

Tensile Properties, Morphology, and Biodegradability of Blends of Starch with Various Thermoplastics

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Received 25 June 2001; accepted 12 April 2002

ABSTRACT: In the present study, blends of starch with different thermoplastics were prepared by a melt blending technique. The tensile properties and morphology of the blends were measured. It was found that with increasing starch content in starch/ionomer blends, the tensile strength and modulus increase. But for starch/low-density polyethylene (LDPE) and starch/aliphatic polyester (APES) blends, tensile strength and modulus decrease with increasing the starch loading. Elongation at break values of all the blend systems decrease with increasing starch loading. The scanning electron micrographs (SEM) support the findings of tensile properties. Better homogeneity is observed in starch/ionomer systems compared with that in starch/APES and starch/LDPE systems. Up to 50% starch content, the starch/

ionomer blends appear as a single phase. The extent of phase interactions of starch/APES system lies in between the starch/LDPE and starch/ionomer systems. From the biodegradability studies of the blends it was found that, although the pure LDPE and ionomer are not biodegradable, the starch/LDPE and starch/ionomer blends are biodegradable with an appreciable rate. The rate of biodegradation of the starch/APES is very high as both the components are biodegradable. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2907–2915, 2002

Key words: starch; polyethylene; low-density polyethylene (LDPE); aliphatic polyester (APES); ionomers; tensile property; biodegradable

INTRODUCTION

Polymeric materials are generally durable and inert towards microbes, thus offering long-term performance. According to the emphasis on environmental pollution problems and land-shortage problem for solid waste management, such as nonavailability of landfills, public perception, and reduction of fertility of lands by accumulation of surface litter, environmentally degradable and 'environmentally friendly' polymers are of interest.¹

Many of the physical and chemical properties of plastics make them ideal materials for a variety of products and applications. Most of the plastics, mainly alkane derived, have poor biodegradability and may have lifetime of over the hundred years when they buried in typical solid waste sites. However, three main classes of biodegradable polymers have become an important concern in modern civilization. Synthetic polymers (polyesters, polyimide, polyacetyl, polyurea, etc.), with vulnerable groups susceptible to hydrolysis attack by the microbes, belong to the first class.² The second class of materials is composed of naturally

occurring processable bacterial polymers, polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). PHB and PHV are truly biodegradable, being attracted by a wide variety of bacteria.³ Blends of polymers and additives, which are readily consumed by microorganisms, are in the third class.

Starch has been considered as a useful material in certain thermoplastic applications because of its biodegradability, availability, non-toxicity, high purity, and low cost.^{4,5} Starch films possess low permeability and thus becomes attractive materials for food packaging. Starch promotes the biodegradability of a non-biodegradable plastic and also starch can be used together with a fully biodegradable synthetic plastic,^{6–11} producing biodegradable blends of low costs. The starch remains in granular form in the plastic matrix and thus may act as a filler. Its lower specific gravity (1.5) compared with that of an inorganic filler, such as clay (specific gravity, 2.6), is an important factor for its use as a filler.

Starch, on mixing, enhances the biodegradability of the synthetic polymer mainly because of the increase in polymer surface created after starch consumption by microorganisms.¹² One more important aspect is the steadily increasing worldwide starch production.

In light of the advantages just discuss, many works have been done on biodegradable starch/thermoplastic blends.^{13,14} Some of the thermoplastics investigated

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to date include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), poly(ϵ -caprolactone, PCL), poly(butylene succinate-co-adipate, PBSA), poly(ethylene-co-vinyl alcohol, EVOH), and so on.^{16–18} The present article deals with comparative studies on the biodegradable blends of starch with various important thermoplastics such as LDPE, aliphatic polyester (APES), and ionomer. Usually, the contents of starch in these blends is < 50 wt % because of the difficulty in the loading of starch. In this article, however, we prepared the blends containing >50 wt % of starch, up to 90 wt %, as well as those containing lower contents of starch, <50 wt % for comparison. Furthermore, to the best of our knowledge, this is the first report to deal with the blends of starch with ionomer. The tensile properties are related to the morphology of the blends, which were investigated by scanning electron microscope (SEM). The biodegradability was studied in activated compost soil mixtures, burring the polymer films. The activated compost soil mixtures are prepared with such a composition, which produces a very good environment for microorganism growth. The detailed composition of the soil is given in the Experimental section.

EXPERIMENTAL

Materials

Low-density polyethylene [LDPE; melt index (MI) (ASTM D 1238), 3.0 g/10 min], which is appropriate for packaging usage, was supplied by Hyundai Petrochemical Company, Korea. Aliphatic polyesters (APES), [poly-(butylene succinate-co-adipate)], grade Skygreen SG-2109 (MI = 14) were supplied by Sunkyong Chemical Company, Korea. The ionomer used in this study was essentially polyethylene (PE) with a small amount of methacrylic acid copolymerized randomly into the ethylene chain, which were neutralized with Na cation. Its density and melt index are 0.920 g/cm³ and 2.0 g/10 min, respectively. The ionomer (Surlyn 2910) was supplied by Dupont.

The starch used in this study was unmodified potato starch (PS) and was supplied by Katayama Company, Japan. Starch was vacuum dried to a moisture content of <1% before blending and processing. Appropriate amounts of thermoplastics were mixed with starch separately to prepare blends of starch with various thermoplastics.

Preparation of blends

Polymers and starch were dried in a vacuum oven by heating at 80°C for >24 hours. Starch was melt blended with LDPE, APES, and ionomer separately in a HAAKE Rheocorder 600 roller mixer for 30 min, at 170°C and 50 rpm. For each system of starch/thermo-

plastic blends, a different level of starch from 10 to 90% by weight were used. The components were physically premixed before being fed into the Rheocorder, and no additional antioxidant was added. Melt temperature and torque were recorded during the mixing period. The blends, after preparation, were placed in tightly sealed vials to prevent any moisture absorption.

Tensile properties

Measurements of tensile properties, such as tensile strength, elongation at break, and tensile modulus (hereafter referred to as modulus), were performed on an UL25 (Hounsfield Company..) mechanical tester according to the ASTM D638, Type V method. Samples were strained at a rate of 20 mm/min at room temperature and 50% relative humidity, with a gauge length of 10 mm. Five replicates were tested for each sample, and average values of the elongation at break, tensile strength, and modulus were determined. The modulus was determined from the slope of the linear portion of the stress-strain curves. The tensile strength is the maximum load divided by the original cross-sectional area.

Morphology

The morphology of the blends was examined by scanning electron microscopy (SEM; HITACHI instrument, model S-4200) on cross-sections of cryogenically fractured samples for undegreded samples. Surfaces were coated with a thin layer of gold. The photographs for the biodegradable sample were taken on films. The details of preparation of films are given in next section (Biodegradation Studies).

Biodegradation studies

The biodegradation of the prepared polymer films by microorganisms was investigated in activated compost soil mixtures. The soil mixtures (soil, 50%; sand, 30%; and composted manure, 20% at pH 7.0 \pm 0.5) were maintained at 60 \pm 5% water holding capacity and incubated in a controlled environment chamber. The detailed composition of the mixture is given in Table I. The polymer samples were pressed at 130°C and 250 atm for 1 min to produce thin film (100–150 μ m thick). The films were buried in each of four soil boxes in the incubator. The temperature of the experiment was monitored at 60°C. At predetermined intervals, polymer specimens were removed from the soil mixtures. They were cleaned by 100, 50, 25, and 0% buffer/ethanol solution followed by drying in a vacuum oven. Dried films were weighed to calculate the weight loss. An average of five measurements was taken for producing each data. The surface morphol-

TABLE I
Physical and Chemical Properties of Soil Mixture and Compost

Soil Mixture		Compost	
Water content (%)	60	Water extract nitrogen: soluble nitrogen (mg/kg dry compost)	1020
pH	7.0	Ammonia	987
		Nitrate	30
		Nitrite	3
Bulk density (kg/L)	0.4	Initial total Kieldahl nitrogen mg/kg dry compost):total nitrogen ^a	2620
Volatile solid (VS) content (%, VS/total solid)	86	Water extract carbon:total carbon (mg soluble COD/kg dry compost)	53,000

^a Carbon/nitrogen ratio is 20:1.

ogy of biodegraded polymer specimen was photographed by SEM, following the aforementioned methods used for fractured surface.

RESULTS AND DISCUSSION

Tensile properties

The variation of tensile strength, elongation at break, and modulus with the starch content in starch/LDPE, starch/APES, and starch/ionomer blends are given in Figures 1, 2, and 3, respectively. Tensile strength values continue to decrease in starch/LDPE and starch/APES blends with increasing starch content in the blends. This result is because hydrophobic LDPE or APES are not compatible with hydrophilic starch. It is a general trend that the better the dispersion of the starch in the thermoplastics matrix, the better are the mechanical properties. These findings are also supported by the SEM photographs, which will be discussed later. In fact, addition of starch generally results in an increase in stiffness, which corresponds to decreasing tensile strength as well as elongation at break.¹⁹⁻²⁴ Again for the starch/LDPE and starch/APES blends, the elongation at break (Figure 2) and modulus (Figure 3) show the same trend of variation with starch loading. This result is also because of the

lack of sufficient phase adhesion, as well as poor dispersion. The reduction in tensile strength and modulus in the starch /APES from the pure APES is more prominent compared with that in starch /LDPE blends.

The greater flow property of APES, because of its higher MI values (i.e., lower molecular weight), may increase the stiffness of the starch, thus reducing tensile strength and elongation at break of the starch/APES blends to a greater extent in comparison with the starch/LDPE blends. The moduli also support this explanation; that is, the stiffer the starch, the poorer are the mechanical properties.

In general, lower concentrations of starch gives higher values of tensile strength. On the other hand, elongation at break mainly depends on the interfacial adhesion.²⁵ However, one more peculiar observation is that all the starch/LDPE blends show higher modulus than pure LDPE, though increasing starch content reduces the modulus, as shown in Figure 3. This result is due to the stiffening effect of the starch granules.²⁰ The stiffening effect is because the modulus of starch is higher than that of semi-crystalline LDPE because of the presence of hydrogen bonding in starch and not in LDPE.

On the other hand, comparison of Figure 1 and Figure 3 clearly shows that starch/ionomer blends

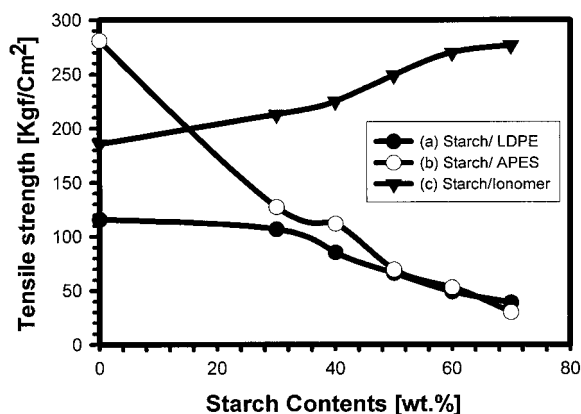


Figure 1 Tensile strength of blends of starch and various thermoplastic polymers: (a) starch/LDPE; (b) starch/APES; (c) starch/ionomer.

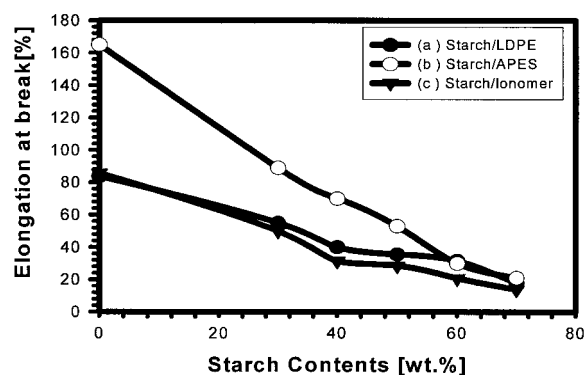


Figure 2 Elongation at break of blends of starch and various thermoplastic polymers: (a) starch/LDPE; (b) starch/APES; (c) starch/ionomer.

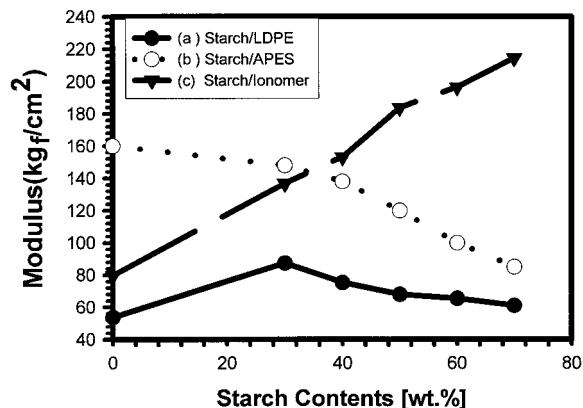


Figure 3 Modulus of blends of starch and various thermoplastic polymers: (a) starch/LDPE; (b) starch/APES; (c) starch/ionomer.

showed results in tensile strength and modulus that are opposite to those of the starch /LDPE and starch /APES blends. The tensile strength and modulus increase with incorporation of starch. This result may be due to the polar interaction between the hydroxyl group of starch and carboxyl group of ionomer. Increased starch increases the compatibility (i.e., phase adhesion) in the starch/ionomer blends. The relationship of morphology and blend compositions will be discussed in detail later. The elongation at break for the starch/ionomer system decreases with increasing starch content, as expected (Figure 2).

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 polymer matrix.²⁶ It should be noted, however, that the elongation at break mainly depends on phase adhesion. In Figure 2, for the starch/APES blends of 50 or 70 wt % starch, elongation at break drops abruptly. This result is because of the phase separation: literally no interfacial adhesion is observed from SEM (Figures 5b and

5c) for these two cases (50 and 70 wt % starch content blends).

Phase morphology of fractured surface by SEM

The morphology of the blends was examined by SEM. The microphotographs are given in Fig 4 (a, b and c) to 6(a, b, c and d) Micrographs, taken after fracture indicate clearly the heterogeneous morphology of the blends, where deformed starch particles are interspersed in the continuous thermoplastic matrix as fillers. Figures 4–6, however, show better compatibility between starch and ionomer compared with other starch/ thermoplastic blends, meaning that the homogeneity between the two components of the starch/ionomer blends is better.

In Figure 4 (a, b, and c) it is obvious that for the starch/LDPE blends, the starch phase is in granular shape. The fractured surface micrographs show that the number of voids during fracture due to the poor interfacial adhesion keeps on increasing with increasing starch content. The poor interfacial adhesion was reflected in the mechanical properties. It is seen that increasing starch loading in starch/LDPE blends decreases the interfacial adhesion and homogeneity. The mechanical properties already discussed also support these findings. Similar results were observed for starch/APES blends, as shown in Figure 5. However, for the starch/ionomer blends, the micrographs of the blends appear like almost single phase materials up to 50 wt % of starch contents, whereas droplets are very prominent for blends containing >70% starch. This result indicates that the compatibility decreases with increasing starch contents. The phase adhesion for the blends of lower starch contents may originate from the interaction of carboxyl group of ionomer with the hydroxyl group of starch, as already mentioned. As a consequence, the tensile strength and the modulus increased with increased starch contents due to such a

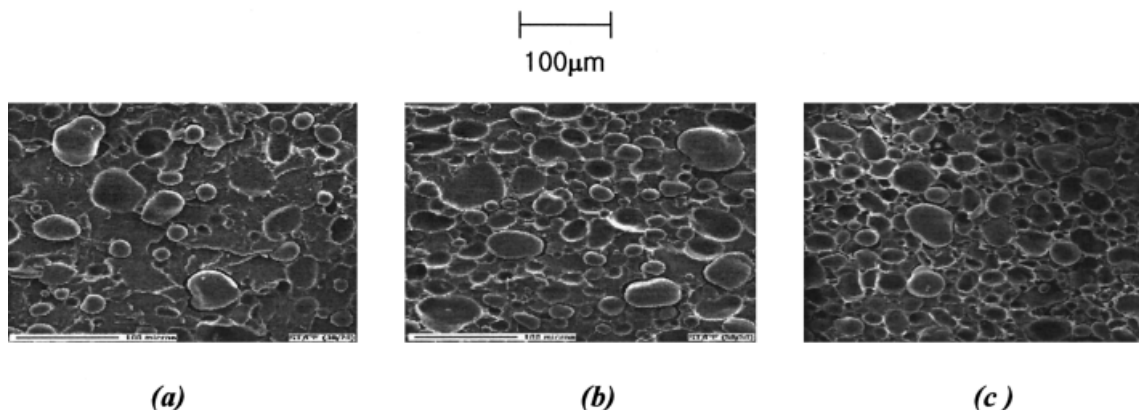


Figure 4 SEM micrographs of starch/LDPE blends (a) starch/LDPE (30/70); (b) starch/LDPE (50/50); (c) starch/LDPE (70/30).

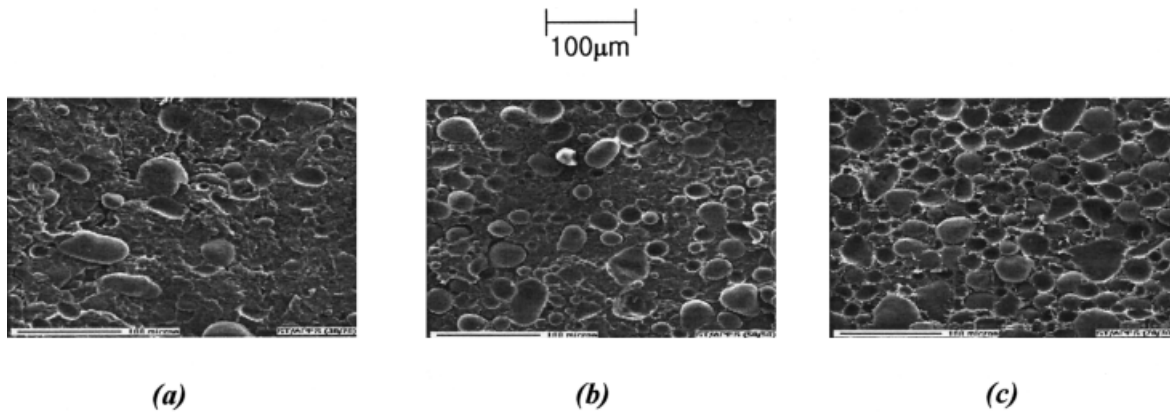


Figure 5 SEM micrographs of starch/APES blends: (a) starch/APES (30/70); (b) starch/APES (50/50); (c) starch/APES (70/30).

partial compatibility, as already seen in Figures 1 and 3.

Biodegradation

The biodegradation of PE/starch blends suggests that microbes consume starch and create pores in the materials, leading to an increase in the surface area of PE matrix and providing susceptible groups for its biodegradation.²⁷ Thiebaud et. Al.²⁸ examined the bio-

degradation of LDPE/starch ester blends by measuring the weight loss due to removal of the starch component by microorganisms, which resulted in a loss in integrity of the mechanical properties.

The weight loss during soil burial up to 60 days is presented in Figure 7. This weight loss is attributed to the starch consumption by microorganism, which should result in the surface of the films being full of holes. This possibility was examined with SEM, and SEM micrographs of these films for various incubation

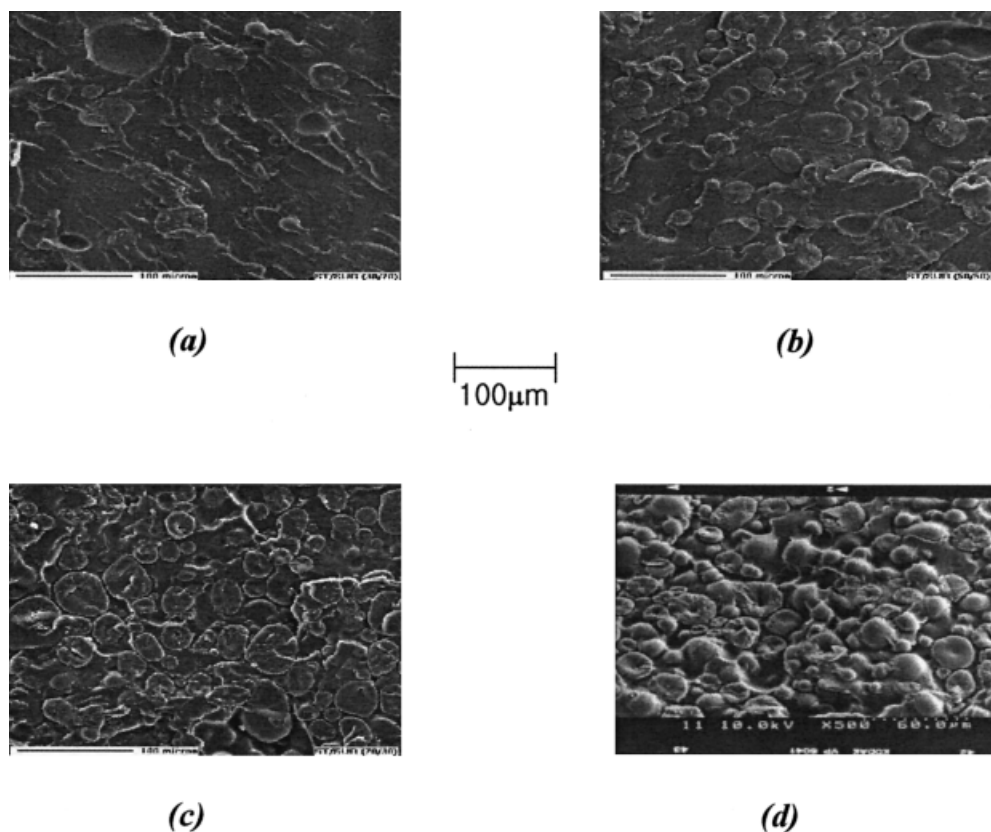


Figure 6 SEM micrographs of the starch/ionomer blends: (a) starch/ionomer (30/70); (b) starch/ionomer (50/50); (c) starch/ionomer (70/30).

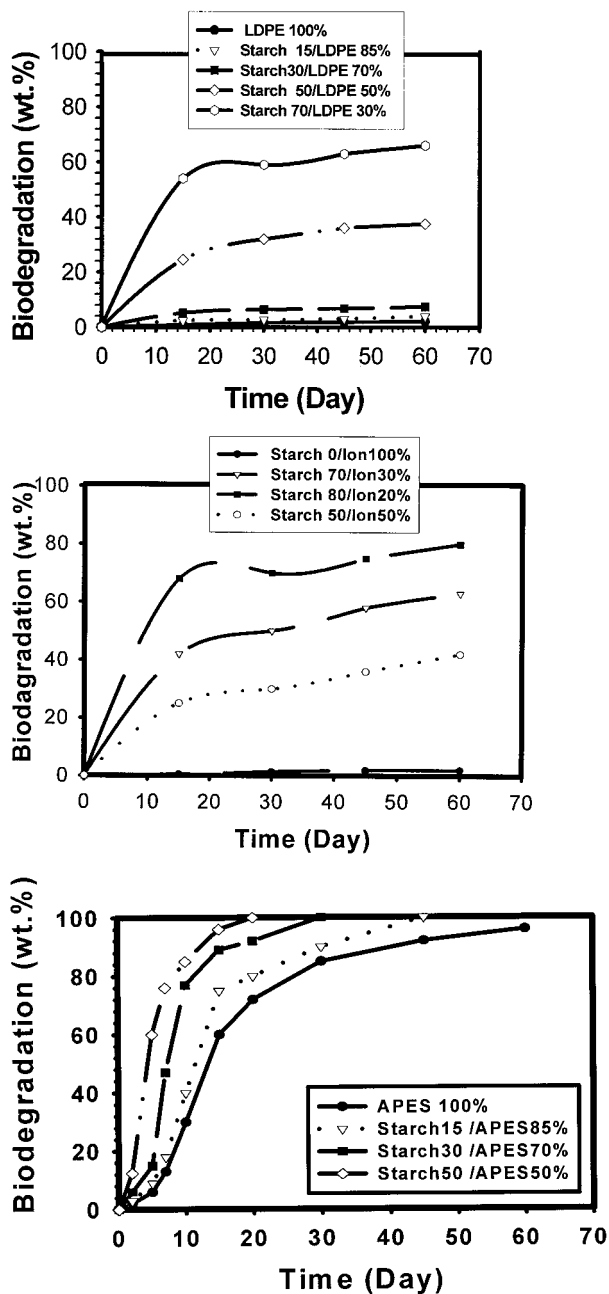


Figure 7 Plot of biodegradation (wt %) versus time (day): (a) starch/LDPE; (b) starch/APES; (c) starch/ionomer.

times are presented in Figures. 8–10. The soil burial method is well known to be a slow process, mainly because of the low percolation rate.²⁹ However, it is noteworthy that the burial soil test reflects the real life condition more than any other test, although soil composition varies from place to place.

From the data in Figure 7a it is obvious that the pure LDPE remains unchanged, even after 60 days, and no weight loss is noticed. This result is supported by SEM (Fig 8a). Again for the starch/LDPE blend of 15% starch content, the weight remained almost stable even after 2 months (60 days) of soil burial (Figure 7a).

This result is because of the very small accessibility of starch to microorganisms, thus keeping the biodegradation rate very slow. For the starch/LDPE blend of 30% starch content (Figure 7a), the weight loss is rapid up to 15 days, and then the blend remains almost unchanged for the next 45 days. The accessible starch has been consumed by first 15 days. In the micrograph shown in Figure 8b, some black droplets surrounded by some white traces are observed. Black droplets are the sites with less thickness compared with the unaffected area of polymer films. The droplets and spots will be further degraded. For 50 wt % starch content blend (Figure 7a), the weight loss is very high. Here also, the degradation is very high for the first 15 days, and then it becomes slow. As seen in the micrograph shown in Figure 8c, within 15 days a large portion of the surface of the 50/50 starch/LDPE blend is consumed. The entire amount of starch content is not removed during the biodegradability experiments. A possible explanation for this result is that starch inclusions in some area of blends are well protected and not easily accessible to microbial/bacterial action.

The increasing starch content speeds up the weight loss. This effect occurs because dispersed parts of starch start to join together and become more interconnected and continuous. Thus, for high starch content blend, a very small amount is protected by thermoplastic components. This observation is in agreement with the predictions of percolation theory in LDPE blends with pure starch.²⁹ The results in Figure 7b indicate that pure ionomer is not biodegradable. Its weight remains unchanged even after 60 days. But when 50, 70, and 80 wt % starch are incorporated, the nature of the time versus weight loss plots appears similar to those for the starch/LDPE systems (Figure 7a). For both cases, because only starch is consumable, unlike the thermoplastics, the trends are similar. Only one micrograph of the starch/ionomer system is shown as a representative example of the starch/ionomer system in Figure 8d.

The time versus biodegradation (wt %) plots for starch/APES blends are given in Figure 7c. The pure APESs are actually synthetic biodegradable polymers. APES show appreciable biodegradability. Up to 30 days it loses weight very sharply and thereafter the rate of weight loss becomes little bit slower. With increasing starch content, the degradability increases, even after 15 wt % starch incorporation the change is noticeable. For 30 and 50 wt % starch loading, weight changes very rapidly within days. For 15, 30, and 50 wt % starch content blend, the films are completely consumed within 45, 30, and 20 days, respectively. From the micrographs in Figure 9 it is seen that for 100% APES, after 10 days, there are some holes, which are prominent at higher magnification (Figure 9b). The change of the surface morphology within days is ob-

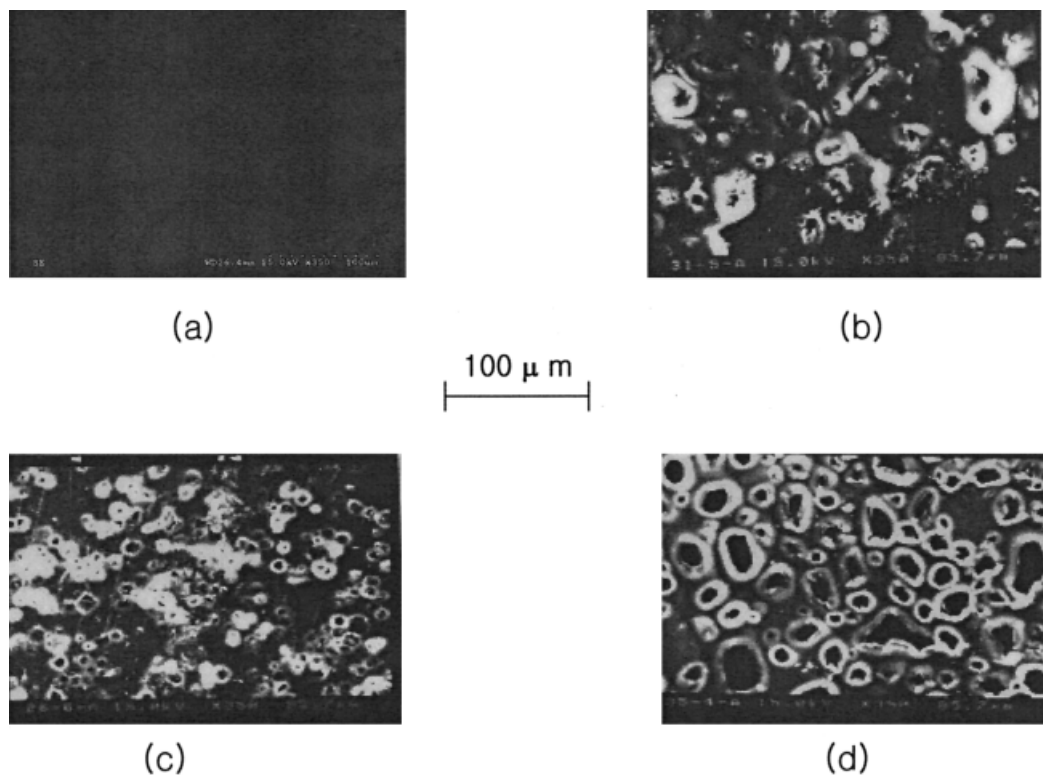


Figure 8 SEM micrographs of biodegraded starch/LDPE or starch/ionomer blends: (a) LDPE 100 wt %; (b) starch/LDPE (30/70); (c) starch/LDPE (50/50); (d) starch/ionomer (80/20). Magnification was 350 \times , and the micrographs were recorded after 60 days for (a) and 15 days for (b)–(e).

vious from micrographs 9a–9d. An increase in number of holes within days following a slower rate proves the consumption of APES by microorganisms.

The results in Figures 10a and 10b indicate that with time (days), the polymers are consumed rapidly. The results in Figures 10c and 10d show that with increasing starch content in starch/APES blends, the degradation increases. Also, with time, the weight loss increases. After 60 days, the starch/APES films were completely degraded.

Comparing the rate of degradation with time, it is revealed that the rates of degradation of starch/LDPE and starch/ionomer blends are almost same, although the phase adhesion is better between starch and ionomer. The phase adhesion of starch/ionomer blends affects the mechanical properties but does not affect the biodegradability appreciably. Both components in the starch/APES system, so the weight loss in this case is very rapid. From the data in Figure 7c, it is also clear that the degradation of starch is more than the pure APES, thus increasing the degradability with increasing starch loading.

CONCLUSIONS

Investigation of the properties of the blends of starch with various thermoplastics indicates that the tensile properties depend on the dispersion of starch in the

thermoplastic matrix. Interfacial adhesion is another important factor of tensile properties (this effect is prominent here mainly on the elongation at break). Starch/ionomer blends showed the best tensile properties among the three types of starch/thermoplastic blends because of the good compatibility that originates from the polar–polar interaction (between hydroxyl group of starch and carboxyl group of ionomer). SEM micrographs are in good agreement in the relation between tensile properties and morphology of the blends. The greater the starch content, the poorer are the mechanical properties, especially for starch/LDPE and starch/APES systems. This relationship is because of the stiffness of the starch. However, for the starch/ionomer system, mechanical properties (mainly, tensile strength and modulus) improve with increasing starch content. Nevertheless, the amount of starch in the blends plays an important role in the biodegradability of the blends, as indicated by the soil burial biodegradability test. The pure LDPE and pure ionomer are not biodegradable but the starch/LDPE and starch/ionomer blends are biodegradable to an appreciable extent. The extent of biodegradation of starch/APES blends is very high because both the components are biodegradable. Because the starch is more biodegradable than APES, it is also seen that with an increase in starch loading, biodegradability increases.

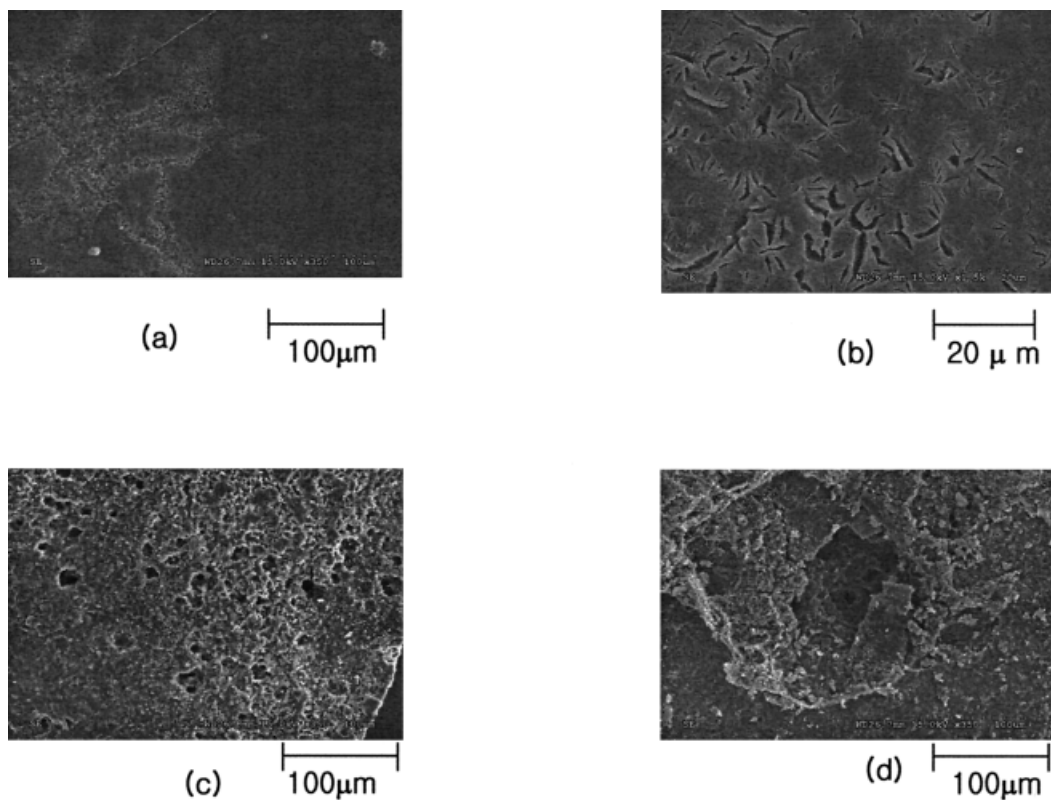


Figure 9 SEM micrographs of biodegraded APES (100 wt %): (a) 10 days, magnification of 350×; (b) 10 days, magnification of 1500×; (c) 30 days, magnification of 350×; (d) 45 days, magnification of 350×.

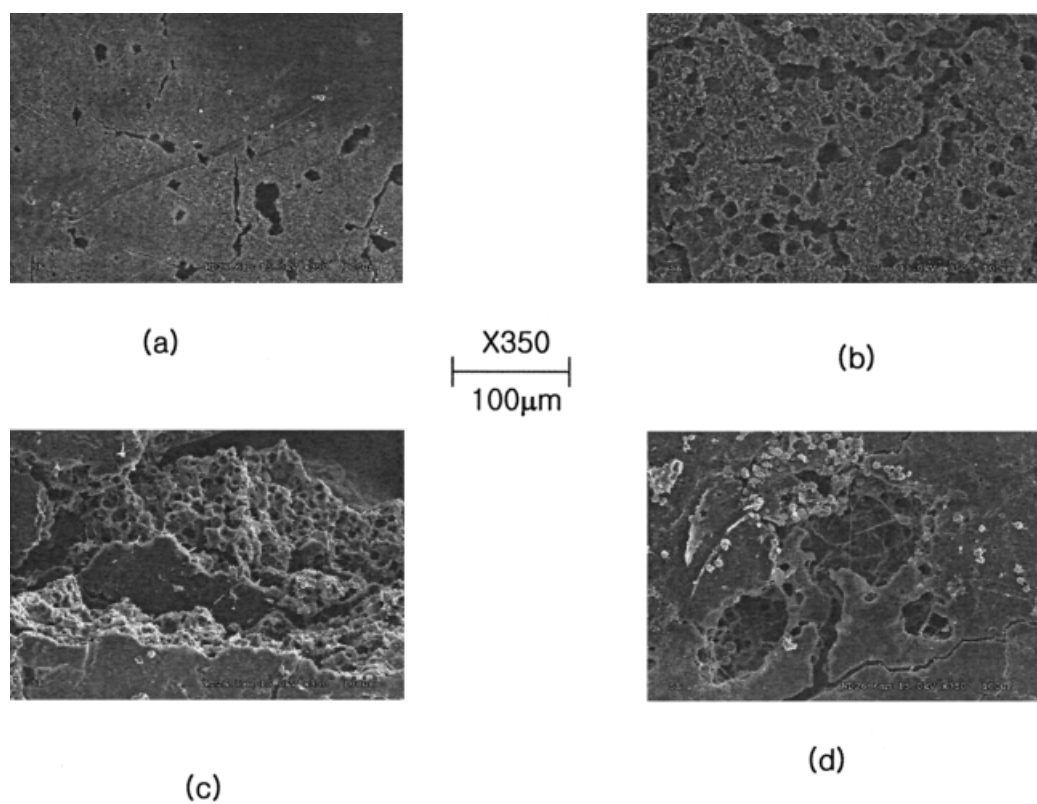


Figure 10 SEM micrographs of biodegraded starch/APES blends for 10 or 30 days: (a) starch/APES (15/85), 10 days; (b) starch/APES (15/85), 30 days; (c) starch/APES (30/70), 10 days; (d) starch/APES (50/50), 10 days.

The authors thank Mr. Yeum-Sek Kang of Pusan National University for his help in biodegradation experiments. The work was supported by the Center for Integrated Molecular Systems, POSTECH, Korea and the Brain Korea 21 Project in 2001.

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