The Characterization of Biodegradable Polybutylene Succinate/Starch Blends Using HDPE-g-Acrylic Acid as a Compatibilizer

S.-M. Lai*, C.-S. Wu and H.-T. Liao

1Dept. of Chemical and Materials Engineering, National I-Lan University, I-Lan 280, Taiwan, ROC
2Dept. of Biochemical Engineering and Graduate Institute of Environmental Polymer Materials, Kao Yuan University, Kaohsiung County 821, Taiwan, ROC

Received: 29 July 2005 Accepted: 24 October 2005

SUMMARY

The properties of polybutylene succinate (PBSU)/starch blends containing 5 phr of compatibilizer, HDPE-g-acrylic acid, are discussed. X-ray diffractograms indicated some disruption of the crystal structure of PBSU with the addition of starch. The melting temperature decreased slightly with increasing amounts of starch. The added starch tended to disrupt the inter-molecular hydrogen bonding interactions between the PBSU chains in the matrix. For blends containing a certain amount of starch, the thermal stability decreased due to a relatively low heat stability of starch. As for mechanical properties, a slight increase in tensile strength was observed when the compatibilizer was incorporated in the blends. Enhanced interaction was deduced from SEM observation. Surface erosion, seen in the optical micrographs, was accompanied by a visible growth of microorganisms particularly at high concentrations of starch. The rate of biodegradation was assessed based on the decrease in tensile strength during 4 weeks of soil burial. The weight loss increased with increasing treatment times and with starch content during extended soil burial.

INTRODUCTION

Biodegradable polymers with ecological advantages such as sustainability have been of great commercial interest because of growing environmental concerns about plastics waste disposal1. In particular, biopolymers derived from annually renewable resources have received considerable attention recently as a good way to form biodegradable blends at low cost.

Starch, one of the most abundant natural food sources, from tubers and grains, is considered an attractive biopolymer filler due to its low cost, low density, non-abrasive nature, biodegradability, and so on. It is a glucose-based biopolymer composed of linear amyllose and highly branched amylepectin. Amylose consists of α-1,4-linked glucose units, while amylepectin is a highly branched structure of α-1,4-linked chains connected by α-1,6-linkages2.

Griffin, in 1975, pioneered the blending of granular starch with plastics3; however, as native starch generally exists in a granular state owing to hydrogen bonding between adjacent molecules, it fails to disperse in sufficiently finely divided form into the plastic matrix. Efforts to minimize this problem have recently led to the development of thermoplastic starch (TPS) prepared by incorporating suitable amounts of water and/or plasticizers, a process termed “gelatinization”4. Properties have been considerably improved when synthetic plastics are blended with gelatinized or thermoplastic starch since then.

However, in some cases, the lack of specific interactions between gelatinized starch and the plastics matrix still gives an incompatible blend because of the difference in polarity. Compatibilizers are often used to further enhance interfacial interactions around the interphase, and to improve the final properties of the blend. As demonstrated...
by Biktas et al., when polyethylene grafted maleic anhydride was used, the compatibility between dispersed gelatinized starch and polyethylene matrix was improved. Unfortunately, a completely degradable blend is often questioned, since polyolefins are resistant to microorganisms attack. So, there have been numerous investigations into the blending of biodegradable polymers with starch,[8] including ethylene-co-vinyl alcohol (EVOH), thermoplastic polyolefin[9], polypropylene (PPLA), polycaprolactone[10,11], polybutylene succinate (PBSU)[12,13], and polylactic acid (PLA).[14] PBSU is an aliphatic thermoplastic polyester, synthesized by reacting butylene glycol with succinic acid[15,16]. Interesting properties, including biodegradability and processibility, have allowed PBSU to generate many types of blends, injection and extrusion products[17-20]. But, starch blends are an attractive way to further reduce costs.

Polybutylene succinate adipate (PBSA)/starch films were prepared with starch contents of 5%-30% by weight and processed by blown film extrusion[21]. Mani et al.[22] tried to improve the compatibility between starch and poly (e-caprolactone) or PCL, and between starch and PBSU (Bionolle 1020), using a compatibilizer with an anhydride functional group incorporated into the polyester backbone and a twin-screw extruder to process the mixture.

The addition of a small amount of compatibilizer significantly increased the strength of the blend. Our recent studies showed that the starch gelatinization was effective in promoting compatibility with PBSU (Bionolle 1001)[23]. In all PBSU blends, the mechanical properties of materials made using gelatinized starch showed higher performance than those made with untreated starch.

In view of studies dealing with starch and PBSA compatibilized blends, this work was undertaken to explore in depth the effect of a compatibilizer (acrylic acid grafted high density polyethylene, HDPE-g-MA) on the physical and mechanical properties of PBSU/starch blend, aiming to produce new generations of low cost biodegradable plastics.

**EXPERIMENTAL**

**Materials**

Samples of polybutylene succinate - PBSU (Bionolle), with melt index of 1.5 (g/10 min), were supplied by the Showa High Polymer Corporation under the trade name of Bionolle 1001 (Mw = 2.6 x 10^5). The melting temperature (T_m) and glass transition temperature (T_g) determined in our laboratory were 112.9 °C and -32.5 °C, respectively. Corn starch, composed of 27% amylose and 73% amylpectin, was obtained from the Sigma Chemical Corporation. HDPE-g-MA (Polyboll 1009) with a grafting ratio of 6 wt% acrylic acid was supplied by the Chrompton-Uniroyal Chemical Corporation (now part of Chemtura).

**Sample Preparations**

All pristine resins were pre-dried for 24 h at 60 °C in a dehumidified air-circulated oven prior to further treatment. 5 phr of HDPE-g-MA (parts per hundred resin based on the total weight of PBSU and starch) were added in the mixing sequence. The mixing of PBSU and starch was carried out using xylene as solvent, to form a uniform suspension, at a rotor speed of 50 rpm for 30 min. at 125 °C. The starch contents were 10, 20, 30, and 40 wt%, respectively.

The batch was then hot pressed to obtain a thin sheet. Tensile test specimens, according to ISO-37 Type (III) standard, were prepared through a die cut. Tensile measurements based on ASTM standard D638 were conducted. Before any test, all samples were stored in a vacuum drier for at least 24 hours.

**Measurements**

The physical and chemical performance of the blends, and biodegradability, were evaluated by chemical and physical characterization using several techniques as described below.

**Structure and Thermal Characterizations**

The infrared spectra of the PBSU/starch blends were recorded on a Fourier Transform Infrared Spectrophotometer (BIO-RAD, FTS-7PC) at a resolution of 4 cm⁻¹ for 64 scans from 4000-500 cm⁻¹. A Rigaku D-max 3V X-ray unit was used to determine the change in crystalline structure at room temperature. An X-ray source of CuKα radiation with a wavelength of 0.154 nm was employed. The diffractograms were scanned in the 2θ range from 5° to 45° at 4°/min. The melting temperature (Tm) and enthalpy (ΔHm) were measured using a DSC (Perkin-Elmer, DSC-7) at a heating rate of 10 °C/min from 25 to 140 °C. The crystallization was performed at a cooling rate of 10 °C/min from 140 to 25 °C. Thermogravimetric analysis (TGA) using a TA instrument 2050 TGA system was carried out.
at a heating rate of 20 °C/min from 30 to 600 °C to evaluate the thermal stability of the blends.

**Mechanical Properties and Morphology**

Measurements of tensile strength and elongation were conducted in accordance with ASTM-D638 at a crosshead speed of 50 mm/min using a Lloyd's 135K Universal Tensile Testing Machine.

The morphology of fractured sample under cryogenic condition was elucidated using a scanning electron microscope (Hitachi, S-4100). All samples were sputtered with gold before further characterization.

**Biodegradability**

These tests were carried out in soil sampled from inside of the campus of Xiang Yuan University. Tensile specimens of all blends were buried in a soil chamber conditioned at 80% relative humidity and 25 °C. Tensile strength was assessed at each week, during a month period of soil burial. The weight loss for extended burial periods, as an indication of biodegradability, was calculated as follows.

\[
\text{Weight loss (\%)} = \frac{(W_0 - W_f)}{W_0} \tag{1}
\]

where \(W_0\) is the original sample weight and \(W_f\) is the final sample weight after soil burial.

**RESULTS AND DISCUSSION**

As this compatibilizer is structurally similar to the aliphatic segment of the PBSU backbone, it is likely that its grafted polar moiety interacts with the hydroxyl groups of starch.

For ease of comparison, a typical blend of PBSU and 20 wt% starch is presented here, unless otherwise stated.

**Structure and Thermal Characterization**

Important regions of the FTIR spectra of PBSU/starch blends, with and without 5 hr of compatibilizer, are depicted in Figure 1 for a comparison. Characteristics absorption ranges of starch include:

(i) absorption bands of O-H (3600-3300 cm\(^{-1}\))

(ii) C-H (2920 cm\(^{-1}\))

(iii) O-H bending of absorbed water (1640 cm\(^{-1}\))

(iv) C-O (1250-900 cm\(^{-1}\)).

In addition, the following PBSU absorption bands were observed:

(i) O-H (3600-3300 cm\(^{-1}\))

(ii) C-H (2941 cm\(^{-1}\))

(iii) C=O (1728 cm\(^{-1}\))

(iv) ester bonding (1264 cm\(^{-1}\)), and

(v) C-O (1140 cm\(^{-1}\)).

In general, when starch was incorporated, most of the typical absorption bands of PBSU remained unchanged but they tended to enlarge. The spectrum intensity of hydrogen bonded C=O (1702 cm\(^{-1}\)) depicting the interaction of hydrogen bonding between O-H bending group on starch and functional group of C=O on PBSU was not strong enough to be revealed clearly near the shoulder of free C=O absorption band, being impossible to distinguish the PBSU/starch blend. When HDPE-g-AA was incorporated, the formation of new absorption bands of carbonyl ester bonding (1737 cm\(^{-1}\)) in Figure 3 (c) was observed because of hydrogen bonding interactions and the formation of an ester group of O-H on starch and acrylic acid bonding of the compatibilizer. Similar findings are seen for other starch blends.

Figure 2 shows the X-ray diffraction patterns used to investigate the crystallinity of PBSU/starch blends. As seen, Figure 2 (a), the characteristic diffraction peaks of pristine PBSU occurred at around 2θ values of 18.1° and 23.2°. Similar values of 19.5° and 23.5° were found for a similar type of PBSU (Bionolle 1020). These peaks changed slightly with the introduction of 20% starch. One tiny peak of 17.6° appeared, Figure 2 (b), indicating that a crystal domain of PBSU has been partly disrupted. Furthermore, with the addition of a compatibilizer, two extra diffraction peaks at 18.1° and 23.2° appeared in Figure 2 (c) as compared with Figure 2 (b). Apparently, this compatibilizer shares similar crystal formation with the blend in this region. This difference in the crystalline regions of the blends, causing changes in their thermal behaviors, will now be discussed.

To investigate the effect of starch content on the thermal behavior of PBSU/starch blends, the melting temperature (Tm) was determined by the differential scanning calorimetry. As seen in
Figure 1. FTIR curves of (a) PBSU and (b) PBSU/20% starch and (c) PBSU/20% starch, 5 phr HDPE-g-AA.

Figure 3, the melting temperature decreased slightly from 113.9 °C to 110.8 °C, for the blend containing 20% starch. The blend containing 40% starch gave a further decrease in melting temperature at 109 °C (not shown here for brevity). Apparently, the added starch tends to disrupt the inter-molecular hydrogen bonding within the PBSU matrix, which causes the entropy of mixing to increase. This increase reduces the melting temperature for thermodynamic reasons. Previous examinations of X-ray analysis also indicate disruption of some crystal domains of PBSU. On the other hand, with the addition of compatibilizer (HDPE-g-MA), better mixing is achieved, which changes the enthalpy of mixing. This change appears to be similar to the change in the entropy of mixing, which accounts for the similar order of melting temperature \( T_m \approx 111.4 \) °C for the blends with or without a compatibilizer. A small melting peak \( T_m \approx 127.0 \) °C and a crystallization peak \( T_c \approx 117.1 \) °C for the compatibilizer were observed, Figure 3(c). As for the crystallization temperature of the blends, a corresponding decrease was also found.

The thermal stability of blends containing various amounts of starch is illustrated in Figure 4, derived from thermogravimetric analysis. The initial loss of weight was attributed to the loss of any remaining water from the starch. As expected, PBSU showed thermal stability with 10% of weight loss up to about 300 °C. For the blend containing 10% of starch, the thermal stability remained at a certain degree, but continued to decrease and the temperature for at about 10% of weight loss was about 360 °C. Further decrease in the thermal stability was found for higher starch contents because of its relatively low heat stability of starch. A decomposition temperature close to 310 °C is associated with
selective dehydration and transglucosidation. Interestingly, the ash content of starch was about 12% up to 600 °C, which might be associated with the tendency to form a thermally resistant char layer with a high residual carbon content. The weight loss at 360 °C of the PBSU/starch blends, containing compatibilizer and various amounts of starch, is given for comparison, as shown in Figure 5. Thus, HDPE-g-AA displayed higher thermal resistance than PBSU and starch probably due to its rather stable main chain with C-C and C-H bonding, which in turn slightly increases the thermal stability of the blends.

Mechanical Properties

Figure 6 shows the effect of the starch content on tensile strength of blends. When the starch
content increased, tensile strength of the blends generally decreased, in agreement with Park et al.\textsuperscript{15} and Ratto et al.\textsuperscript{16} For PBSU blended with starch, tensile strength progressively decreased from 26.3 ± 1.6 MPa to 13.8 ± 1.0 MPa. When the compatibilizer was incorporated, it improved the mixing of PBSU and starch, as observed by an average increment of about 16% in tensile strength. This increase is rather limited when compared with our previous approach using gelatinized starch, for which tensile strength increased up to as much as 100%.\textsuperscript{17}

Throughout this study, the mechanical properties of PBSU/starch blends with a compatibilizer conferred higher performance than those without it. These findings were supported by an investigation of
Figure 6. The effect of starch content and compatibilizer on tensile strength of PBSU/Starch blends

the morphological characteristics of PBSU/Starch blends with HDPE-g- AA. Yet, it is interesting to see whether any ageing effects on the mechanical and thermal properties might occur during prolonged storage. The suspicion that hydrolysis might cause sample properties to deteriorate because of a scission of the polyester chains needs further studies especially at higher starch contents.

The SEM micrographs of PBSU/Starch blends are shown in Figure 7. Cavities surrounding starch granules were observed in Figure 7 (b), reflecting a lack of interaction between PBSU and starch, and confirming the previous findings relating to mechanical properties. When the compatibilizer was incorporated, finer micro-cavities were evident as shown in Figure 7 (d), which implied improved interaction between the constituents of the mixture.

Biodegradability

Typical optical photomicrographs of PBSU/Starch blends, taken after various periods in a soil test, are shown in Figures 8 to 10. Figure 8 illustrates the surface behavior of PBSU after various burial periods. Virtually no difference was observed with treatment time, probably because of the hydrophobic character of PBSU that limits the degree of the material degradation. Similar findings for the PBSU blend containing 20% starch after similar treatment procedures are shown in Figure 9. Although starch degrades quickly because of its hydrophilic character, only a slow degradation was observed for these blends, probably because the amount of starch present was still limited.

However, after varying the starch content in the compatibilized blends, a visible growth of microorganisms was detected, particularly at high concentrations of starch as shown in Figure 10, after 4 weeks of burial. The incorporation of compatibilizer did not prevent the formation of microorganisms; there was not much effect on sample degradation.

To further assess the biodegradability of PBSU/Starch blends, tensile strength of the samples subjected to burial tests was determined. Tensile strength is a function of the microorganism-induced decomposition and should provide an index of biodegradation. Tensile strength of uncompatibilized and compatibilized PBSU/Starch blends, containing 20% starch, is shown in Figure 11. Tensile strength of PBSU decreased from 26.3 ± 1.0 to 17.8±0.5 MPa over this short term of investigation. Apparently, PBSU was subjected to invisible micro-organisms attack, which caused its molecular weight to decrease. With the addition of compatibilizer, tensile strength still decreased slightly with burial time. As for typical blends containing 20% starch, tensile strength of compatibilized and uncompatibilized blends decreased with burial time as well. However,
Figure 7. The SEM micrographs of (a) PBSU and (b) PBSU/20% starch and (c) PBSU/20% starch, 5 phr HDPE-g-AA

(a) PBSU  
(b) PBSU/20% starch

(a) PBSU/20% starch/HDPE-g-AA (5 phr)

Figure 8. Photographs of PBSU at various burial periods

(a) 1 week  
(b) 2 weeks  
(c) 3 weeks  
(d) 4 weeks
Figure 9. Photographs of PBSU/starch blends containing 20% starch after soil burial for (a) 1 week (b) 2 weeks (c) 3 weeks (d) 4 weeks

PBSU/starch (20 wt%)/HDPE-g-AA (5 phr)

(a) (b) (c) (d)

PBSU/starch (20 wt%)

(a) (b) (c) (d)

Figure 10. Photographs of compatibilized PBSU/starch after 4 weeks of soil burial at various starch contents (a) 10% (b) 20% (c) 30% (d) 40%
tenile strength of compatibilized blends was higher than that of uncompatibilized ones, indicating a slower degradation because of improved interaction between PBSU and starch. Starch is a natural polymer and could be readily used as a carbon source by the microorganisms. Thus, the decline in tenile strength does appear to indicate a certain degree of biodgradation, even though previous surface observation showed a limited degradation.

To further assess the biodogradability of PBSU/ starch blends, the samples were buried in a conditioned soil environment and the weight loss due to microorganisms attack was recorded according to Equation (1). The results for blends with or without compatibilization are depicted in Figure 12. PBSU, with or without compatibilizer, was quite stable in this short term of investigation, with no significant effect when it was present. On the other hand, an intensive biodgradation was found for blends containing starch, with a profound increase in the weight loss for blends containing 40% of starch, reaching up to 41% for blends without compatibilizer. When the treatment period increased, the values of the weight loss increased, meaning that starch, a natural polymer, could be readily used as a carbon source by the microorganisms. This would cause a measurable amount of weight loss in the treatment period. In addition, the slight difference in weight loss observed for blends, with or without compatibilizer, indicated an enhanced interaction between PBSU and starch due to the presence of compatibilizer.

CONCLUSIONS

The properties of polybutylene succinate (PBSU)/ starch blends containing 5 phr of compatibilizer, HDPE-g-acrylic acid, have been discussed. X-ray diffractograms indicated some disruption of the crystalllography of PBSU with the addition of starch. The melting temperature decreased slightly with higher dosages of starch, due to the added starch, which tended to disrupt the inter-molecular hydrogen bonding within the PBSU matrix. For blends containing a certain amount of starch, the thermal stability decreased. On the other hand, the presence of the compatibilizer helped to improve the thermal properties and tenile strength. The gelatinization of the starch significantly improved the mechanical properties according to our previous work; however, interaction was still limited using this type of compatibilizer. Surface erosion shown in optical micrographs indicated a visible growth of microorganisms, particularly at high concentrations of starch. The rate of biodgradation was assessed from the decrease in tensile strength and viscosity during 4 weeks of soil burial. The assessment of biodogradability indicated an increasing weight loss with longer treatment periods and higher starch contents.

Figure 11. The effect of burial time on tensile strength of PBSU, PBSU/starch blends and compatibilized PBSU/starch blends

![Graph showing the effect of burial time on tensile strength](image)

374

20 Polymers & Polymer Composites, Vol. 14, No. 4, 2008
ACKNOWLEDGEMENT

Partial grants-in-aid from R.O.C. government (Contract number of NSC 94-2216-E-197-001) are gratefully acknowledged. Some experiments carried out by M.-J. Chen and D.-Y. Lin are also appreciated.

REFERENCES