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## Processing, performance and biodegradability of a thermoplastic aliphatic polyester/starch system

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### Abstract

Composites of a biodegradable thermoplastic aliphatic polyester, polybutylene succinate adipate (PBSA), with granular corn starch were investigated for processability, mechanical and thermal properties, and biodegradability. The PBSA/starch films were prepared with starch contents of 5%–30% by weight and processed by blown film extrusion. Increasing the starch content led to an increase in modulus and decreases in tensile strength, elongation to break and toughness. The rate of biodegradation in soil, as measured by respirometry, increased significantly as the starch content was increased to 20% and then plateaued. Scanning electron microscopy revealed that the starch granules were embedded in the continuous-phase PBSA and that starch promotes the biodegradation of PBSA. Gel permeation chromatography indicated a molecular weight decrease for the PBSA after soil exposure and confirmed that biodegradation was enhanced by the presence of starch. The results demonstrated that the biodegradable PBSA/starch system has mechanical properties useful for blown film applications. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Biodegradable film; Starch; Polybutylene succinate

### 1. Introduction

Poly(butylene succinate adipate) (PBSA) is a commercially available, aliphatic thermoplastic polyester with many interesting properties, including biodegradability, melt processability, thermal and chemical resistance [1–6]. PBSA is synthesized by the reaction of glycols with aliphatic dicarboxylic acids and is available in molecular weights ranging from 10 000 to 100 000 g/mol for use in a variety of applications. Earlier studies have demonstrated that PBSA, in the form of films and molded objects, exhibits significant biodegradation within 2 months of treatment in soil, water with activated sludge, and sea water [2,6]. Despite these many attractive properties; however, the commercialization of PBSA has been slowed by its relatively high cost. Therefore, our research focuses on the addition of low cost, biodegradable corn starch to PBSA as a route to generating biodegradable composites

with improved cost competitiveness, while maintaining good mechanical properties and processability.

Starch is composed primarily of amylose, a linear polymer of  $\alpha$ -1,4-linked glucose units, and amylopectin, a highly branched polymer of  $\alpha$ -1,4-linked chains connected by 1,6-linkages. (Fig. 1(b)) Whereas native corn starch contains approximately 25% amylose, the amylose content of starch can range as high as 85% or as low as 0% – depending on its source. With the application of heat and shear in the presence of water, the granular structure of starch can be removed and the starch can be processed as a thermoplastic [7]. A number of studies have been carried out on starch/polymer blends for applications such as packaging film and agricultural mulch [8–22]. Limited studies have been performed with the PBSA and starch [23, 24]. One study concerns our initial results of processing the PBSA with starch and the other study uses a formulation consisting of starch plasticized with 23% ethylene glycol and then blended with 70% PBSA to obtain water resistant films and blow molded pots for seedlings [24]. Pure PBSA film has been constantly studied and recently considered for agricultural film applications and bags for compost [25].

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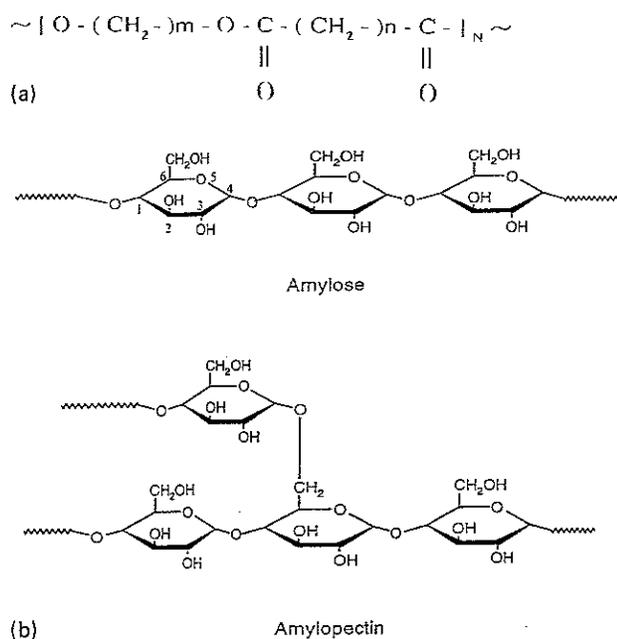


Fig. 1. Structure of (a) PBSA and (b) starch.

Starch has also been used in its granular form as a rigid filler in polymeric systems [26–34]. As is the case with other rigid filler particles, the addition of starch generally results in an increase in stiffness with corresponding decrease in tensile strength and elongation to break. Mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and the degree of adhesion of the filler to the polymeric matrix. Willett [26] evaluated the mechanical properties of low-density polyethylene/starch composites as a function of starch content and granule size; a compatibilizer was included to improve adhesion between the starch granules and the polymer matrix. Elongation to break and tensile strength were found to agree with theoretical predictions. Schroeter [27] et al. studied the effects of starch as a filler in polycaprolactone and epoxy resin. The modulus of the polycaprolactone/starch system increased with starch content, while no such effect was seen in the epoxy/starch system [27]. Endres [28] et al. have studied blends of biodegradable polymers, including polycaprolactone and cellulose acetate, with potato, wheat, and corn starch, with starch contents of up to 40%. Theoretical predictions indicated that the mechanical properties of these blends would be somewhat improved by the addition of starch granules. It was demonstrated that insufficient mixing as well as the size of the starch granules can have a significant influence on the interfacial quality and therefore on the mechanical properties.

One potential advantage of starch as an additive is enhanced biodegradability of the polymer. Indeed, Ramsey [29] et al. found that the biodegradability of solvent cast films of poly-(hydroxy butyrate co-hydroxy valerate) was enhanced by the incorporation of starch at a content of 50% by weight. The addition of starch also resulted in a decrease

in tensile strength and an increase in modulus. Evangelista et al. [30] studied linear low density polyethylene with native and modified (octenyl succinate) corn starch. Samples containing native cornstarch exhibited faster rates of biodegradation than samples containing modified corn starch, with the rate of biodegradation controlled by the degree of accessibility of the granules.

Here, we report on the processability, mechanical and thermal properties, and biodegradability of PBSA/starch composite films containing up to 30% cornstarch by weight. We began by investigating the processing conditions for blown film extrusion. We then characterized the mechanical and thermal properties of the films and, finally, assessed their biodegradability in soil.

## 2. Experimental

### 2.1. Materials

PBSA (trade name Bionolle), blown film grade 3001 (Fig. 1) and a 50/50 masterbatch of 3001 and granular corn (maize) starch were obtained as pellets from Showa Highpolymer Co., Ltd. The pure PBSA was processed in its original pellet form and the PBSA/starch formulations were first cryogenically milled into powders and mixed before processing. A Purnell International Type FM 10/4-4 Henschel mixer was used to mix powdered PBSA 3001 with powdered PBSA/starch masterbatch at 200–1700 rpm for several minutes. The final (test) blends contained 5%, 10%, 15%, 20%, 25% and 30% by weight of starch. The molecular weight of the PBSA is 293 000 g/mol as determined by gel permeation chromatography (GPC).

### 2.2. Extrusion blown film processing

All PBSA and PBSA/starch samples were dried at 55°C or 70°C for several hours before processing. These drying temperatures were chosen based on the recommendations from Showa Highpolymer. The mixed powders were processed into blown films using a Brabender single screw extruder with four heated zones and a blown film die. The screw diameter was 22 mm; the blown film die had an interior diameter of 2.54 cm and a gap size of 0.05 cm. The screw speed was 40 rpm; processing temperatures in zones 1 through 4 were 160°C, 165°C, 175°C, and 180°C, respectively. During each run, the radius of the blown film varied from approximately 80–100 mm. Consequently, the film thickness varied from .07–.18 mm. The blow-up ratios were maintained at 3 : 1 and 4 : 1.

### 2.3. Methods of analysis

#### 2.3.1. Capillary rheometry

An Instron Model 3213 Capillary Rheometer with Rheosoft software was used to perform rheological

measurements at various shear rates. The capillary was circular, with a length/diameter ratio of 40 (i.e. 5.080 cm length, 0.126 cm inner diameter). For each trial, melt was continuously extruded until the force reached a constant value. The samples were tested in the temperature range of 120°–180°C (in increments of 10°C) over identical shear rate profiles. The Rabinowitsch correction method was used to account for shear rate at the capillary wall. All samples were dried before testing.

### 2.3.2. Mechanical testing

Tensile properties were measured using an Instron Model 4204 tensile tester with a 91 kg load cell and a crosshead speed of 12.7 mm/min. Rectangular samples (25.4 mm wide) were used, with a gauge length of 25.4 mm. For each sample, 10 replicates of the films in the extrusion direction were tested at each condition. Most films were conditioned at three relative humidities ( $32 \pm 5$ ,  $56 \pm 5$ , or  $75 \pm 5\%$ rh) for at least 14 days; other samples were oven-dried at 55°C for 24 h. Each tensile test was performed immediately after removing the film from the humidity chamber or oven.

### 2.3.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of the pure PBSA and PBSA/starch blends was carried out with a Seiko DMS 210 instrument with the following parameters: frequency = 1 Hz; scan rate = 4°C/min; temperature range = –150°C to 130°C. Films were tested in the tension mode. Before the experiment, films were dried at 100°C in the chamber for 15 min to remove any residual bulk water. The dynamic storage modulus ( $E'$ ), loss modulus ( $E''$ ), and mechanical loss tangent ( $\tan \delta = E''/E'$ ) were measured.

### 2.3.4. Biodegradation testing

Polymer mineralization (i.e. conversion of polymer-C to CO<sub>2</sub>) was measured using a respirometric method based on that described by Bartha and Pramer [35]. Film samples totalling ca. 250 mg polymer-C (i.e. 450–480 mg total weight depending on the starch content) were cut into 10 mm × 10 mm pieces and buried in test reactors (250 ml biometer flasks; Belco Glass Inc., Vineland, NJ) containing 50 g of a standard soil mix (1:1:0.1 w/w/w mix of potting soil, sand, and composted manure; pH  $7.0 \pm 0.5$ ) maintained at  $60\% \pm 5\%$  water-holding capacity and incubated in a controlled environment chamber at 30°C. Immediately prior to initiating the tests, the soil was supplemented with inoculum ( $10.0 \pm 0.4$  mg inoculum g<sup>-1</sup> soil; *Recycle® Compost Maker – formulated for grass clippings*; Ringer Corp., Minneapolis, MN) and 1.0 ml of a combined macro-/micro-nutrient solution. Carbon dioxide produced during the biodegradation process was trapped in 20 ml of 0.40 M NaOH added to the side-arm portion of the biometer flasks. The CO<sub>2</sub> traps were changed at 24–168 h intervals and a 4 ml aliquot of the NaOH from each trap was titrated with 0.10 M HCl. Daily and cumulative CO<sub>2</sub> production

(total and net) and percent mineralization were calculated relative to a control flask (without added polymer films).

### 2.3.5. Scanning electron microscopy

Electron micrographs were obtained on samples collected before and after biodegradation testing in soil. Samples were cut and, if there was visible soil adhering to the film, carefully cleaned using a soft bristled brush. The samples were sputter coated with AuPd in a Balzers SCD040 sputter coater to impart conductivity. The surface of each sample was examined with an Amray 1000A at 10 kV and a working distance of 12 mm, as well as on a Zeiss CSM 950 SEM at 10 kV and a working distance of 16–18 mm. Polaroid Type 52 film was used to record the images.

### 2.3.6. Gel permeation chromatography

Molecular weights and polydispersities of the PBSA and PBSA/starch blends were determined by GPC using a Waters Model 510 pump, Model 410 refractive index detector, and Model 717 plus autosampler with ultrastayragel columns of 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> and 10<sup>6</sup> Å. Samples were eluted using chloroform at a flow rate of 1.0 ml/min. Solutions were filtered through a 0.45 µm cellulose acetate syringe filter and samples (100 µl) were injected at a concentration of 0.5% (w/v). PBSA solutions of varying concentration were used to prepare a calibration curve of molecular weight. Number-average ( $M_n$ ), weight average ( $M_w$ ), and peak ( $M_p$ ) molecular weights were calculated using the Waters Chromatography Millennium software (version 2.15). Note, however, that because of the insolubility of starch in chloroform, only the PBSA component of the blends was detected in the chromatograms.

### 2.3.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were made with a Perkin-Elmer DSC-7 with a liquid nitrogen cooling accessory. A scan rate of 10°C/min was used in the temperature range –40°C to 130°C. The enthalpy of melting of PBSA for the films was determined both before and after biodegradation testing.

### 2.3.8. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to determine if there was any water in the samples. A TA Instruments Model 2950 using a scan rate of 10°C/min.

## 3. Results and discussion

### 3.1. Processing

Capillary rheometry studies in the temperature range of 120°C–140°C were performed for the PBSA and PBSA/starch filled systems to determine optimal blown film processing conditions. There is a significant change in the viscosity with temperature. The temperature of processing

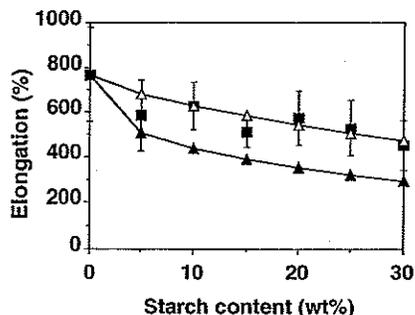


Fig. 2. Elongation to break of the PBSA/starch films as a function of starch content. (■) experimentally measured values and (▲) predicted values are for the extreme cases of perfect adhesion and (△) no adhesion between the filler and the polymer matrix.

was chosen to be in the temperature range of this data. The trends and data are explained elsewhere.

Problems with melt strength and processing arose at starch contents > 30%; consequently, the films used in the mechanical, thermal, and biodegradation testing phases of this study were processed containing a maximum of 30% starch. The selected processing temperatures were not significantly altered for the homopolymer and starch-based systems; i.e. temperatures were controlled to within a few degrees depending on the amount of starch. Based on SEM analyses, it was determined that the starch remained as granules throughout the processing into films.

### 3.2. Mechanical properties

The stress–strain behavior of the PBSA 3001 and PBSA/starch films is similar to that of polypropylene; i.e. after a yield point, the polymer begins to neck. The neck was more transparent than the unnecked material and, in general, necking was much more pronounced in the 100% PBSA films than in the PBSA/starch films. The neck did not propagate continuously, but in sudden jumps, producing a pattern of horizontal stripes (approximately 1 mm wide) along the necked region. Accordingly, oscillations occurred in the measured stress, as evidenced by the apparent noise in the stress/strain curves. Strain hardening began to take place after the yield point, and continued until failure. The broken

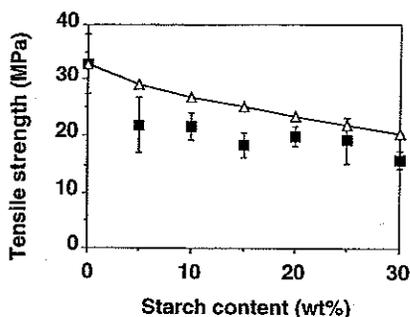


Fig. 3. Measured (■) and theoretical (△) tensile strengths for the PBSA 3001 and PBSA/starch systems.

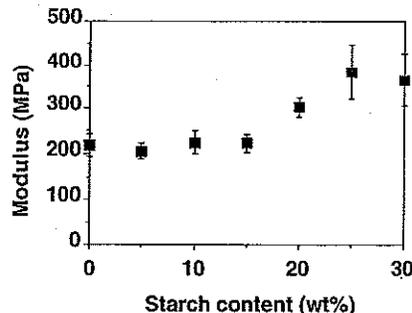


Fig. 4. Modulus of the PBSA/starch systems as a function of the starch content.

samples showed fibrillation around the break, behavior indicative of strain-induced crystallization.

Mechanical properties were measured on films that were dried at 55°C and also on films that were equilibrated at relative humidities between 30% and 70%. Conditioning at various humidities had no apparent effect on mechanical properties, as had been previously found by Willett [33]. This trend is in contrast to systems containing gelatinized starch, in which moisture content has a large effect on mechanical properties [7,24]. The following discussion of the mechanical properties of the PBSA/starch system is based on the results of the films dried at 55°C.

Elongation to break (Fig. 2) decreased with increasing starch content, as expected. Small amounts of starch significantly altered the elongation; however, the negative impact of starch additions on elongation appeared to plateau at the higher starch concentrations. Predicted values for the extreme cases of (i) perfect adhesion and (ii) no adhesion between the filler and the polymer matrix also are included in Fig. 2. The equations used are [37]

$$\epsilon'/\epsilon = 1/(1 - \phi_F^{1/3}) \quad (1)$$

for perfect adhesion, and

$$\epsilon'/\epsilon = 1(1 - \phi_F^{2/3}) \quad (2)$$

for poor adhesion, where  $\epsilon'$  and  $\epsilon$  are the elongation to break (defined as  $(L - L_0)/L_0$ ) of the unfilled and filled systems, respectively, and  $\phi_F$  is the volume fraction of filler [40]. The experimental results agree approximately with Eq. (2), suggesting that there is a poor adhesion between the starch granules and the PBSA matrix.

This interpretation is consistent with the tensile strength results. Fig. 3 shows the experimental results along with the theoretical values predicted by Nielsen [37] for the case of poor adhesion between the filler and the matrix:

$$\sigma = \sigma_0(1 - \phi_F^{2/3})S, \quad (3)$$

where  $\sigma$  and  $\sigma_0$  are the tensile strengths of the filled and unfilled systems respectively,  $\phi_F$  is the volume fraction of filler, and  $S$  is a stress concentration function. For simplicity, we assume no stress concentration ( $S = 1$ ). As expected, the

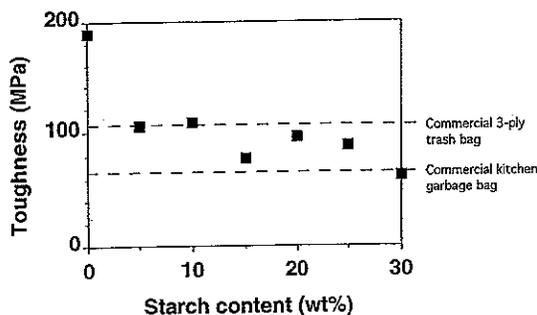


Fig. 5. Toughness of the PBSA/starch systems as a function of the starch content.

addition of starch to the PBSA system results in a decrease in the tensile strength. However, the tensile strength does not vary significantly as the starch content is increased from 5% to 30%. The measured values are slightly lower than the theoretical values, particularly for starch contents between 5% and 15%.

The modulus (Fig. 4) increases at the higher starch contents, with the maximum value (380 MPa) occurring at a starch content of 25%–30%. Interestingly, at starch contents less than 20% the modulus of the blends is essentially the same as that of pure PBSA. Nevertheless, the overall increase in modulus with filler content is typical for filled polymeric systems.

The effect of starch additions on toughness (defined as the area under the stress/strain curve) is illustrated in Fig. 5. The addition of 5%–30% starch results in approximately a 50% decrease in toughness. This is not unexpected; however, the toughness values for films containing up to 25% starch are still comparable to those of the commercially available trash bags, suggesting that the starch/PBSA system may be suitable for such an application. PBSA/polylactic acid blends containing up to 50% PBSA, which have been considered for the trash bag applications [38], have exhibited mechanical properties comparable to the starch/PBSA systems in the current study.

Representative DMA data ( $E''$  vs. temperature (Fig. 6(a));  $E'$  vs. temperature (Fig. 6(b)) for PBSA 3001 and PBSA 3001/starch are shown in Fig. 6(a) and (b). There is a broad  $E''$  peak in the range of  $-70^{\circ}\text{C}$ – $-20^{\circ}\text{C}$  with a peak maximum at approximately  $-55^{\circ}\text{C}$ , which corresponds to the glass transition temperature of the PBSA. There was no significant change in the  $T_g$  for PBSA in any of the PBSA/starch blends. There are no transitions from starch visible in the DMA data. Melting of the PBSA is represented by a dramatic decrease in modulus at approximately  $85^{\circ}\text{C}$ . The value for the storage modulus (Fig. 6(b)) for the PBSA is slightly lower than the PBSA/starch systems containing 20% and 30% of starch, indicating increased rigidity in the PBSA/starch system. Vaidya [10] studied the effect of various parameters on DMA and found the  $T_g$  of starch in an 80/20 starch/ethylene propylene-*g*-maleic anhydride blend to be in the same temperature range as the melting of PBSA.

However, the  $T_g$  of starch can vary significantly with the amount of moisture in the system. Thus, noting that the PBSA/starch filled materials have low moisture contents, as observed from TGA, we would expect the  $T_g$  of starch to be much higher than the melting of PBSA.

### 3.3. Biodegradation

Despite the considerable amount of work that has been carried out with starch filled polymers, there remains little information regarding the environmental biodegradability of these materials. For the PBSA and PBSA/starch systems, respirometric tests were carried out to document polymer biodegradation in a soil environment. Unlike weight loss, which reflects structural changes in the film,  $\text{CO}_2$  evolution provides an indicator of the ultimate biodegradability (i.e. mineralization) of the polymer films. Test exposures were carried out until cumulative net mineralization reached approximately 70%, at which point the exposures were terminated and any residual material recovered. The time required to reach this pre-determined endpoint varied with the starch content of the films – ranging from about 60 days for the films with the highest starch contents to about one year for the pure PBSA 3001 (Fig. 7(a) and (b)). These data clearly indicates that the biodegradability of the PBSA component of the blends was enhanced significantly by incorporation of the starch filler. For example, whereas pure PBSA 3001 had a half-life of 231 days, the incorporation of only 5% starch in the blend yielded films with a half-life of only 80 days (Table 1). Increasing the starch content of the blends to as much as 20% resulted in enhanced rates of mineralization and, hence, significant decreases in polymer half-life (Table 2). However, increasing the starch content of the blend to 25% or 30% yielded no further enhancement in polymer biodegradability (i.e. cumulative net mineralization,  $r_{\text{max}}$ , or  $t_{1/2}$ ). Indeed, after about 25 days, net mineralization curves for the films containing 20%–30% starch were essentially the same as the curve obtained for the positive control (i.e. cellophane). It should be noted that the current FDA test protocols state that an organic compound can be presumed “biodegradable” if more than 50% of its carbon content is converted to  $\text{CO}_2$  during the test exposure [39]. Thus, based on this criterion, the PBSA 3001 can be considered totally biodegradable.

Electron micrographs of the pure PBSA 3001 film taken before and after the soil test exposures are presented in Fig. 8(a)–(d). At time zero (i.e. prior to the test exposure) the pure PBSA film exhibited a relatively smooth surface marked by striations (Fig. 8(a)), which presumably were a result of film processing. However, the film was already beginning to show signs of degradation after a soil test exposure of only 28 days (Fig. 8(b)); i.e. a number of surface irregularities, as well as a few small holes, were clearly evident in the film. After six months in the soil (net mineralization  $\approx 43\%$ ), there was significant fragmentation of the surface layers and large holes were clearly evident

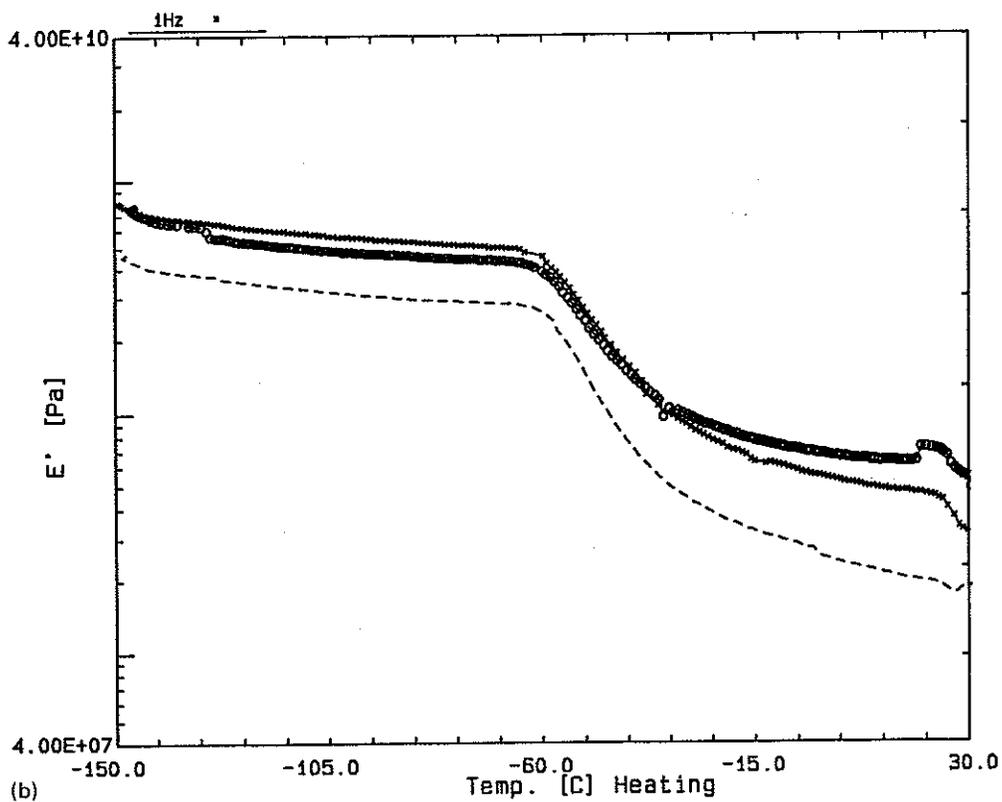
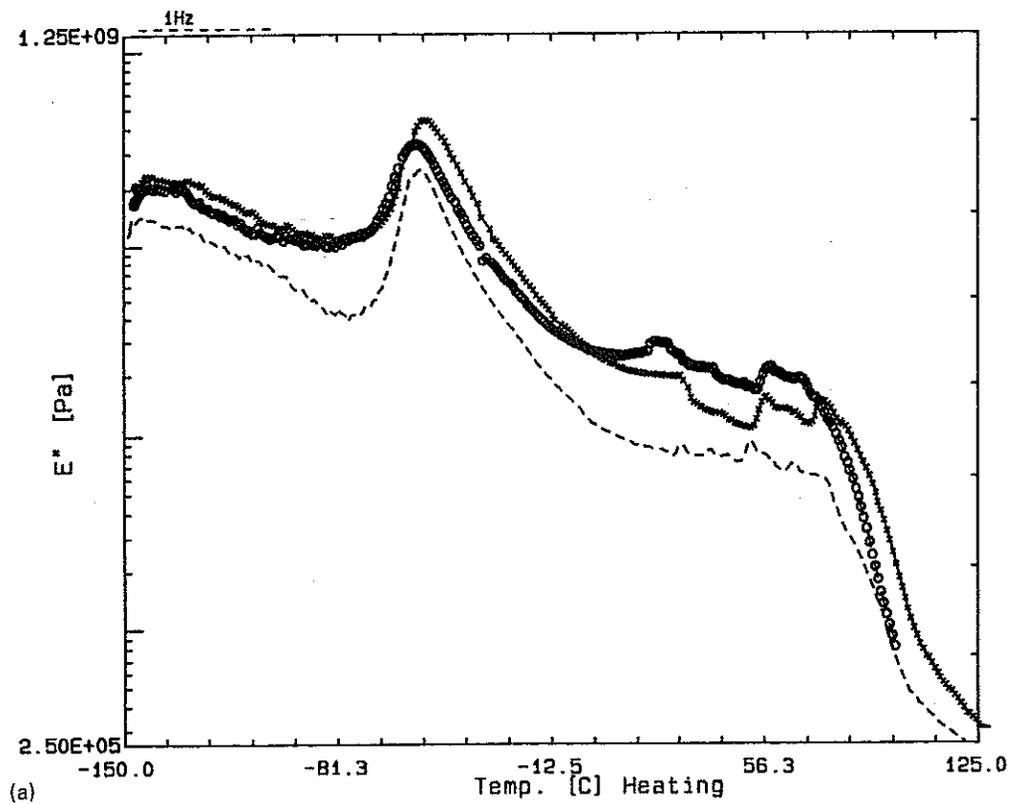


Fig. 6. DMA of the PBSA 3001 and PBSA/starch systems. (a)  $E''$  vs. temperature (---) 100/0, (x) 70/30 and (o) 80/20; (b)  $E'$  vs. temperature (---) 100/0, (x) 70/30 and (o) 80/20.

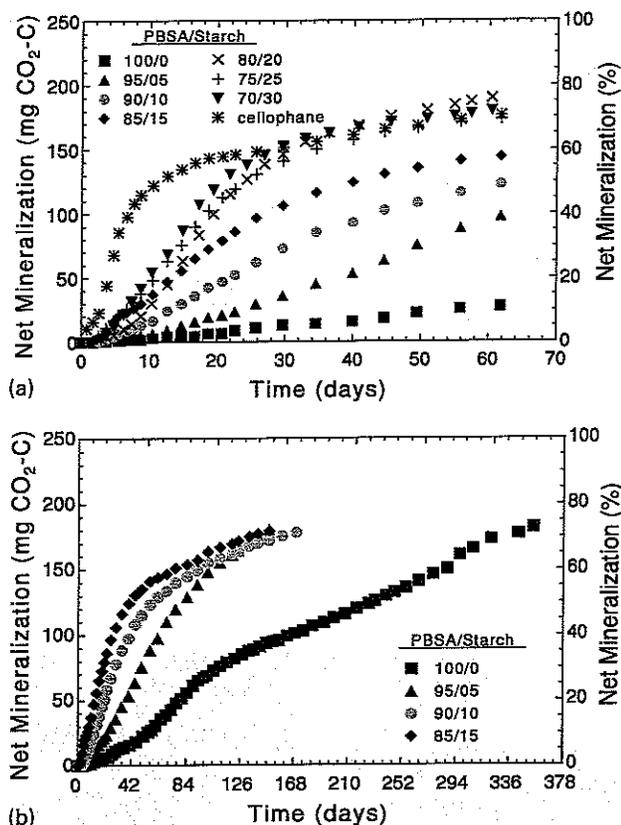


Fig. 7. Net mineralization of the PBSA 3001 and PBSA/starch systems in soil at 30°C and a moisture content of 60% WHC: (a) soil test exposure = 0–62 days; (b) test exposure = 148–368 days.

(Fig. 8(c)). Only a few small fragments of residual film could be recovered from the soil after a test exposure of about one year ( $t = 368$  days; net mineralization  $\approx 73\%$ ); however, the SEM photographs of these fragments revealed

that they were heavily pitted and marred by large fissures (Fig. 8(d)). Whereas the photographic evidence suggests that degradation of the PBSA 3001 occurred gradually over the entire surface, we postulated that starch added to the PBSA would be selectively hydrolyzed and that this would create localized micropores in the film, giving rise to an increase in the surface area and a concomitant increase in the rate of degradation.

Electron micrographs of the 90/10 PBSA/starch blend are presented in Fig. 9. Whereas starch granules are clearly visible in the undegraded film (Fig. 9(a)), they are almost totally absent from the film exposed to soil for 28 days (Fig. 9(b)). Indeed, after 28 days there were numerous holes in the film corresponding in size to that of the starch granules (i.e. 20–50  $\mu\text{m}$ ). Films exposed to the soil for 110 days exhibited numerous interconnecting holes and fractures throughout the surface, with fractures radiating from the holes that once contained starch granules (Fig. 9(c)). As the starch content increases in the system, more starch granules are viewed on the surface. High magnification (2500 $\times$ ) SEM photographs of the 80/20 PBSA/starch system are presented in Fig. 10. Whereas the undegraded film is characterized by a contiguous surface incorporating the starch granules (Fig. 10(a)), films exposed to the soil test environment for only seven days exhibit voids left from the preferential degradation of the starch granules. Further, fractures are clearly visible both on the surface and in the holes themselves. Clearly, the photographic evidence shows that the starch is degraded preferentially and that incorporation of the starch filler enhances degradation of the PBSA component of the films.

Gel permeation chromatographs (GPC) for both the original (undegraded) and degraded PBSA 3001 films are presented in Fig. 11. It is interesting to note that samples

Table 1  
Aerobic biodegradability of PBSA 3001 and PBSA/starch blends in soil at 30°C and a moisture content of 60% WHC. Films were extrusion blown using a Brabender single screw extruder with four heated zones and a blown film die

PBSA/starch (wt/wt)	Exposure time (days)	Net mineralization			$r_{\text{max}}^a$ (mg CO <sub>2</sub> -C d <sup>-1</sup> )	$t_{1/2}^b$ (days)
		(mg CO <sub>2</sub> -C d <sup>-1</sup> )	(%)	RBI <sup>c</sup>		
100/0	60	30.68	12.3	0.17	1.02	231
	368	182.10	72.8	1.03	(0.41) <sup>d</sup>	
95/5	62	97.50	39.0	0.55	1.85	80
	148	180.32	72.1	1.02		
90/10	60	122.66	49.0	0.70	3.08	59
	168	177.91	71.2	1.01		
85/15	62	143.87	57.5	0.82	4.10	40
	148	179.49	71.8	1.02		
80/20	60	189.67	75.9	1.08	7.49	24
75/25	62	173.41	69.4	0.98	6.56	24
70/30	60	179.70	71.9	1.02	7.40	20
Cellophane	62	176.26	70.5	—	15.67	11

<sup>a</sup> Relative biodegradation index = (mg CO<sub>2</sub>-C from the TEST SAMPLE  $\div$  mg CO<sub>2</sub>-C from the POSITIVE CONTROL); positive control = cellophane.

<sup>b</sup> Maximum rate of mineralization.

<sup>c</sup> Half-life; i.e. number of days to achieve 50% mineralization.

<sup>d</sup> The net mineralization curve for pure PBSA 3001 film was biphasic; i.e. was characterized by two distinct rates of CO<sub>2</sub>-C evolution (see Fig. 7(b)).

Table 2  
Weight average molecular weight of PBSA/starch samples. Values obtained from GPC chromatograms taken before and after the soil test exposures

PBSA/starch (%/%)	$M_w$ of sample removed from biometer (g/mol)			
	Exposure time (days)			
	0	28	180	365
100/0	293 000	281 000	196 000	136 000
90/10	260 000	195 000	—	—
80/20	244 000	177 000	—	—

degraded for up to one year exhibited only a single modal distribution, which is consistent with random degradation of the polymer [40]. Conversely, the GPC chromatograms for all the starch filled polymers exhibited a bimodal distribution after soil test exposures of at least 28 days. The evolution of this distribution is illustrated in the chromatograms for the

80/20 PBSA/starch sample (Fig. 12); note that evidence of the second (low molecular weight) peak was visible after a soil test exposure of only 14 days. These data indicate that the incorporation of starch in the blend resulted in a different mode of attack on the PBSA component of the films. Given that PBSA is a polyester, it is conceivable that incorporation of the starch filler resulted in a disruption of some of the ester linkages.

The weight average molecular weights of PBSA 3001 in the pure and starch filled systems are presented in Table 2. As anticipated, the incorporation of starch filler into the blend resulted in a reduction in the molecular weight of the polymer systems. Decreased molecular weights of the starch filled systems may be explained from the shear mixing of high modulus materials and processing – where more mechanical stress is needed at higher starch contents. Regardless, the addition of starch to the PBSA resulted in a more rapid decrease in the molecular weight of the PBSA

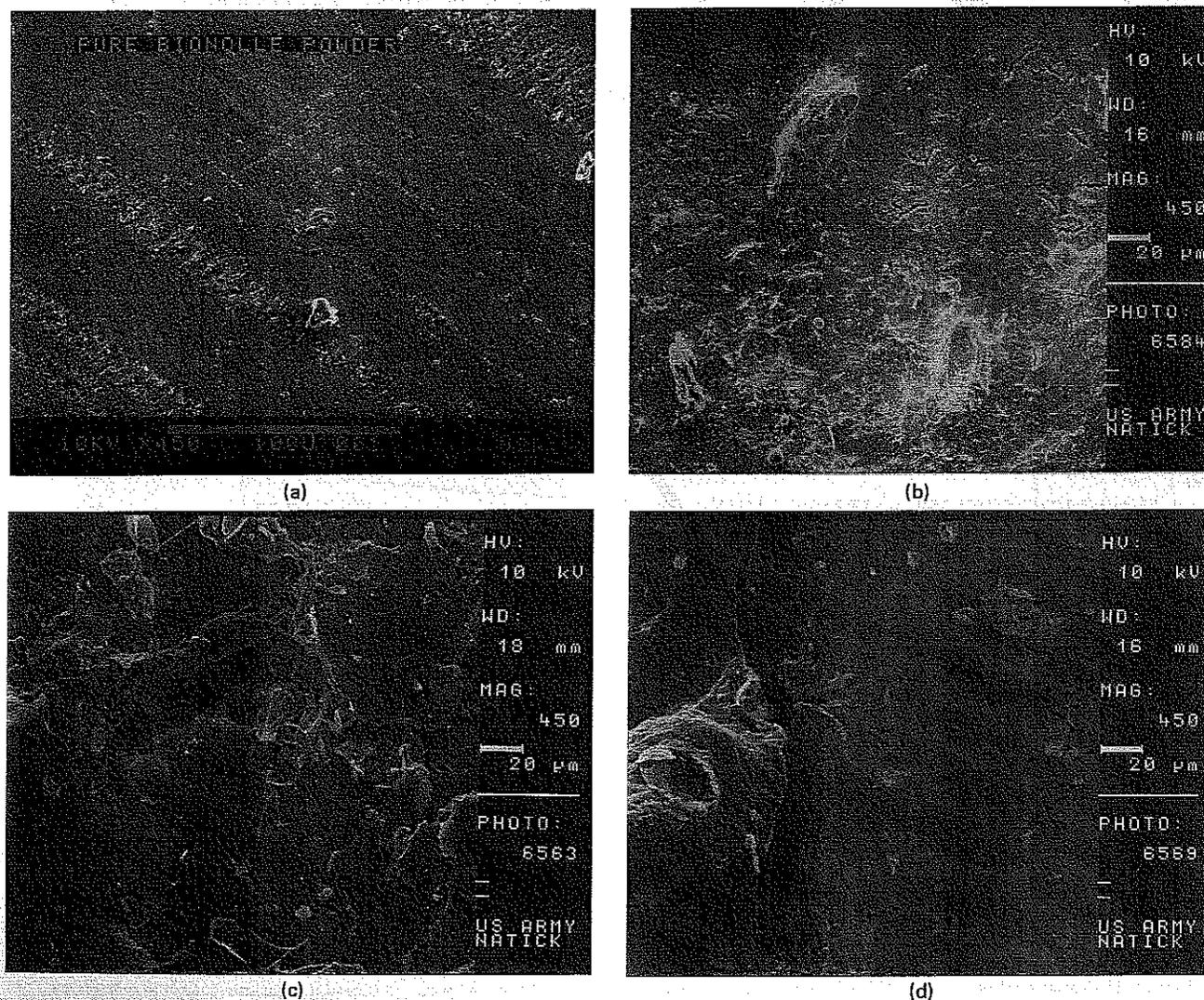


Fig. 8. SEM photographs of the PBSA 3001 films (450 × magnification): (a) undegraded film; (b) after a 28 day test exposure; (c) after a 180-day test exposure; and (d) after a 1 year test exposure.

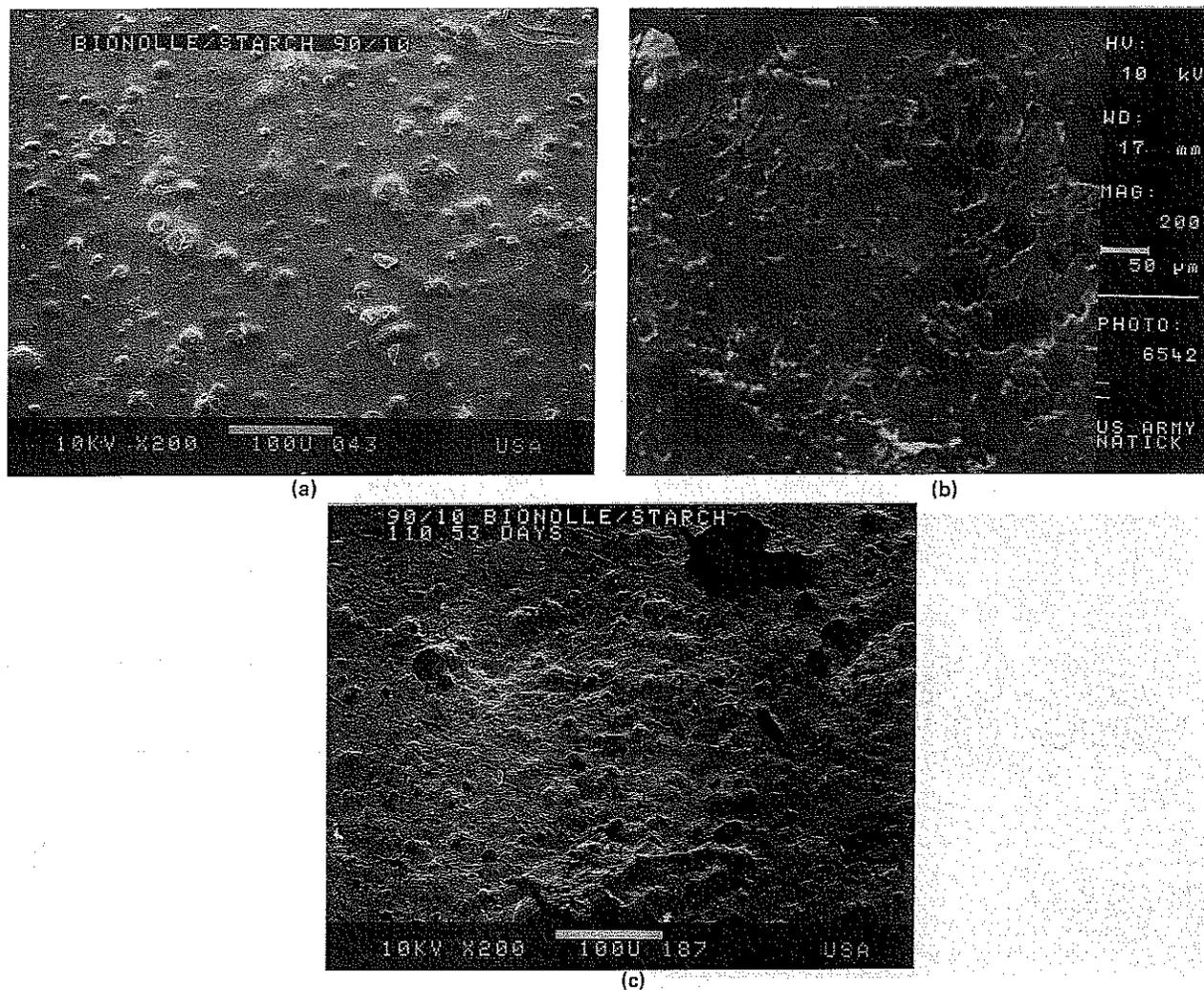
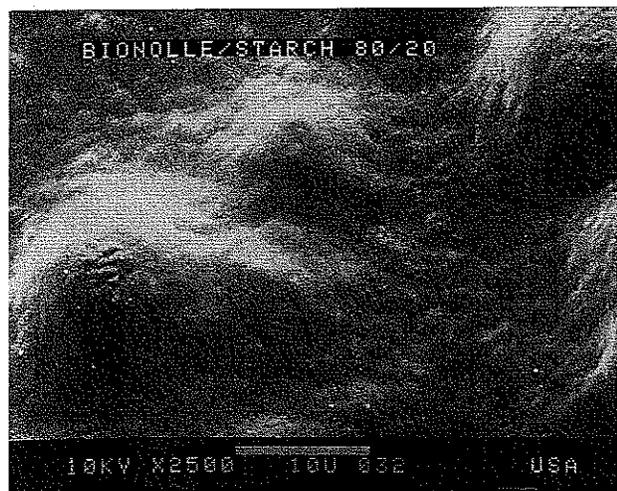


Fig. 9. SEM photographs of the 90/10 PBSA/starch films (200 $\times$  magnification): (a) undegraded film; (b) after a 28 day test exposure; and (c) after a 110 day test exposure.

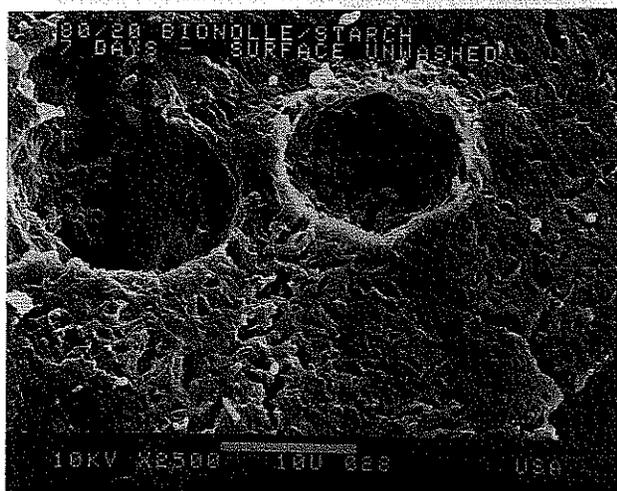
during soil test exposures. For example, whereas there was only a 4% reduction in the molecular weight of the pure PBSA 3001 after a 28 day test exposure, the molecular weight of the PBSA component of the 90/10 and 80/20 PBSA/starch systems decreased by more than 25% during the same exposure period. Nevertheless, the pure PBSA 3001 exhibited a 37% decrease in  $M_w$  after 180 days in the soil and a 54% decrease in  $M_w$  after one year. These results correlate well with those obtained from the polymer mineralization studies.

Typical DSC scans of the pure PBSA and 80/20 PBSA/starch systems are presented in Fig. 13. Although the reported  $T_g$  for PBSA ( $-55^\circ\text{C}$  DMA data from this report;  $-45^\circ\text{C}$  for DSC<sup>2</sup>) is not visible in the DSC scans, there is a  $T_g$ -like transition that appears at  $45^\circ\text{C}$  for both the pure PBSA and starch filled samples. This transition, which does not shift with blend composition or upon cycling of the sample, appears on second heating and is presumably a reflection of the structure of the PBSA [36].

Enthalpy values (obtained from the first heat DSC data) for the PBSA component of the test samples, as a function of exposure time in the soil test environment, are presented in Fig. 14. Both the 80/20 and 70/30 compositions exhibited an increase in enthalpy—peaking at DAY 14 and decreasing significantly thereafter. In light of the results of the polymer mineralization studies, these data are consistent with preferential degradation of the starch, followed by degradation in the amorphous regions of the PBSA, and finally by degradation in the crystalline regions of the PBSA. The initial decrease in enthalpy can be attributed to the disappearance of the starch, which results in an increase in the PBSA/starch ratio and, consequently, an increase in the proportion of crystalline PBSA in the residual polymer. The subsequent decrease in enthalpy is clearly linked to the degradation of the PBSA itself. The  $\Delta H$  of pure PBSA remained almost constant, indicating slow degradation in the crystalline regions of the polymer. However, the GPC data (Table 2) indicate a dramatic decrease in molecular weight as a



(a)



(b)

Fig. 10. SEM photographs of the 80/20 PBSA/starch films (2000 $\times$  magnification): (a) undegraded film and (b) after a 7 day test exposure.

function of time, which confirms that degradation of the PBSA occurs first in the amorphous zones.

#### 4. Conclusions

Composites of PBSA and granular corn starch, with starch contents up to 30% by weight, can be processed into films by blown film extrusion. Constant mix times, screw speeds and temperature profiles for the extrusion process were maintained to minimize any alternations in the films and to minimize effects from processing parameters. The extrusion blown film processing resulted in consistent films at all starch contents. Although the addition of starch alters the mechanical properties of the resulting films, these materials retain the toughness properties as well as a useful range of mechanical properties that lend themselves to trash bag applications. Another feature of these films is that there are no shifts in the mechanical properties

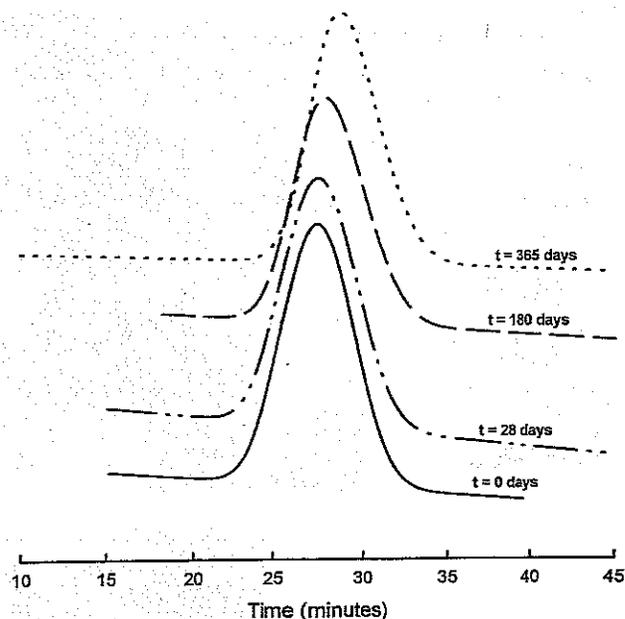


Fig. 11. GPC chromatograms of the PBSA 3001 system; film samples recovered from the soil test after exposures of 0, 28, 180 and 365 days.

at different moisture content and no development of brittleness in these films after extended storage of the films in the laboratory.

The mechanical properties of the starch-filled films are consistent with theoretical models for filled systems with

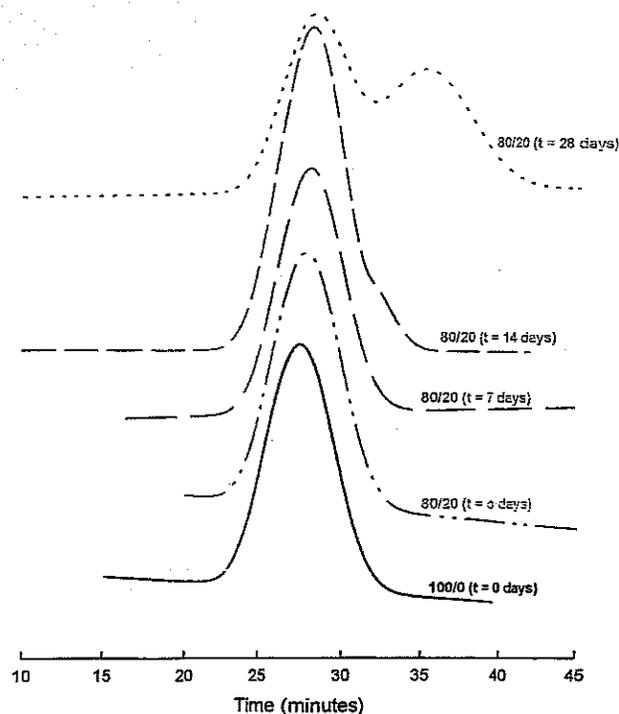


Fig. 12. GPC chromatograms of the 80/20 PBSA/starch systems; film samples recovered from the soil test after exposures of 0, 7, 14 and 28 days. The chromatogram for the PBSA 3001 sample is included as a reference.

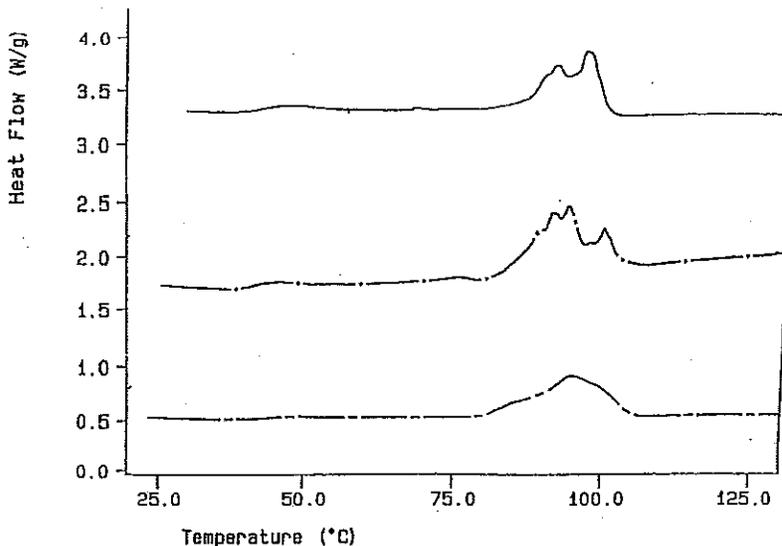


Fig. 13. DSC scans of the PBSA 3001 and 80/20 PBSA/starch systems. (100/0 second heat data (—), 80/20 first heat data (— · —), 80/20 second heat data (---)).

poor adhesion between filler and matrix. In particular, elongation and tensile results suggest that there is no adhesion between the matrix and the starch. This was confirmed by SEM and DMA analysis of the blown films. Moreover, the biodegradation results demonstrate that although the PBSA

3001 is inherently biodegradable, addition of the starch filler significantly improves the rate of degradation of the PBSA component of the polymers, presumably through its effect on surface area.

Investigations of PBSA, and PBSA/starch systems have

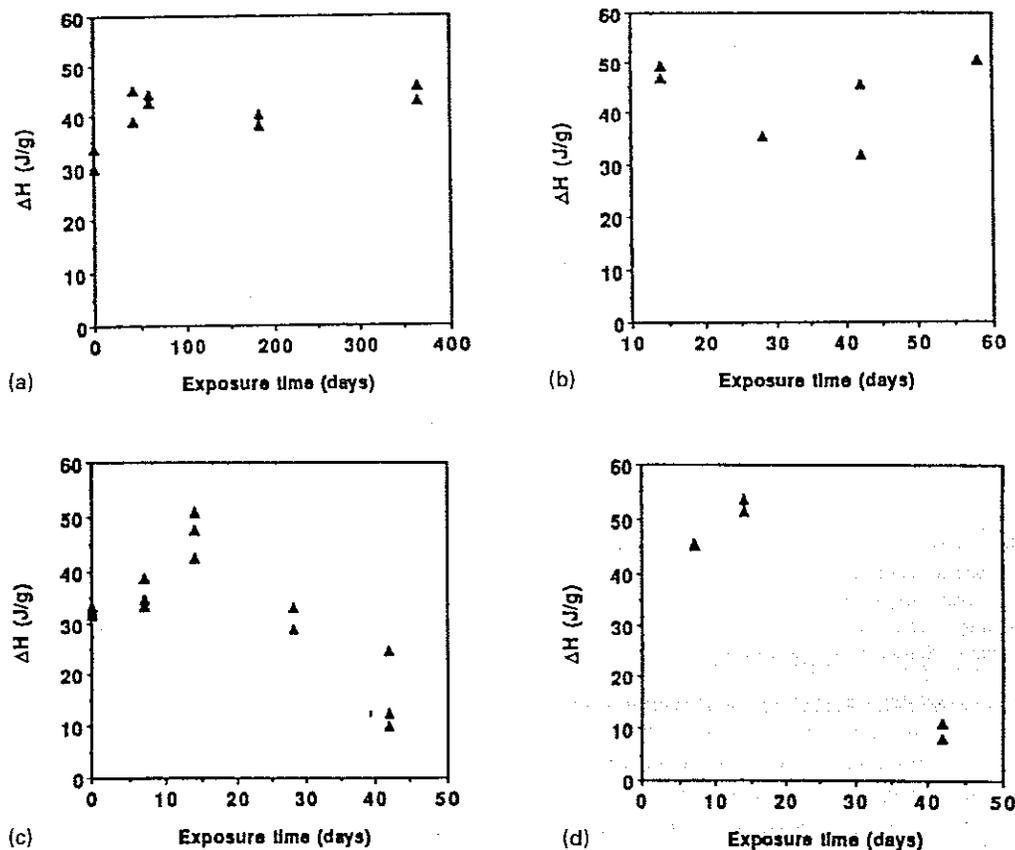


Fig. 14. Enthalpy ( $\Delta H$ ) data for the 1st heat melting peak of the PBSA/starch systems; film samples recovered from the soil test after exposures of up to one year. (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30.

contributed to our understanding of the thermal and mechanical behavior of blown films composed of biodegradable polymers. Our investigation explores the role of starch as a biodegradable filler. Further investigations should include the use of compatibilizers to perhaps create adhesion between the starch and PBSA or the pursuit of selective plasticizers for each component; e.g. where the starch can be gelatinized to act as a thermoplastic.

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