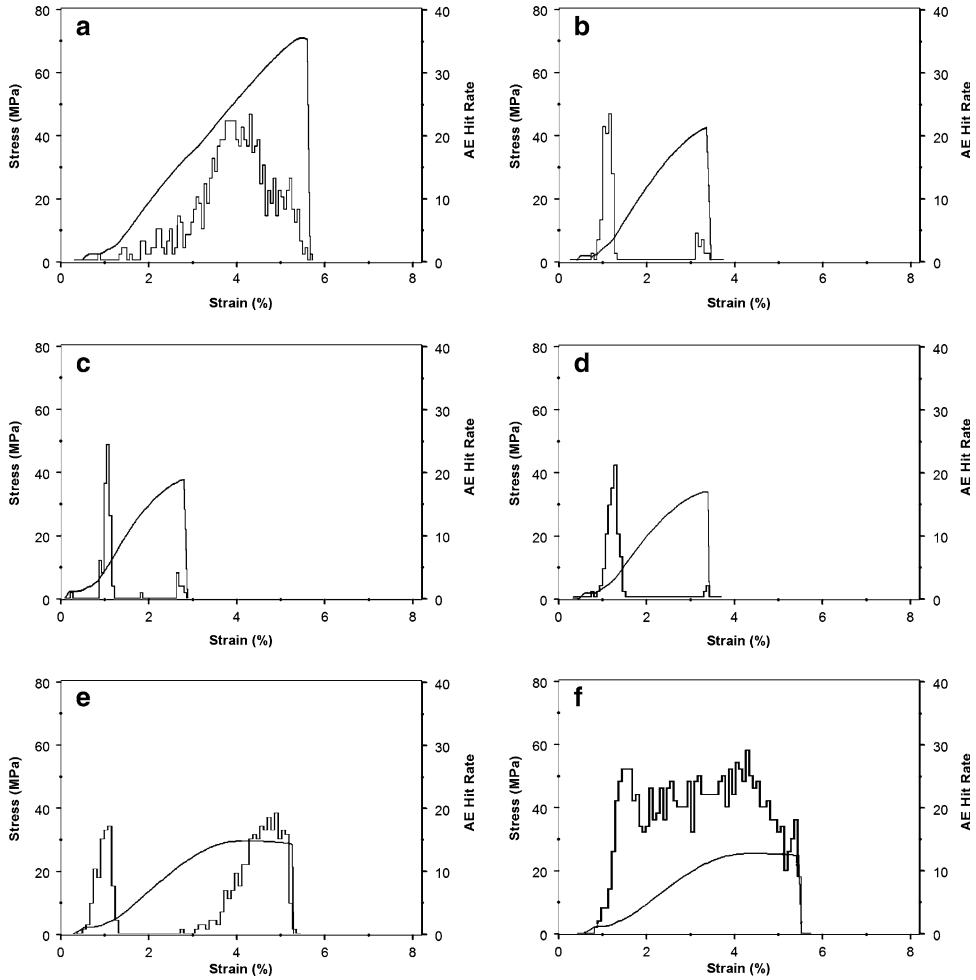

Fig. 5 Acoustic emission and stress–strain curves for glycerol-plasticized SBP–PLA composites (**a**) 100% PLA, (**b**) 0% glycerol, (**c**) 10% glycerol, (**d**) 20% glycerol, (**e**) 30% glycerol, and (**f**) 40% glycerol

fracture peak. In previous work with SBP and PLA, correlated debonding and fracture was found to occur at high levels of filler [18]. The AE of plasticized SBP–PLA composites with 10% and 20% sorbitol had similar AE propagation and exhibited a slight yield at the highest stress–strain rate (Fig. 4c, d). The debonding stress for 0% plasticizer was around 20 MPa and decreased with the addition of sorbitol. The debonding stress for 10% and 20% sorbitol was 10 MPa and 5 MPa, respectively. This reflected the lubricating effect of sorbitol at the SBP–PLA interface and the plasticization of SBP as the particles were softened by sorbitol. The second peak became more dominant as sorbitol content increased to 20%. At 30% plasticizer, the AE spectra showed significantly different behavior and the stress–strain yield became more pronounced (Fig. 4e). The debonding and fracture became uncorrelated and the composite elongation increased. The plasticized SBP–PLA composite exhibited ductile behavior which could be an indication of the formation of a network between SBP and PLA rather than a particle-matrix system. At 40% sorbitol, ductile behavior was still present but less pronounced and appears to be correlated; this may reflect the inability of SBP to absorb high levels of sorbitol (Fig. 4f).

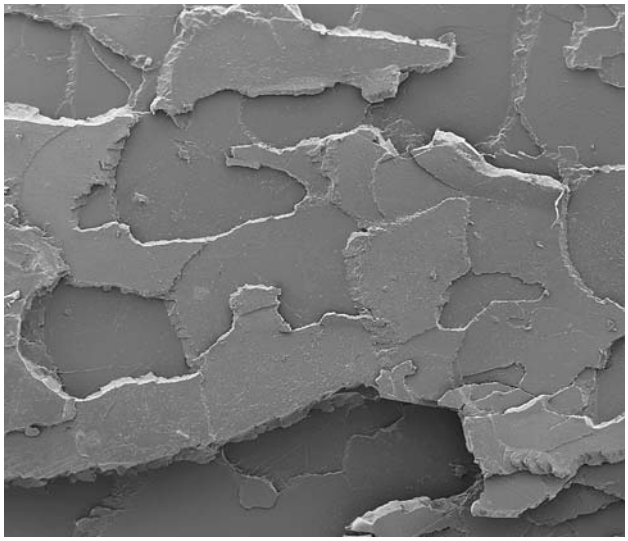

Fig. 6 SEM image of PLA fracture surface

The addition of glycerol as a plasticizer instead of sorbitol had a similar effect on the AE signature and stress–strain

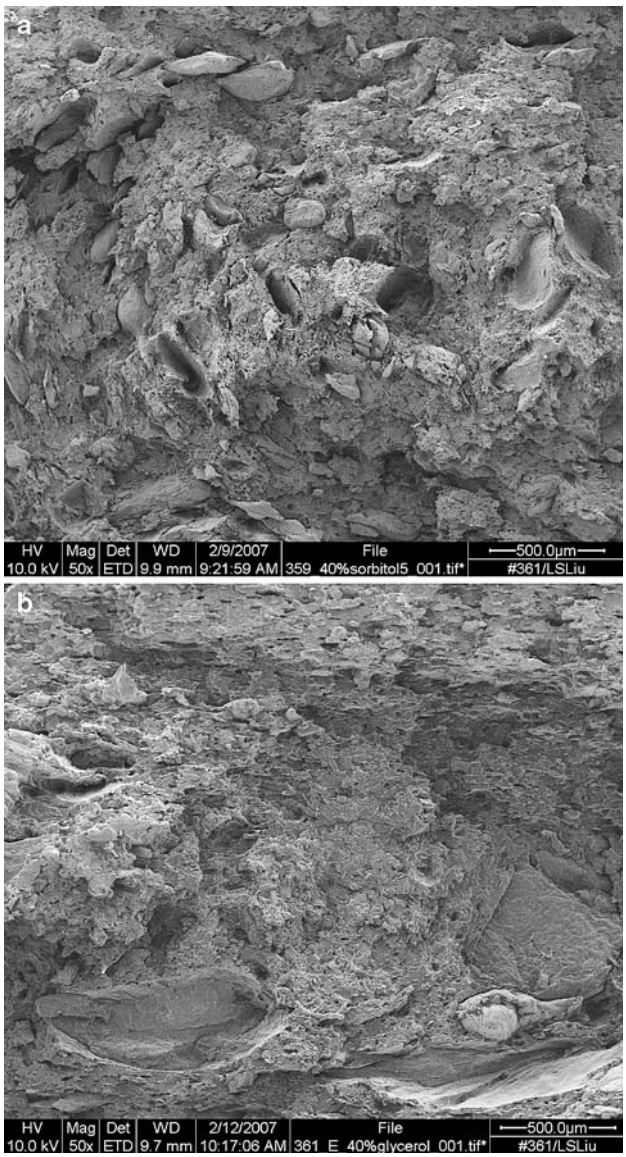

Fig. 7 SEM images of plasticized SBP–PLA green composites with 40% (**a**) sorbitol and (**b**) glycerol

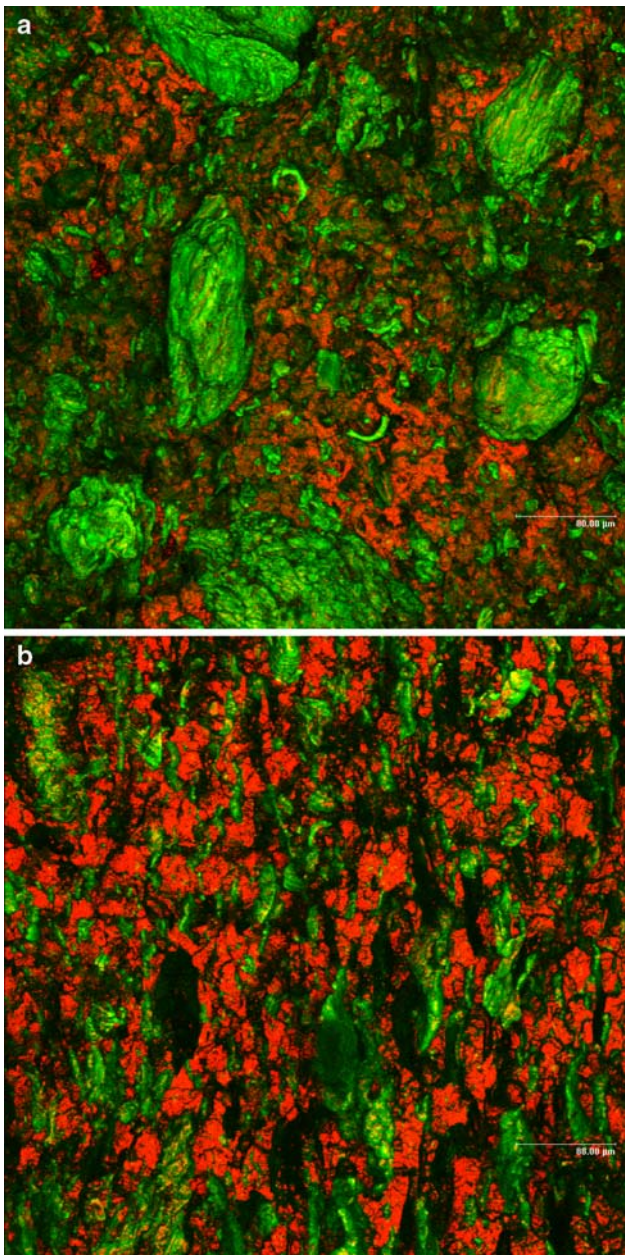

Fig. 8 Confocal reflective and fluorescent microscopy of SBP–PLA composites plasticized with 40% (**a**) sorbitol and (**b**) glycerol. PLA is depicted in red; SBP in green

relationships of SBP–PLA composites. The addition of glycerol up to 20% showed comparable behavior to sorbitol plasticized SBP–PLA with a larger debonding peak and correlated fracture mechanics (Fig. 5c, d). The debonding energy was significantly lower than the corresponding value for sorbitol. This is probably because glycerol is a liquid at room temperature while sorbitol is solid although the sorbitol is solvated in the SBP, and the lubricating effect of glycerol was higher than sorbitol. At 30% glycerol, the debonding and fracture are uncorrelated similar to 40% sorbitol (Fig. 5e). The most interesting AE data was plasticized SBP–PLA composites with 40% glycerol. The single broad AE peak began at 1% strain, accompanied by a slight material yield in the stress–strain curve, and continued until fracture suggesting a type of interacting network between SBP and PLA. Adhesion of SBP to PLA did not occur as indicated by the tensile strength (Fig. 2a); if adhesion occurred, the tensile strength would increase (reinforcement) or the loss in tensile strength would not be as great.

Microscopy

A typical fracture surface of PLA is shown in Fig. 6. Under the PLA surface layer, plasticized SBP was well dispersed

although some aggregation can be seen in composites with lower plasticizer content. The fracture surfaces of 40% sorbitol and glycerol plasticized SBP–PLA composites showed that 30% SBP was well-dispersed in the PLA matrix (Fig. 7a, b). This result is consistent with our previous findings where the freeze-fractured surface indicated good dispersion of SBP in the PLA [17, 18]. Sorbitol plasticized SBP–PLA had larger particles and generally larger aggregates than glycerol plasticized SBP–PLA composites. Examining the SEM images of 40% plasticizer, it appears that the glycerol plasticized SBP–PLA has significantly smaller particles and is more oriented (see top right of Fig. 7b) than sorbitol plasticized SBP–PLA composites. Confocal microscopy allowed the detailed examination of the structure of plasticized SBP–PLA composites. Under fluorescence and reflection the PLA phase reflected light from the 488 nm laser line (pseudo-colored red), and SBP fluoresced green under excitation. In general, PLA–SBP composites with sorbitol as a plasticizer or low levels of glycerol were well dispersed but did not mix well with the PLA matrix (Fig. 8a). For the composite with 40% glycerol, the plasticized SBP and PLA phases were co-continuous (Fig. 8b) in which the glycerol plasticized SBP (green) formed tendrils that were aligned with and penetrated the PLA phase.

Conclusion

The addition of sorbitol and glycerol plasticized SBP–PLA green composites. In general, glycerol was a better plasticizer than sorbitol. Plasticized SBP with 40% glycerol formed a co-continuous phase with PLA. Green polymer composites of SBP–PLA could be used where cost reduction is needed for packaging, utensils, and light weight construction materials.

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