

Preparation and Properties of Biodegradable Poly(butylene succinate)/Starch Blends

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Received 8 July 2004; accepted 14 October 2004

DOI 10.1002/app.21679

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The vital differences between the use of untreated starch and gelatinized starch in blends with poly(butylene succinate) (Bionolle) were thoroughly examined in this study. The melting temperature decreased slightly with increasing dosages of untreated and gelatinized starch. The added starch perhaps tended to disrupt the intermolecular hydrogen bonding within the Bionolle matrix. On the other hand, a large increase in the crystallinity was seen with the addition of starch. Starch appeared to play a nucleating role in the blends. The trend of the glass-transition temperature decreasing with the starch level was similar to the trend of the melting temperature. For the same starch content, the glass-transition temperature showed some variations. For blends containing a certain amount of gelatinized starch, the thermal stability remained to a certain degree but continued to decrease. This was ascribed to the relatively low heat stability of starch. As for the mechanical properties, a sig-

nificant increase in the tensile strength (up to 2 times) was observed when untreated starch was replaced with gelatinized starch in the blends. Similarly, the tear strength increased up to 1.5 times if gelatinized starch was employed. Apparently, the gelatinization of starch was efficiently achieved for promoting its compatibility with Bionolle. In all cases, the mechanical properties of Bionolle blended with gelatinized starch were better than those of Bionolle blended with untreated starch. A morphological investigation provided evidence in support of these findings. This relatively low-cost gelatinization approach provides an alternative to a high-cost compatibilizer approach for improving the performance of biodegradable blends. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 257–264, 2005

Key words: biodegradable; blends; polysaccharides

INTRODUCTION

Biodegradable polymers featuring ecological advantages for sustainable development have attracted great commercial interest because of growing environmental concerns.¹ Several internationally renowned corporations, such as DuPont, ICI, Cargill-Dow, and Union Carbide, are devoted to the development of performance/cost-competitive products. Biodegradable polymers such as poly(lactic acid) (PLA), poly(hydroxy alcanoate), poly(vinyl alcohol), and poly(butylene succinate) (PBSU) are available as commercial products. However, the prices of these biodegradable polymers are generally high, and thus blending with low-price resins becomes an alternative approach to resolving this problem. In particular, biopolymer fillers derived from annually renewable resources and used to form biodegradable blends have received much attention recently.

Starch, one of most abundant natural food sources for most plants, has been considered an attractive biopolymer filler because of its low cost, low density, nonabrasive nature, biodegradability, and so forth. Starch is primarily composed of amylose and amylopectin. Amylose is a linear polymer of α -1,4-linked glucose units, whereas amylopectin is a highly branched polymer of α -1,4-linked chains connected by 1,6-linkages.² Griffin³ in 1975 pioneered blending with granular starch with plastic materials. Unfortunately, native starch generally exists in a granular state because of the inherent hydrogen bonding between adjacent molecules. Therefore, starch fails to disperse on an extremely fine scale into a plastic matrix. Efforts to solve this problem have led to the recent development of thermoplastic starch prepared by the incorporation of suitable amounts of water, plasticizers, or both; this is called *gelatinization*.⁴ The properties have been considerably improved for synthetic plastics blended with gelatinized or thermoplastic starch since then. However, in some cases, the lack of specific interactions between the gelatinized starch and plastic matrix still produces an incompatible blend. To further enhance the interfacial bonding around the interphase, compatibilizers are often required. By employing

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Contract grant sponsor: Republic of China; contract grant number: NSC 91-2621-Z-197-002.

polyethylene-grafted maleic anhydride as a compatibilizer, Bikiaris and Panayiotou⁵ reported that the compatibility between dispersed gelatinized starch and a polyethylene matrix could be improved. Unfortunately, a completely degradable blend was often questioned. Thus, numerous works have been published regarding the blending of biodegradable polymers with starch.^{6–12}

George et al.⁶ investigated the processing and physical properties of poly(ethylene-co-vinyl alcohol) (EVOH) and gelatinized starch blends for various types of starches, including waxy maize starch (70% amylose), corn starch (30% amylose), and specially treated high-amylose corn starch. Among them, waxy maize starch provided the best stiffness. High-amylose starch provided better elongation at a low dosage of EVOH. At a dosage of EVOH greater than 50%, not much effect of the starch types was seen. Seidenstücker and Fritz⁷ compared the effects of starch and gelatinized starch on their blends with thermoplastic polyurethane (TPU) through a twin-screw extrusion process. The strain at break for gelatinized starch blended with TPU, reaching 1200%, was five times that of an untreated starch blend, and this indicated an enhanced interaction between the gelatinized starch and TPU. Park et al.⁸ studied the effect of the glycerol content on the crystalline morphology and mechanical properties of gelatinized starch and PLA. Gelatinized starch also played a nucleating role in promoting the crystallinity of PLA. When the water/glycerol ratio was 100/40, the blend reached optimum toughness. Unfortunately, the elongation was still limited. In another study, binary blends of poly(hydroxy butyrate) (PHB) were prepared with natural starch, starch adipate, and grafted starch-urethane derivatives by Innocenti-Mei et al.⁹ The PHB blends were characterized in terms of their mechanical and thermal properties. Significant decreases in both the glass-transition temperature (T_g) and melting temperature (T_m) were observed for all the formulations. The best results were obtained with grafted starch-urethane blends with poly(propylene glycol).

Although many biodegradable polymers have been reported to blend with starch, studies discussing PBSU/starch blends have been limited. PBSU is an aliphatic thermoplastic polyester synthesized by the reaction of glycols with dicarboxylic acids.^{13,14} Interesting properties, including biodegradability and processibility, have allowed PBSU to generate many types of blend, injection, and extrusion products.^{15–21} For the further reduction of the cost of PBSU, a starch blend provides an attractive approach. Poly(butylene succinate adipate) (PBSA)/starch films were prepared with starch concentrations of 5–30 wt % and were processed by blown-film extrusion.²² Increasing the starch content led to an increase in the modulus and decreases in the tensile strength, elongation to break,

TABLE I
Formulations for Gelatinized Starch

Sample	Starch		Water		Glycerol	
	g	wt %	g	wt %	g	wt %
CSG00	30	50	30	50	0	0
CSG08	30	50	25	42	5	8
CSG17	30	50	20	33	10	17
CSG33	30	50	10	17	20	33

and toughness. The results demonstrated that the biodegradable PBSA/starch system had mechanical properties useful for blown-film applications. Mani and Bhattacharya²³ tried to improve the compatibility between starch and PBSU; a compatibilizer containing an anhydride functional group incorporated onto the polyester backbone was used. The blends were melt-compounded with a twin-screw extruder. The addition of a small amount of the compatibilizer increased the strength significantly over that of the uncompatibilized blend.

Because few studies have dealt with PBSU/starch blends, this work was undertaken to examine in depth the effect of starch and gelatinized starch on the physical and mechanical properties of PBSU/starch blends. Different degrees of gelatinization were used with various amounts of glycerol. The blends were characterized with thermal analysis, including differential scanning calorimetry (DSC) and thermogravimetric weight loss. The tensile strength and tear strength were evaluated and elucidated in a morphology study with scanning electron microscopy. In summary, this study could lead to a better understanding of blend performance and pave the way to producing a new generation of biodegradable plastics for our environment.

EXPERIMENTAL

Materials

The materials were PBSU and starch. PBSU with a melt index of 1.5 g/10 min was supplied by Showa High Polymer Corp. (Showa Denko K.K., Tokyo, Japan) under the trade name of Bionolle 1001. T_m and T_g determined in our laboratory, were 114 and -32.5°C , respectively. Corn starch was purchased from Roquette (Barcelona, Spain).

Sample preparation

All the pristine resins were predried for 24 h at 50°C in a dehumidified air-circulated oven before further treatment. The gelatinized starch was prepared by the addition of various amounts of water and glycerol according to Table I. Gelatinization was completed in

TABLE II
Untreated Starch and Gelatinized Starch Contents for Blending with Bionolle

Sample	Bionolle		Starch		Glycerol	
	g	wt %	g	wt %	g	wt %
05CS	52.5	95	2.75	5	—	—
10CS	49.5	90	5.5	10	—	—
15CS	46.75	85	8.25	15	—	—
20CS	44	80	11	20	—	—
05CSG00	52.5	95	2.75	5	—	—
10CSG00	49.5	90	5.5	10	—	—
15CSG00	46.75	85	8.25	15	—	—
20CSG00	44	80	11	20	—	—
05CSG08	52.5	95	2.53	4.6	0.22	0.4
10CSG08	49.5	90	5.06	9.2	0.44	0.8
15CSG08	46.75	85	7.59	13.8	0.66	1.2
20CSG08	44	80	10.12	18.4	0.88	1.6
05CSG17	52.5	95	2.28	4.1	0.47	0.9
10CSG17	49.5	90	4.56	8.3	0.94	1.7
15CSG17	46.75	85	6.85	12.5	1.40	2.5
20CSG17	44	80	9.13	16.6	1.87	3.4

a Brabender Plastograph internal mixer (Brabender OHG, Duisburg, Germany; South Hackensack, NJ) at a rotor speed of 50 rpm for 30 min at 90°C. The gelatinized starch was then stored in a vacuum drier. The mixing of PBSU (Bionolle) and starch was carried out with an internal mixer at a rotor speed of 80 rpm for 10 min at 145°C. The mixing formulations are shown in Table II. The prepared batch was then hot-pressed to obtain a thin sheet. For ease of comparison, various sample codes are used here. x CS indicates x wt % untreated starch in the blend. CSG y refers to gelatinized starch containing y wt % glycerol. x CSG y indicates x wt % gelatinized corn starch in the blend and y wt % glycerol in the gelatinized starch. The tensile test specimens, which complied with the ISO-37 Type (III) standard, were then prepared with a die cut. Tensile measurements based on ASTM Standard D638 were conducted. Trousers tear test specimens, approximately 1 mm thick, were prepared with backing cloth on one side and with a center groove 0.2 mm deep on both sides to guide crack propagation. Thus, the thickness remaining to be torn was approximately 0.6 mm. At least 1 day of storage in a vacuum drier after sample preparation was kept before any measurements were taken.

Measurements

All test specimens were preconditioned in a vacuum drier for at least 24 h before the tests. T_g was determined via dynamic mechanical analysis (DMA 7e, PerkinElmer, Boston, MA) under a three-point-bending mode at a frequency of 1 Hz at a heating rate of 5°C/min from -50 to 20°C. T_m was measured with DSC (TA2010, TA Instruments, NewCastle, DE) at a heating rate of 10°C/min from 25 to 160°C. The crys-

tallinity was calculated as the heat of fusion divided by the enthalpy required for 100% crystallinity.²⁰ Thermogravimetric analysis (TGA; TGA6, PerkinElmer, Boston, MA) was used to evaluate the thermal stability of the blend at a heating rate of 20°C/min from 50 to 600°C.

The tensile measurements were conducted according to ASTM D 638 at a crosshead speed of 10 cm/min with a Universal GY6040A4 tensile testing machine (Chunyen, Taiwan). The tensile strength and elongation at break were recorded. A Trousers tear test was carried out under similar conditions to determine the fracture energy (G_c) for this type of blend:

$$G_c = 2F/t \quad (1)$$

where F is the minimum force required to propagate a crack and t is the tear thickness.

The morphology of the fractured samples under cryogenic conditions was elucidated with scanning electron microscopy (JSM-6335F, JEOL, Tokyo, Japan). All samples were sputtered with gold before further characterization.

RESULTS AND DISCUSSION

For ease of comparison, a typical blend of Bionolle and CSG08 is presented here because the mechanical properties are in the optimum range, unless otherwise stated.

Thermal characterization

To investigate the effect of the starch content on the thermal behavior of the Bionolle/starch blends, we determined T_m , the heat of fusion, and the crystallinity

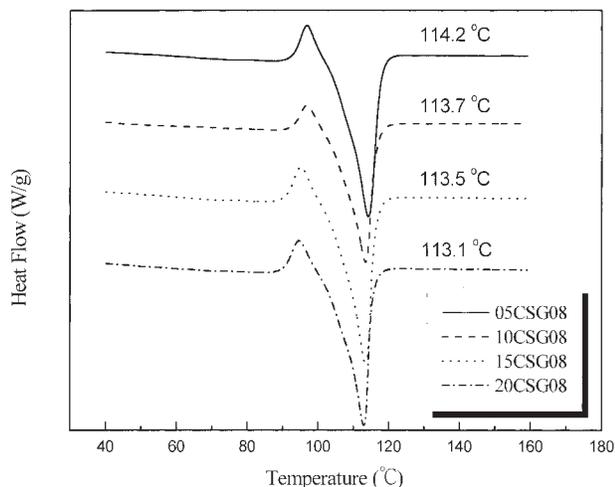


Figure 1 DSC curves of the Bionolle/CSG08 blends.

with DSC. Typical thermographs of the Bionolle/CSG08 blends are shown in Figure 1. For blends containing various amounts of gelatinized starch treated with 8% glycerol, T_m decreased slightly from 114.2 to 113.1°C. T_m of the pristine resin was approximately 114°C and remained roughly unchanged after the incorporation of starch. The measurements carried out for the other formulations are shown in Figure 2. Again, for other dosages of the untreated and gelatinized starch, T_m decreased slightly. Perhaps the added starch disrupted the intermolecular hydrogen bonding within the Bionolle matrix, and this caused the entropy of mixing to increase. This increase would have reduced T_m from a thermodynamic point of view. Likewise, for the same amount of added starch, as the glycerol content increased, the mixing goodness was improved because of the better compatibility between the gelatinized starch and Bionolle. The gelati-

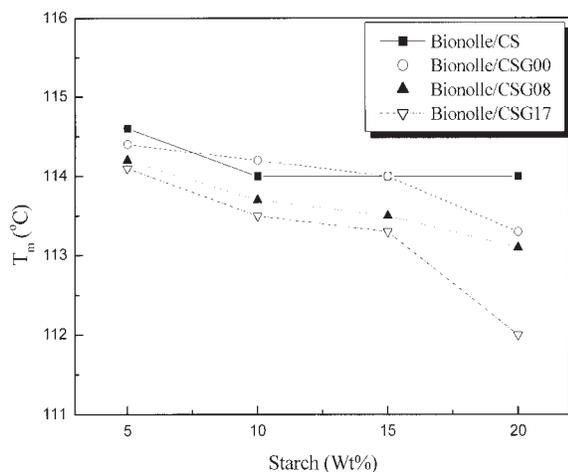


Figure 2 Effect of the starch content on T_m of the Bionolle/starch blends.

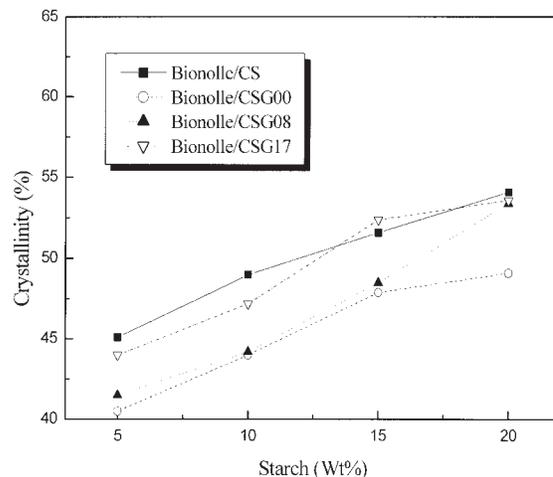


Figure 3 Effect of the starch content on the crystallinity of the Bionolle/starch blends.

nized starch could be depicted by a disruption of hydrogen bonding within the starch molecules. This would result in large deformation (D) because of the reduction of the viscosity ratio (λ) of the dispersed starch and Bionolle matrix according to the following relationship proposed by Taylor:²⁴

$$D = \frac{\mu\gamma R}{\Gamma} - \frac{19\lambda + 16}{16(\lambda + 1)} \quad (2)$$

where μ is the viscosity of the matrix, γ is the shear rate, R is the radius of the droplet (dispersed phase), and Γ is the surface tension.

Good mixing also implied high interaction between the dispersed phase and matrix. The change in the enthalpy of mixing appeared to be slightly smaller than the change in the entropy of mixing, and this accounted for the marginal reduction of T_m .

The crystallinity determined from the DSC measurements is shown in Figure 3. Basically, a large increase in crystallinity occurred with the addition of starch. Perhaps starch played a nucleating role in the blend.⁸ For the same amount of starch, the crystallinity of the untreated starch was slightly larger than that of the gelatinized starch. This might be attributed to the inherent filler nature of the untreated starch. As for the effect of the gelatinized starch, the crystallinity increased with an increasing degree of gelatinization because better mixing was achieved.

To further elucidate the effect of added starch on T_g of Bionolle/starch blends, we show in Figure 4 typical graphs recorded with a dynamical mechanical analyzer for Bionolle/CSG08 with various starch contents. The peak values of the loss modulus were used as an indication of T_g .²⁵ All the measured values were slightly lower than T_g of pristine Bionolle (-32.5°C). The T_g values of the other blends with various starch

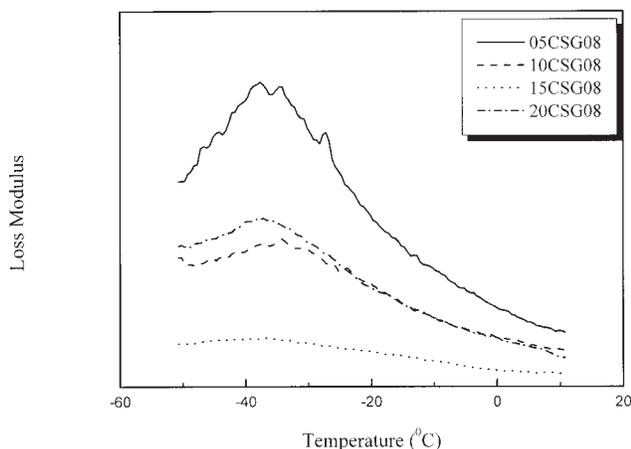


Figure 4 Typical curves of the loss modulus recorded with a dynamic mechanical analyzer for the determination of the T_g values of the Bionolle/CSG08 blends with various starch contents.

contents under different degrees of gelatinization are illustrated in Figure 5. The trend of a decrease in T_g with the starch level is similar to that for T_m . T_g for the blend of Bionolle and the untreated starch (Bionolle/CS) was slightly higher than that of the blend of Bionolle and the water-gelatinized starch (Bionolle/CSG00). As mentioned earlier, the added untreated starch tended to disrupt the intermolecular hydrogen bonding within the Bionolle matrix, and this caused the entropy of mixing to increase. This increase reduced T_g from a thermodynamic point of view. When a certain amount of water-gelatinized starch was incorporated, better mixing was achieved, and this further increased the flexibility of Bionolle and reduced its T_g .

As a matter of fact, water gelatinization is not as efficient as water/glycerol gelatinization because the

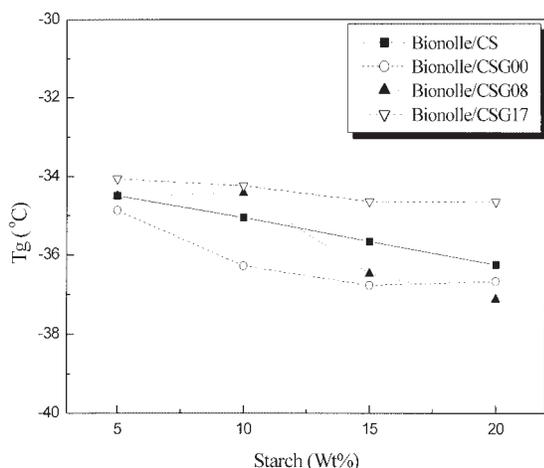


Figure 5 Effect of the starch content on T_g of the Bionolle/starch blends.

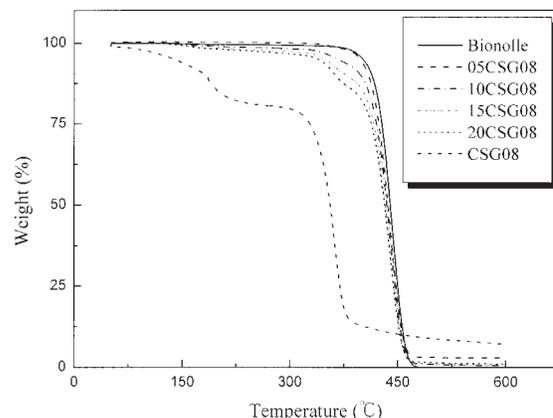


Figure 6 TGA curves of Bionolle, gelatinized starch, and Bionolle/CSG08 with various starch contents.

former may suffer a chance of re-formation of hydrogen bonding after the gelatinization of starch.⁸ Thus, further gelatinization with water/glycerol was carried out. It appeared to further increase the goodness of the mixing and to render specific hydrogen-bonding interactions between Bionolle and the gelatinized starch. Eventually, this effect reduced the molecular mobility of Bionolle, which in turn caused an increase in T_g . This was demonstrated by an increase in T_g for Bionolle/CSG17 in comparison with the T_g values of Bionolle/CSG08 and Bionolle/CSG00. Apparently, the phenomena were different from that seen for T_m . The competition between the entropy of mixing and the enthalpy of mixing governed to a different degree the variations of T_m and T_g .

The thermal stability of the blends containing various amounts of the gelatinized starch is illustrated in Figure 6 with TGA. A representative Bionolle/CSG08 blend, pristine Bionolle, and CSG08 were evaluated for comparison. As expected, Bionolle showed thermal stability up to about 400°C with 5% weight loss. For the blends containing a certain amount of the gelatinized starch, the thermal stability remained to a certain degree but continued to decrease, and the temperature at 5% weight loss was approximately 350°C. This was ascribed to the relatively low heat stability of starch. The initial loss of the gelatinized starch (CSG08) indicated that a small portion of water remained after the gelatinization. Interestingly, the ash concentration for the gelatinized starch was kept at approximately 7% up to 600°C. This might be associated with its chemical structure, which is prone to form a thermal resistance layer and, therefore, yield a high degree of residual carbon.

Mechanical properties

Figure 7 shows the effect of the starch content on the tensile strength of the blends. As the starch content

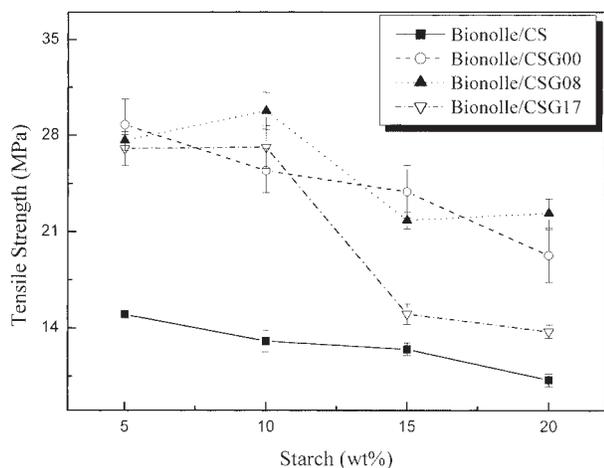


Figure 7 Effect of the starch content on the tensile strength of the Bionolle/starch blends.

increased, the tensile strength of the blends generally decreased. These findings agree with the literature.^{8,22} For Bionolle blended with untreated starch (Bionolle/CS), the tensile strength progressively decreased from 15 ± 0.1 MPa to 10.2 ± 0.5 MPa. To improve the mixing of Bionolle and starch, we used a water/glycerol gelatinization approach for starch. A significant increase in the tensile strength, up to 2 times, was observed. The maximum value was 28.8 ± 1.9 MPa for the Bionolle/CSG00 blend and was close to the tensile strength of unmodified Bionolle (29.1 ± 1.8 MPa). Apparently, the gelatinization of starch was efficiently achieved, and it promoted the compatibility of starch with Bionolle. No clear difference in the gelatinization degree with respect to the tensile strength appeared. However, at a higher dosage of glycerol (Table II), for Bionolle/CSG17, the tensile strength tended to decrease marginally, perhaps because of some plasticizing effect.

The elongation at break of the Bionolle/starch blends is shown in Figure 8. Basically, the elongation at break remained largely unchanged with the addition of starch for all the prepared blends, except for Bionolle/CSG17. This might be attributed to a relatively high concentration of glycerol in the formulations of the gelatinized starch. The plasticizing effect perhaps reduced the elongation at break to some degree. However, the values were still higher than those of Bionolle blended with untreated starch. At the optimum loading of glycerol for Bionolle/CSG08, the elongation at break reached the highest value of approximately $119.9 \pm 0.5\%$, which was close to that of unmodified Bionolle ($126.5 \pm 1.8\%$). Again, a suitable degree of gelatinization of starch was critical for achieving the best performance. The reasons for these observations have already been examined in the discussion of the tensile properties.

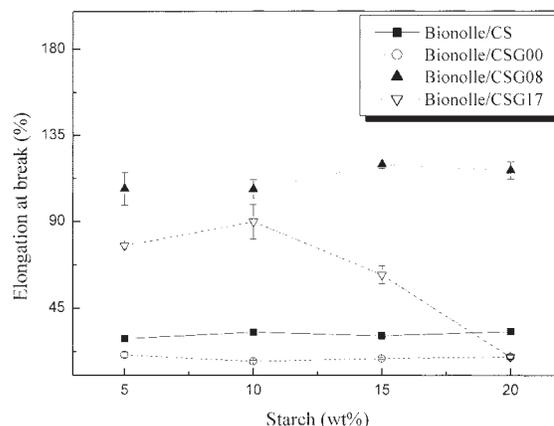


Figure 8 Effect of the starch content on the elongation at break of the Bionolle/starch blends.

To determine the importance of gelatinization on the mechanical properties of the Bionolle/starch blends, we performed a tear test to measure G_c (tear strength). Figure 9 depicts the effect of the starch content on the tear strength of the blends. As shown by the tensile properties, the tear strength progressively decreased with increasing starch content. For Bionolle blended with the untreated starch, the tear strength decreased from 16.5 ± 0.3 to 13.0 ± 0.4 kJ/m². As the untreated starch was replaced with the gelatinized starch in the blends, the tear strength increased up to 1.5 times. Apparently, the gelatinization of starch was beneficial for improving the strength of the blends, and this was attributed to better mixing and high interaction for the blends. However, a higher glycerol content reduced the tear strength of the blends because of a plasticizing effect mentioned earlier. This was manifested in the Bionolle/CSG17 blend.

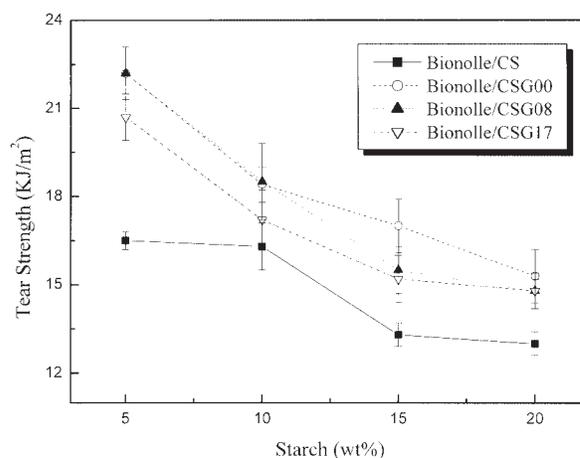


Figure 9 Effect of the starch content on the tear strength of the Bionolle/starch blends.

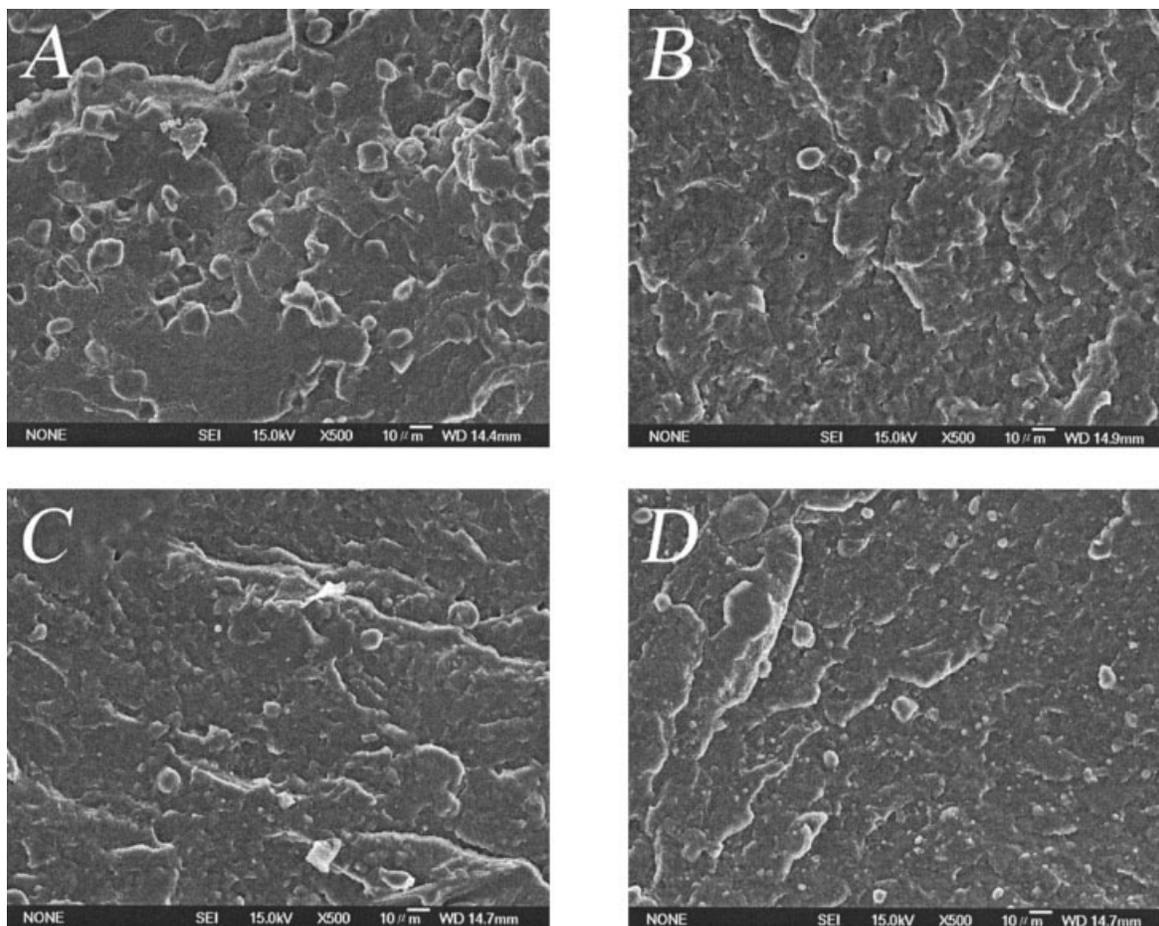


Figure 10 SEM micrographs of the Bionolle/starch blends containing 20 wt % starch: (A) 20CS, (B) 20CSG00, (C) 20CSG08, and (D) 20CSG17.

In all cases of this study, the mechanical properties of Bionolle blended with the gelatinized starch were greater than those of Bionolle blended with the untreated starch. The following morphological investigation provides evidence in support of these findings. It would be interesting to determine whether an aging effect on the mechanical and thermal properties could occur during prolonged storage. Moreover, hydrolysis might degrade the properties of samples because of a reduction of the polyester chains. Further study is needed to consider this effect, especially with higher starch contents. This relatively low-cost approach, rather than a high-cost compatibilizer approach, might provide an alternative way of improving the performance of biodegradable blends.

Morphological observations

SEM micrographs of Bionolle/starch blends containing 20 wt % starch are shown in Figure 10. In all cases, the starch granule was approximately 10 μm in size. Figure 10(A) presents Bionolle blended with the untreated starch. Figure 10(B–D) shows Bionolle blended with

starch gelatinized with various formulations. Some visual cavities can be observed in Figure 10(A), and they reflect a lack of interaction between Bionolle and the untreated starch. This confirms the previous findings concerning the mechanical properties. In particular, the tensile strength was more sensitive to microcracking, and so the blends with the untreated starch had a low strength. As the untreated starch was replaced with the gelatinized starch, the mechanical properties improved to some degree, which depended on the gelatinization formulations and degrees. Fewer microcavities were found in Bionolle blended with gelatinized starch [Fig. 10(B–D)], and this implied that a certain interaction was achieved in the mixtures. Unfortunately, no clear difference could be made in terms of the interaction for those blends. However, these results did provide supporting evidence for the differences in the mechanical properties due to the untreated and gelatinized starch.

CONCLUSIONS

The vital differences between the use of untreated starch and gelatinized starch for blends with Bionolle

were thoroughly examined. T_m slightly decreased with increasing dosages of untreated and gelatinized starch. The added starch perhaps tended to disrupt the intermolecular hydrogen bonding within the Bionolle matrix. For the same amount of added starch, as the glycerol content increased, the goodness of mixing improved because of the better compatibility between the gelatinized starch and Bionolle, which caused a further decrease in T_m . On the other hand, a large increase in the crystallinity occurred with the addition of starch. Perhaps starch played a nucleating role in the blends. The trend of a decrease in T_g with the starch level was similar to the trend for T_m . With the same starch content, T_g for a blend of Bionolle and the untreated starch (Bionolle/CS) was slightly higher than that of a blend of Bionolle and the water-gelatinized starch (Bionolle/CSG00). In addition, an increase in T_g for Bionolle/CSG17, in comparison with the T_g values of Bionolle/CSG08 and Bionolle/CSG00, was observed. The results are probably related to the different degrees of interaction between Bionolle and the gelatinized starch. For the blends containing a certain amount of gelatinized starch, the thermal stability remained to a certain degree but continued to decrease, and the temperature at 5% weight loss was approximately 350°C. This was ascribed to the relatively low heat stability of starch. As for the mechanical properties, a significant increase in the tensile strength, up to 2 times, was observed when the untreated starch was replaced with the gelatinized starch in the blend. Apparently, a gelatinization of starch was efficiently achieved and promoted its compatibility with Bionolle. At the optimum loading of glycerol for Bionolle/CSG08, the elongation at break reached its highest value, approximately $119.9 \pm 0.5\%$, which was close to that of unmodified Bionolle ($126.5 \pm 1.8\%$). Again, a suitable degree of gelatinization of starch was critical for achieving the best performance. Similarly, the tear strength increased up to 1.5 times when the gelatinized starch was employed. In all cases of this study, the mechanical properties of Bionolle blended with the gelatinized starch were greater than those of Bionolle blended with the untreated starch. The morphological investigation provided evidence in support of these findings. This relatively low-cost ge-

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Grants-in-aid from Taiwan, Republic of China government under the contract number of NSC (91-2621-Z-197-002) are greatly acknowledged. Partial financial support from Plastics Industry Development Center are appreciated.

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