Compatibilization of Low-Density Polyethylene/ Cassava Starch Blends by Potassium Persulfate and Benzoyl Peroxide

Varaporn Tanrattanakul, Wannarat Panwiriyarat

Bioplastic Research Unit, Polymer Science Program, Faculty of Science, Prince of Songkla University, Hatyai, Songkla, Thailand 90112

ABSTRACT: Low-density polyethylene (LDPE) was melt-blended with native cassava starch in an internal mixer. The unplasticized starch content was in the range of 30–70 wt %. Potassium persulfate and benzoyl peroxide were used as initiators to generate free radicals in starch and LDPE, leading to graft copolymerization during melt blending. An enhancement of interfacial adhesion due to initiators was observed directly in scanning electron micrographs and was proven indirectly with many experiments, including tensile property testing, tear strength testing, water absorption testing, dynamic mechanical thermal analysis, thermogravimetric analysis, and soil burial testing. The tensile strength and Young's modulus of all blend compositions increased with the addition of initiators, whereas the tear strength increased in blends containing 50 wt % or more starch. The water uptake of the samples decreased significantly when initiators were added. Starch exhibited a strong effect on the α-relaxation process of LDPE. Blends containing initiators provided higher α-relaxation temperatures than blends without initiators. The increase in the interfacial adhesion of the blends also affected the biodegradation of starch. A lesser biodegradation rate of starch was observed in the blends containing initiators; this was shown by a reduction in the weight loss and more starch left in the samples after soil burial testing. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 742–753, 2009

Key words: biodegradable; biopolymers; blends; polyethylene (PE); renewable resources

INTRODUCTION

Low-density polyethylene (LDPE) has been used as a commodity product for more than 50 years. Plastic waste causes problems with respect to waste management. Every year, there is a tremendous increase in plastic waste that cannot be completely eliminated because there are limited landfill sites. The pyrolysis of plastic wastes may produce carcinogens such as dioxin, and the pyrolysis process also consumes a lot of energy and generates greenhouse gases such as carbon dioxide. With respect to these environmental problems, the degradation of plastics becomes an important issue. Although biodegradable plastics such as poly(lactic acid), poly(butylene adipate-*co*-terephthalate), and poly(3-hydroxylbutyrate) have been launched recently, their cost is very high in comparison with conventional plastics. Bioplastics are a new class of plastics representing plastics derived from renewable biomass sources such as starch and vegetable oils, whereas fossil fuel plastics are derived from petroleum. Bioplastics may not have biodegradation characteristics. The ASTM D 6866 method has been developed to certify the biologically derived content of bioplastics. There is an important difference between biodegradability and biobased content. Blends of conventional fossil-based plastics and starch are called bioplastics as well. Their biobased content depends on their starch content. LDPE blended with starch is one example of bioplastics. Blends of LDPE and starch have been widely studied in the last 3 decades, and they are still an important subject to be studied and researched now. Starch has been used as a biofiller in LDPE to reduce the cost and increase the degradation of plastic products. Starch is a natural polymer and is an abundant, inexpensive, and renewable resource. Starch is degraded by microorganisms and is suitable for preparing bioplastics and biodegradable polymers. Unfortunately, the mechanical properties of thermoplastic polymer/starch blends are low because of the immiscibility of the blends. The hydrophilic nature of starch and the hydrophobic nature of LDPE make LDPE/starch blends incompatible. Therefore, many published articles concerning LDPE/starch blends have frequently reported on

compatibilization methods. Moreover, the degradation of LDPE/starch blends has also been reported, although they are not fully biodegradable polymers.

There are many kinds of starches used for blending with LDPE, such as corn starch,[1–17] potato starch,[18–21] wheat starch,[22] sago starch,[23] rice starch,[24] banana starch,[25] mango starch,[26] and cassava starch.[27–32] To increase the compatibility of LDPE/starch blends, modified or nonnative starch has been used, such as pregelatinized starch,[11] crosslinked starch,[14] octanoated starch,[18,19,33] starch acetate,[20] hydropropylated starch,[21] and phthalated starch.[34] Polyethylene graft copolymers have been widely used as compatibilizers with other polymers; they include polyethylene grafted with maleic anhydride (PE-*g*-MA),[1,3,5,6,17,24,25,35,36] polyethylene grafted with glycidyl methacrylate,[10,27] LDPE grafted with dibutyl maleate,[31] LDPE grafted with itaconic acid,[32] an ethylene/acrylic acid copolymer,[16,37] and polyethylene grafted with styrene-*co*-maleic anhydride polymer.[38] Other polymers used as compatibilizers include an ethylene/vinyl acetate copolymer,[2] an ethylene/vinyl alcohol copolymer,[28] and a functionalized metallocene copolymer.[39] One-step reactive blending of LDPE and starch by the addition of maleic anhydride and peroxide has been reported.[9,12,13,15]

In situ graft copolymerization is one effective method for increasing the compatibilization of polymer blends. The graft copolymerization of a thermoplastic polymer onto starch has been widely studied. Potassium persulfate (PPS), a water-soluble initiator, is effective for starch graft copolymerization.[40] It is well established that benzoyl peroxide (BPO) can be used as an initiator for polyolefins. To the best of our knowledge, there is no report of blending LDPE and cassava starch with the addition of PPS and BPO. The objective of this study was to enhance the compatibility of LDPE/cassava starch blends by the addition of PPS and BPO to increase interfacial adhesion between the LDPE matrix and starch granules. The hypothesis was that PPS and BPO would induce free radicals in starch and LDPE, leading to graft copolymerization and improved interfacial adhesion at the interphase between LDPE and granular starch. This study focused on the effect of PPS and BPO on the mechanical properties and characteristics of the blends, but verification of the graft copolymer was beyond the scope of this study.

EXPERIMENTAL

Materials

LDPE (EL-Lene 1905F/FA) with a melt flow index of 5.0 g/10 min was produced by Thai Polyethylene Co., Ltd. (Bangkok, Thailand). Native cassava starch was kindly supplied by General Starch, Ltd. (Bangkok, Thailand). Starch was dried at 100°C for 48 h and kept in a desiccator before use. PPS and BPO were analytical-grade and were used as received.

Blend preparation

Blends containing 30–70 wt % starch were prepared with an internal mixer (model 350E, Brabender, Duisburg, Germany). Mixing was carried out at 120°C with a rotor speed of 100 rpm for 8 min. LDPE was initially melted for 3 min before the addition of starch. The PPS content was 0.5 pphr (0.5 parts per hundred parts of starch), whereas the BPO content was 1.0 pphr (1.0 parts per hundred parts of LDPE). Starch was mixed with a PPS aqueous solution in a blender for 3 min at room temperature before blending with LDPE and BPO in the internal mixer. LDPE/starch blends were compression-molded into sheets (∼ 1.0 mm thick) with a KT-7014 compression molding machine (Kao Tieh, Ltd., Taipei, Taiwan) at 120°C for 5 min. Sample sheets were cooled to room temperature and then kept in the desiccator before mechanical property testing and characterization.

Mechanical property testing

The die-cut specimens were prepared from the compression-molded sheets. The tensile properties (ASTM D 412C) and tear strength (ASTM D 624 for the right-angle specimen) were determined with a universal testing machine (LR10K, Lloyd, Fareham, England) at a crosshead speed of 50 mm/min. Before the measurements, the samples were conditioned at 50 ± 5% relative humidity for 24 h in the desiccator. Testing was performed at 25 ± 2°C and 50 ± 5% relative humidity, and eight specimens were tested for every sample. The average values and standard deviations were reported. Young's modulus was determined from the slope of the linear portion of the stress–strain curves.

Blend characterization

Water absorption was measured with 25.0 mm × 25.0 mm × 3.0 mm samples (width × length × thickness) according to ASTM D 570. It involved total immersion of the samples in distilled water at room temperature. The samples were dried in a vacuum oven at 50°C for 24 h. Then, they were cooled in the desiccator and weighed [dry mass (m_{dry})] close to ±0.0001 g. At regular time intervals, each sample was removed from the water, dried by wiping with blotting paper, and subsequently weighed [wet mass (m_{wet})] to determine the water uptake. The samples were placed back into the water after

each measurement and were investigated over a period of 2 months. The water uptake was calculated with eq. (1):

$$\text{Water uptake (\%)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \qquad (1)$$

The thermal properties were evaluated with a TGA7 thermogravimetric analyzer (PerkinElmer, Norwalk, CT) and a DSC7 differential scanning calorimeter (PerkinElmer). Thermogravimetric analysis (TGA) was carried out at a heating rate of 10°C/min from 30 to 600°C under a nitrogen atmosphere. DSC thermograms were recorded with a scan rate of 10°C/min for both heating and cooling at temperatures between 20 and 160°C. The crystallization temperature was detected with the first cooling scan, whereas the melting temperature and degree of crystallinity were determined with the second heating scan. The fusion heat of 100% crystalline LDPE was 277.1 J/g.[11] The degree of crystallinity was normalized with the weight fraction of LDPE in the blends. Dynamic mechanical thermal analysis (DMTA) was performed with a Rheometric Scientific (Piscataway, NJ) DMTA V. The experiments were carried out in the dual-cantilever bending mode at a frequency of 1 Hz with a strain control of 0.01%, and the heating rate was 3°C/min. The temperature range was −40 to 100°C. A scanning electron microscope (JSM-5800LV, JEOL, Tokyo, Japan) was used to observe the blend morphology before and after soil burial testing. Freeze-fractured surfaces were investigated, and samples were coated with gold before observation.

Soil burial test

Soil for the soil burial test was obtained from mixtures of fertile soil and general ground under trees and was kept in 30-cm-high baskets. Samples were dried in a vacuum oven at 60°C for 24 h. Then, they were cooled in the desiccators and weighed close to ±0.0001 g. The samples were buried at the center of the baskets and placed outside the building. The samples were removed periodically after a fixed time interval, washed thoroughly with water, and then vacuum-dried at 60°C for 24 h. The weight of the samples was recorded and used to calculate the extent of biodegradation of the samples. The weight-loss percentage was calculated with eq. (2):

$$\text{Weight loss (\%)} = \frac{W_a - W_b}{W_b} \times 100 \qquad (2)$$

where W_a and W_b are the weights of the samples after and before the soil burial test, respectively. After the soil burial test, the samples were also investigated with TGA and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Blend morphology

It is known that LDPE/starch blends are immiscible; therefore, phase separation is obtained. Figure 1 shows SEM micrographs of the blends containing 30 wt % starch with and without initiators. Unplasticized starch granules dispersed in the LDPE matrix. No adhesion between the starch granules and LDPE matrix appeared in the blend without initiators, as shown in Figure 1(a,b). With the addition of 0.5 pphr PPS and 1.0 pphr BPO, good adhesion between the starch granules and LDPE matrix was achieved, as displayed in Figure 1(c,d). The arrow in Figure 1(d) indicates the superior interfacial adhesion between the starch granules and LDPE matrix. On the basis of the preliminary study, PPS promoted adhesion between the starch granules, as shown by arrows in Figure 2(a). The connection of starch granules in the blends without PPS was slightly noticeable. Without BPO, we could not notice good adhesion between the starch granules and LDPE matrix, as shown in Figures 1(d) and 2(b). As a result, it was necessary to use both PPS and BPO to increase the interfacial adhesion between starch and LDPE. The blend morphology indicated that a grafting reaction between starch and LDPE may have occurred at the interphase. This agrees with the assumption of this study: PPS plays an important role in the grafting reaction of starch granules, whereas BPO induces free radicals in LDPE, leading to an interfacial graft copolymer between starch and LDPE. We believe that a graft copolymer (LDPE-g-starch) formed in these blends, although there was no characterization of the graft copolymer. Besides the evidence from the blend morphology, there were many proofs implying the formation of this graft copolymer, which are discussed next.

Mechanical properties

Figure 3(a–c) shows the tensile properties of LDPE/starch blends. The blends with and without initiators showed similar trends as the starch content increased. Young's modulus increased whereas the tensile strength (stress at break) and elongation at break decreased as the amount of starch increased, as reported by many researchers.[3,4,6,10,24,30] Superior modulus and tensile strength were displayed by the blends containing initiators. Among the blends without initiators, the maximum modulus, 261 MPa, appeared for the blend containing 60 wt % starch. With initiators, the modulus increased from
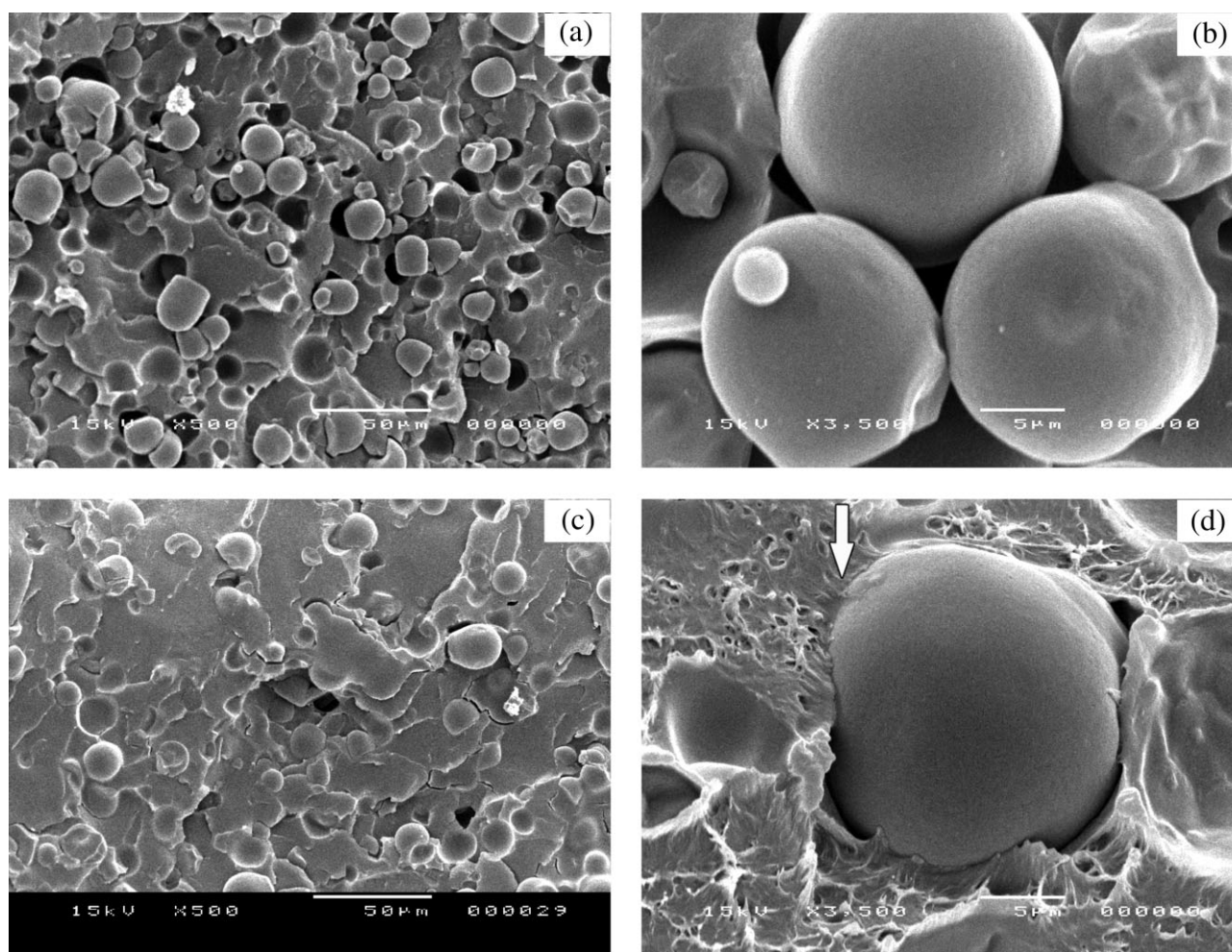
Figure 1 SEM micrographs of LDPE/starch blends containing 30 wt % starch: (a,b) without initiators and (c,d) with initiators.

214 MPa to a maximum of 508 MPa in the blend containing 50 wt % starch. The increase in the modulus due to the addition of initiators to these blends was greater than that for the LDPE/corn starch blends compatibilized with polyethylene grafted with glycidyl methacrylate,[10] by which the modulus increased from 240 to 300 MPa. The tensile strength also increased with the addition of initiators. This improvement was clearly noticed in the blends containing 40 wt % or more starch. The tensile strength of the blends containing 50 wt % or more starch with initiators was 8–9 MPa, which was slightly higher than that of LDPE/cassava starch blends reported by Huang et al.,[30] which was approximately 2–8 MPa. Compared to LDPE containing 30–50 wt % corn starch,[1,10,11] these blends showed higher tensile strength of 8.9–10.7 MPa, whereas those blends showed tensile strength in the ranges of 5.7–8.0, 6–10, and 5–7 MPa, respectively. The addition of initiators reduced the elongation at break of the blends containing 40 wt % or less starch, and no effect of the initiators was observed in the starch-rich blends. The elongation at break of the blends containing 50 wt % or more starch with initiators, shown in Figure 3(c) (6.6–55.6%), was higher than that reported by Huang et al. (3–18%). Compatibilizers may show effects on the elongation at break in various ways. For example, polyethylene grafted with glycidyl methacrylate, used as a compatibilizer in LDPE/corn starch blends,[10] showed insignificant changes in the elongation at break (5–5.5%) in blends containing 30–50 wt % starch. Bikiaris and Panayiotou[1] showed the effect of the compatibilizer content on the enhancement of the elongation at break of LDPE/corn starch blends; that is, 0.4 and 0.8 mol % PE-g-MA provided elongations at break of 30 and 100%, respectively. The tensile properties of polymer blends strongly depend on the parent polymers. LDPE is tough and ductile, whereas starch is hard and brittle. The degree of crystallinity and glass-transition temperature of starch are quite high. The glass-transition temperature of granular starch is approximately 210–230°C, and it is very close to the degradation temperature (ca. 225–250°C).[1]
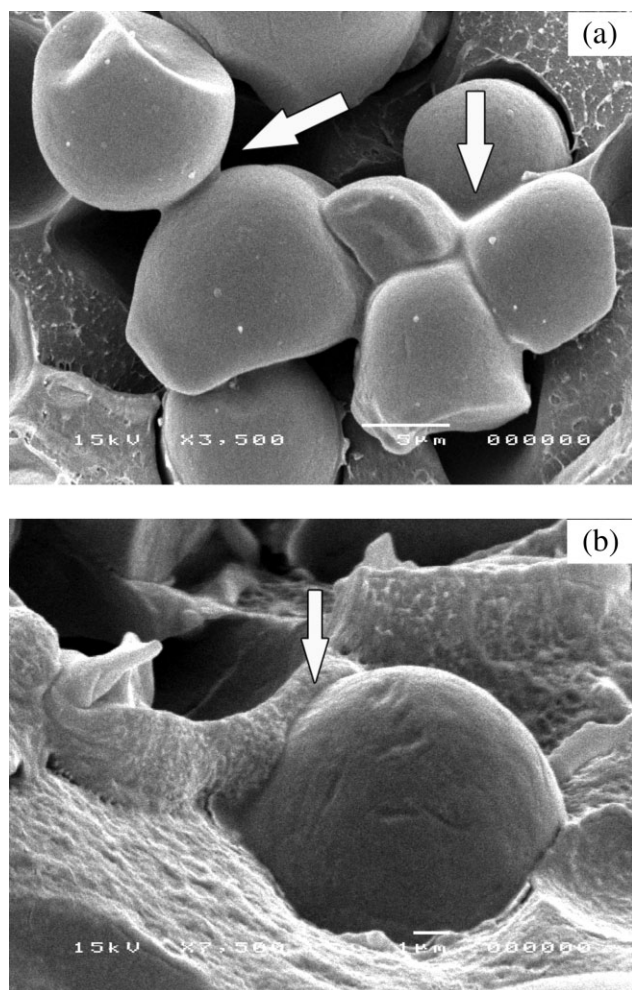
Figure 2 SEM micrographs of LDPE/starch blends with 50 wt % starch and different initiators: (a) 0.5 pphr PPS and (b) 0.5 pphr PPS and 0.5 pphr BPO.

Furthermore, starch is stiffer than LDPE because of its high crystallinity and intermolecular attraction by hydrogen bonding. Therefore, granular starch added to LDPE would act as rigid particles in LDPE and bring about an enhancement of the modulus of the blends. The tensile strength and elongation at break of polymer blends are more sensitive to the miscibility and morphology of the blends. Unfortunately, we cannot measure the tensile properties of granular starch; thus, we are unable to determine the deviation from the rule of mixture. A reduction in the tensile strength and elongation at break is always derived for an LDPE/granular starch blend because of immiscibility; consequently, compatibilization is essential for this blend. The particle size of starch granules is very large ($\sim$ 20 μm), causing premature failure during loading. Normally, the particle size of the dispersed phase should be small (e.g., <1 μm) to improve the mechanical properties. Both the brittleness and too large particle size of the starch granules contributed to the decrease in the tensile strength

and elongation at break for the blends. Because of the initiators, there was increased interfacial adhesion in the blends, which enhanced the modulus and tensile strength. In general, an increase in interfacial adhesion improves load transfer between the dispersed phase and the matrix, resulting in higher mechanical properties. Although the interfacial adhesion was improved, a lower elongation at break for the blends containing initiators was derived. This could be explained as follows: during the application of the load, load transfer between LDPE and starch occurred more in the blends with initiators than in the ones without initiators. After the transfer of the load to starch, the high brittleness and too
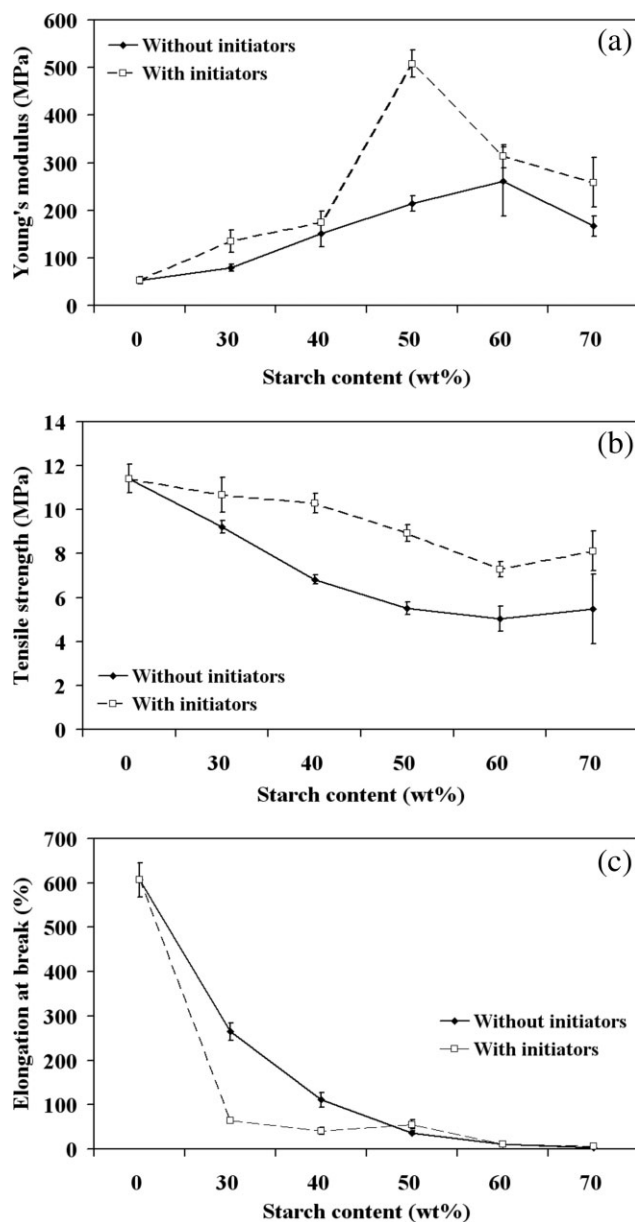

Figure 3 Tensile properties of LDPE/starch blends: (a) modulus, (b) stress at break, and (c) elongation at break.
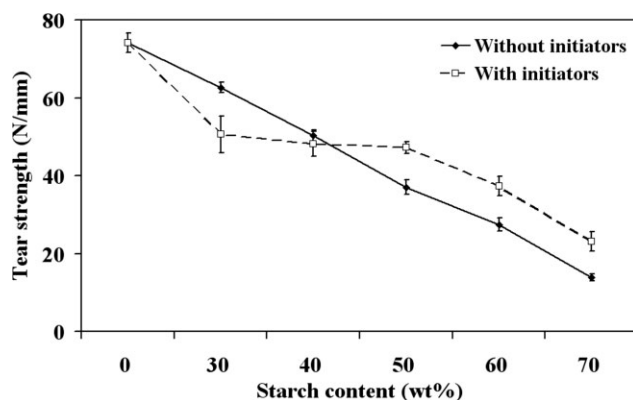
Figure 4 Tear strength of LDPE/starch blends.

large particle size of the starch played important roles in the ductility of the blends. In fact, BPO was able to crosslink LDPE, and this resulted in the decreased elongation at break. The tear strength of all blends containing initiators had to be higher than that of the blends without initiators if crosslinking occurred. However, the results in Figure 4 do not support this assumption. When the starch content was 30 or 40 wt %, the tear strength of the blends without initiators was higher than that of the blends containing initiators. Moreover, a swelling test in *p*-xylene at 80°C revealed that the blends containing initiators dissolved in the solvent. This confirms that crosslinking in LDPE did not take place in these blends.

The yield stress did not change significantly when less than 60 wt % starch was added. It was in the ranges of 8.6–12.6 and 6.1–8.9 MPa for the blends with and without initiators, respectively. Apparently, the initiators increased the yield stress of the blends as well. The initiators did not change the tensile behavior of all blend compositions. With and without initiators, the blends exhibited ductile fracture when the starch content was 50 wt % or less. The blends became brittle and no yield point was detected when the starch content was 70 wt %.

Although the blends containing 60 wt % starch showed a yield point, the elongation at break was as low as 11%. The tear strength of the LDPE/starch blends decreased with increasing starch content, as shown in Figure 4. The initiators had a positive effect in the blends containing 50 wt % or more starch, whereas a significant decrease was found for the blend containing 30 wt % starch. The initiators led to synergistic behavior of the tear strength for certain blend compositions. On the other hand, the synergistic behavior of the modulus and tensile strength due to the initiators appeared in all blend compositions.

Blend characterization

One disadvantage of LDPE/starch blends compared with LDPE is greater hydrophilicity in the blends due to the nature of starch. Practically, a reduction in the hydrophilic behavior of starch is one approach to the improvement of blends. Table I shows the water uptake percentage in the blends with and without initiators. The enhancement of water absorption with increasing starch content and soaking time can be seen. Obviously, water absorption diminished in the blends containing initiators, and a great reduction was observed in the blends containing 50 wt % or more starch. This behavior could have arisen from the good adhesion between LDPE and starch [Figs. 1(d) and 2(b)] and between starch granules [Fig. 2(a)], as described earlier for the blend morphology. This was attributed to a decrease in the surface area of the starch granules in the blends containing initiators. The lesser surface area of starch yielded lower water uptake of the blends. The results for water absorption indirectly implied the presence of a graft copolymer on the starch surface. Different compatibilization methods could generate different characteristics for the blends. For example, PE-*g*-MA in the LDPE blended with plasticized corn starch acted as an emulsifier, and this was attributed to a finer dispersion of the plasticized

TABLE I
Water Absorption of LDPE/Starch Blends

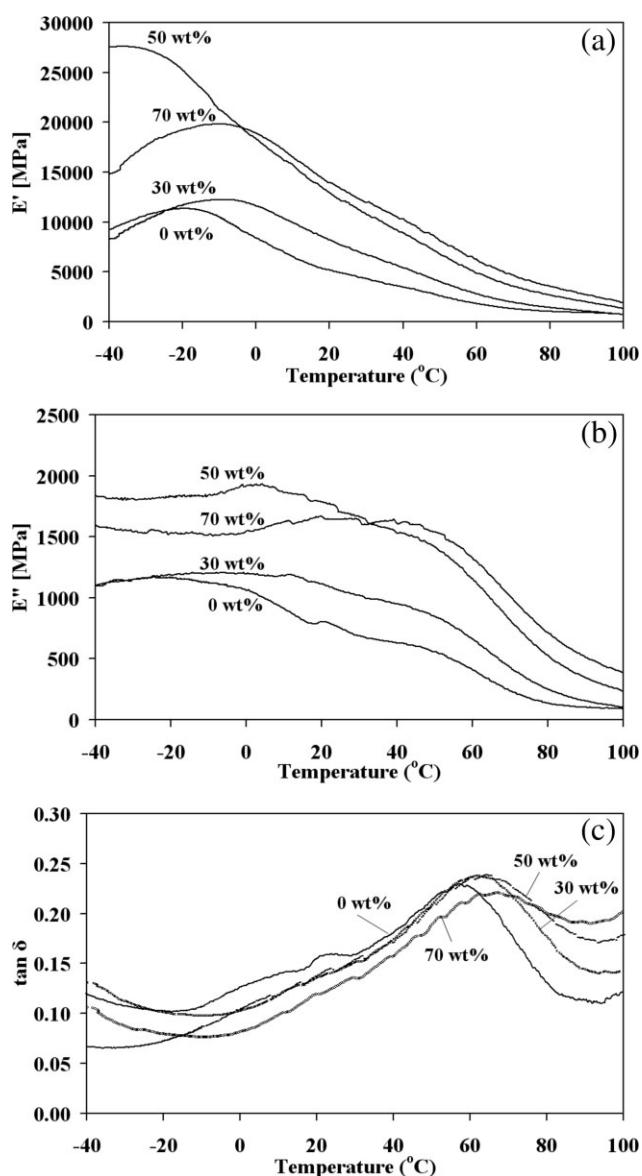| Time (days)	Water uptake (%)					
	Starch content without initiators (wt %)			Starch content with initiators (wt %)		
	30	50	70	30	50	70
1	0.5 ± 0.0	2.0 ± 0.2	8.0 ± 0.3	0.4 ± 0.0	0.7 ± 0.0	2.4 ± 0.2
6	1.0 ± 0.0	4.5 ± 0.5	21.7 ± 0.8	0.9 ± 0.0	1.6 ± 0.0	5.4 ± 0.4
12	1.5 ± 0.0	6.1 ± 0.7	22.9 ± 1.0	1.1 ± 0.1	2.2 ± 0.0	7.2 ± 0.5
18	1.8 ± 0.1	7.4 ± 0.8	22.9 ± 1.1	1.4 ± 0.1	2.6 ± 0.1	8.6 ± 0.5
24	2.1 ± 0.1	8.4 ± 0.9	22.9 ± 1.0	1.6 ± 0.1	2.9 ± 0.0	9.7 ± 0.5
30	2.2 ± 0.1	9.4 ± 1.1	22.9 ± 1.0	1.8 ± 0.0	3.3 ± 0.0	11.0 ± 0.6
60	2.4 ± 0.0	10.9 ± 1.2	22.6 ± 1.1	2.1 ± 0.1	3.8 ± 0.0	12.8 ± 0.7

Figure 5 DMTA thermograms of LDPE/starch blends without initiators: (a) storage modulus (E'), (b) loss modulus (E''), and (c) tan δ.

starch in the LDPE matrix.[1] Those blends showed increased water absorption after the addition of PE-g-MA. Finer particles provide more surface area, and PE-g-MA is more hydrophilic than LDPE. On the contrary, the particle size of unplasticized starch in these blends did not change, although the graft copolymer occurred on the surface of starch. Therefore, those results differed from the findings in this study.

Viscoelastic properties of the blends without initiators are illustrated in Figure 5. Starch increased the storage modulus of the blends; this was similar to the increase in Young's modulus. This result reveals that granular starch acted as a reinforcing filler for LDPE. Starch also increased the loss modulus of the

blends and showed a peak or shoulder at approximately 60°C or less. The tan δ peaks of LDPE and the blends appeared in the temperature range of 57–67°C within the measured temperature range of −40 to 100°C. Three relaxations are commonly observed in DMTA thermograms of polyethylene and are designated the α, β, and γ relaxations.[41,42] The γ relaxation typically appears at a very low temperature (e.g., −150 to −90°C) and is related to the crankshaft motion. The β relaxation is observed between −30 and 20°C, and there is no general conclusion about the origin of molecular motion in this relaxation. However, it is believed that the β process can be attributed to the segmental motions in the noncrystalline phase in either the amorphous phase or the interfacial phase. The α relaxation is usually found at a relatively high temperature (30–120°C), depending on the grade of polyethylene. There were different assumptions involving the α relaxation; for example, this relaxation was due to molecular motion within the crystalline phase or due to deformation of amorphous regions occurring as a result of reorientation within the crystallites. The maximum temperatures of tan δ peaks in LDPE and the blends are listed in Table II. Starch strongly increased the α-transition temperature of LDPE (e.g., from 57 to 67°C after the addition of 70 wt % starch). This finding suggests that starch interfered with the α-relaxation process of LDPE. The α-transition temperature increased more with additional initiators, as illustrated in Table II and Figure 6. The higher transition temperature appeared for all blend compositions. This is probably due to the effect of the graft copolymer. The good interfacial adhesion between starch and LDPE may have obstructed the molecular mobility of LDPE. The effects of initiators on the storage and loss moduli of the blends are demonstrated in Figures 7 and 8, respectively. Small changes in the storage modulus were obtained, and the initiators decreased the loss modulus of the blends, particularly at temperatures below the α-transition temperature. Although starch and initiators played a role in the α-relaxation process of

TABLE II
Temperature at the Tan δ Maximum (α-Transition Temperature) for LDPE/Starch Blends With and Without Initiators

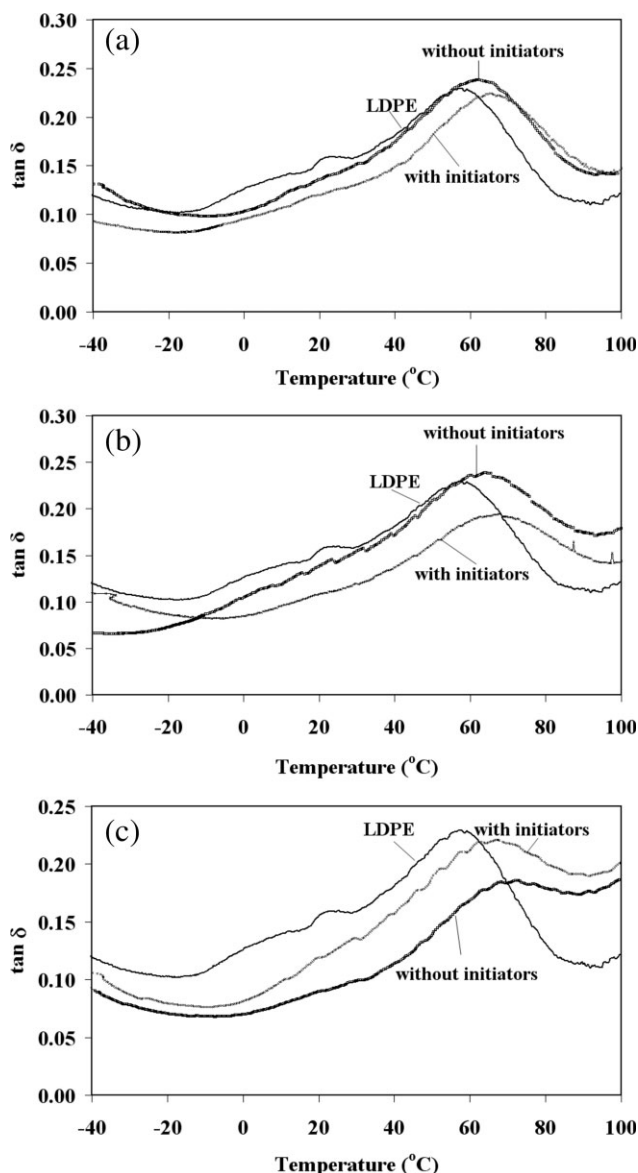| Starch content (wt %)	Temperature at the tan δ maximum (°C)	
	Without initiators	With initiators
0	57.1	57.1
30	62.0	65.1
50	64.4	67.1
70	67.2	72.5

Figure 6 Tan δ–temperature curves of LDPE/starch blends containing 30–70 wt % starch: (a) 30, (b) 50, and (c) 70 wt % starch.

LDPE; there were only small changes in the crystallization and melting temperatures and degree of crystallinity of LDPE in the blends according to the DSC measurements listed in Table III. The degree of crystallinity of the blends containing 30 or 70 wt % starch increased only 1%, and that of the 50 wt % starch sample increased only 5%. These values were not high enough to affect the mechanical properties and water uptake of the blends. Therefore, changes in the properties after the loading of the initiators were not due to the increase in the crystallinity. No significant changes in the crystallization and melting temperatures were reported in the LDPE/corn starch blends with and without PE-g-MA.[6] DSC thermograms of LDPE and the blends recorded from the

first heating scan and the first cooling scan showed a change in the heat capacity at 55.1–56.5°C, but this disappeared in the second heating scan. This phenomenon was also reported by other researchers[6,43] and was claimed to be the glass-transition temperature of LDPE.[43] It is inconclusive in this study because it was not detected in the second heating scan. However, this transition temperature may be related to the α relaxation, which was observable from DMTA thermograms.

The TGA results for the blends with and without initiators produced similar thermograms, as shown in Figure 9. Two decomposition temperatures at approximately 350 and 500°C were noticed for the
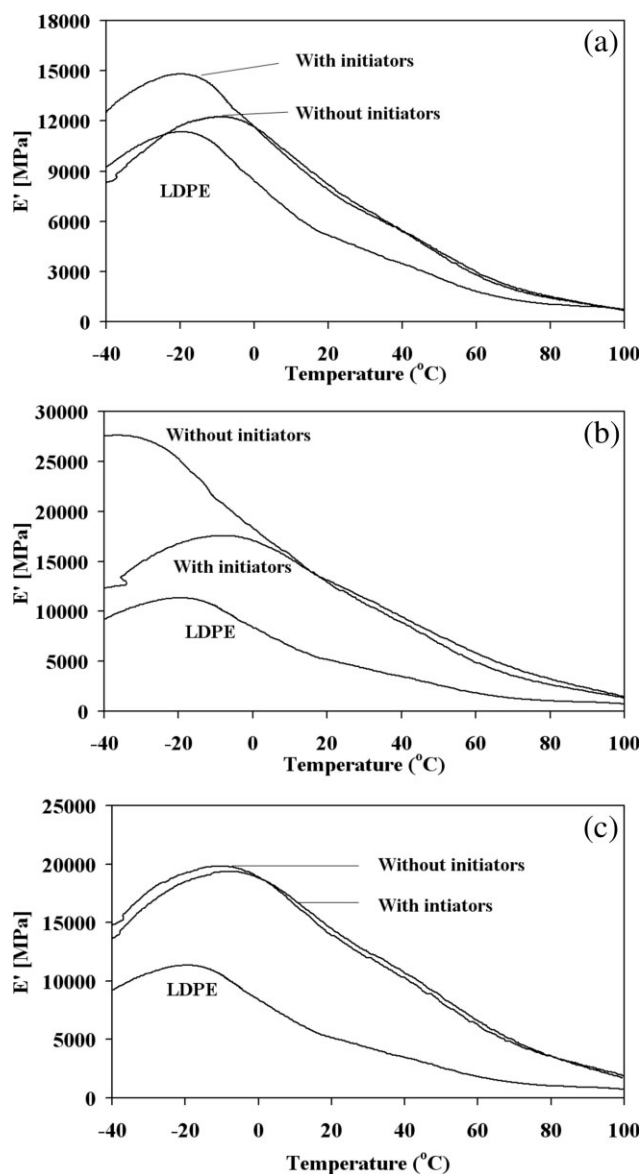

Figure 7 Storage modulus (E')–temperature curves of LDPE/starch blends with and without initiators: (a) 30, (b) 50, and (c) 70 wt % starch.
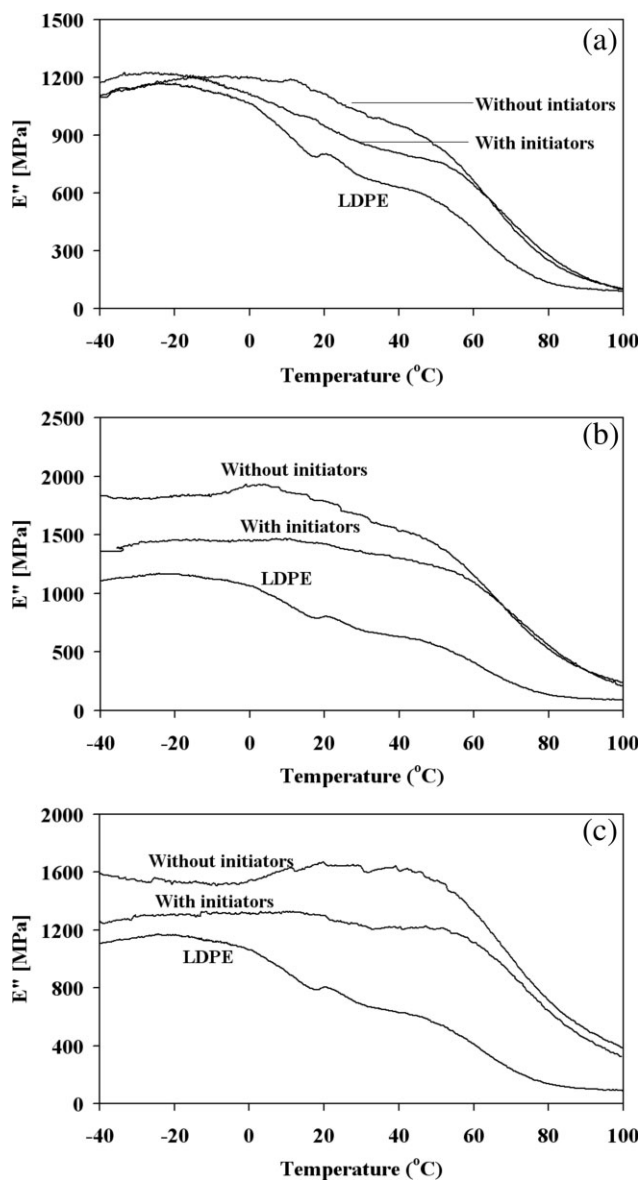
Figure 8 Loss modulus (E'')–temperature curves of LDPE/starch blends with and without initiators: (a) 30, (b) 50, and (c) 70 wt % starch.

TABLE III
Crystallization Temperature (T_c), Melting Temperature (T_m), and Degree of Crystallinity (X_c) of LDPE/Starch Blends With and Without Initiators

Starch (wt %)	Without initiators			With initiators		
	T_c (°C)	T_m (°C)	X_c (%)	T_c (°C)	T_m (°C)	X_c (%)
0	94.0	109.9	20.8	—	—	—
30	95.0	109.5	19.1	95.8	109.2	20.1
50	95.3	109.4	15.2	95.6	109.5	20.1
70	95.6	109.5	17.3	95.1	108.7	16.0

the relative lost weight of the blends increased tremendously with increasing time duration of the soil burial and starch content. The maximum weight loss at 24 weeks increased from 10 to 70% when the starch concentration was increased from 40 to 70 wt %. During soil burial, biodegradation in the starch phase took place, generating weight loss of the samples. Thus, more degradation of the samples provided more weight loss. Remarkably, a great reduction in the weight loss was achieved when initiators were added to the blends. With initiators, the weight of the blends containing 50 wt % or less starch remained constant or decreased slightly ($\leq 3\%$), whereas the blends containing 60 or 70 wt % starch showed a maximum weight loss of 18 or 26%,
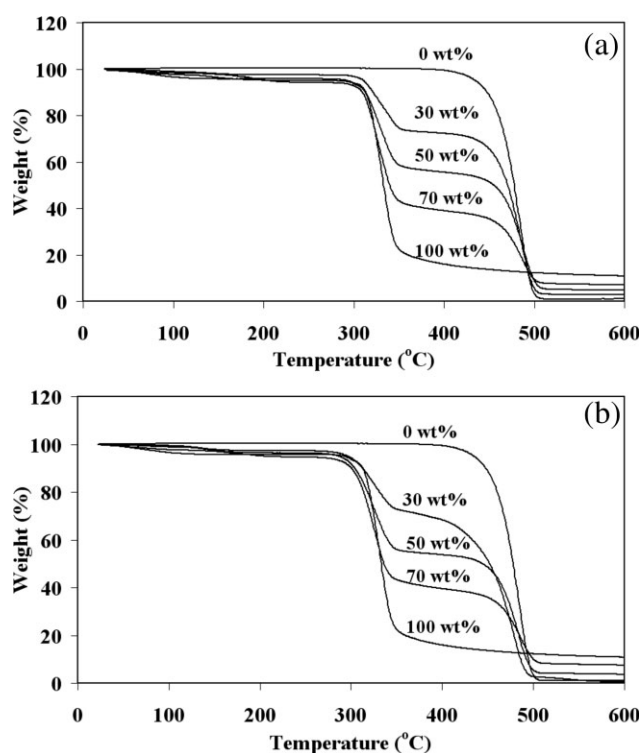
blends. The amount of ash in the blends also corresponded to the starch content. The initiators showed no effect on the degradation behavior of the fresh samples (i.e., samples not soil-burial-tested). The effect of increased interfacial adhesion due to initiators on degradation was observed in the soil-burial-tested samples, as discussed next.

Characteristics after the soil burial test

One of the most common methods for estimating the biodegradation rate is the weight loss of samples during soil burial. Figure 10 exhibits the weight loss of samples according to eq. (1). Without initiators,

Figure 9 TGA thermograms of LDPE/starch blends: (a) without initiators and (b) with initiators.
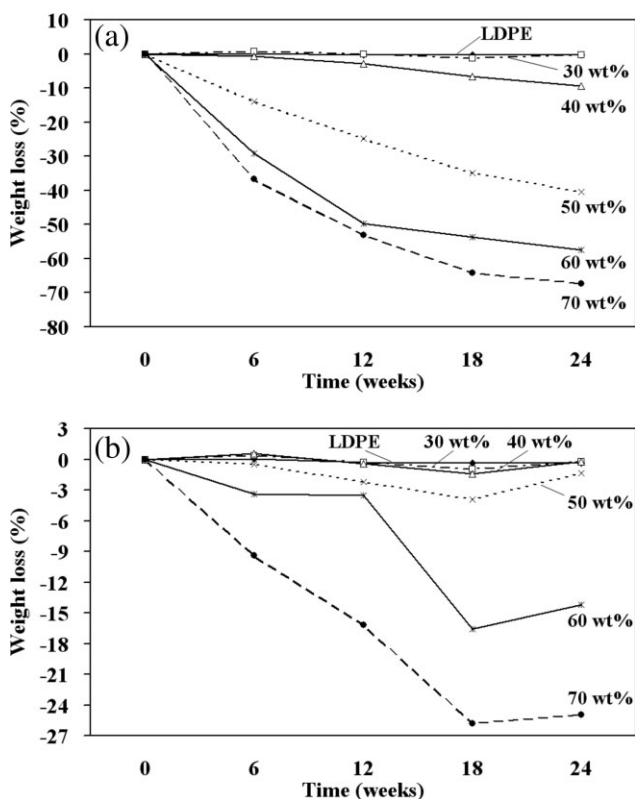
Figure 10 Weight loss after the soil burial test of LDPE/starch blends: (a) without initiators and (b) with initiators.

respectively. Slight changes in the weight loss of the blends containing 30 wt % starch were observed in accordance with observations by others.[1] Natural macromolecules such as starch and cellulose are generally degraded in a biological system by hydrolysis followed by oxidation.[44] The decrease in water absorption in the blends containing initiators caused a low biodegradation rate because water is essential for fungus growth and physical factors affecting the activity of enzymes. Figure 10(b) substantiates the assumption that the graft copolymer occurred on the surface of the starch granules and inhibited or delayed the biodegradation of the starch portion.

After the soil burial test, the blends containing 50 or 70 wt % starch were selected to be investigated by TGA. Figure 11 presents TGA thermograms of the blends with and without initiators after soil burial testing of 6–24 weeks. Samples tested for longer burial times showed lower starch contents for all the blends, except the blend containing 50 wt % starch with initiators [Fig. 11(c)], which was less affected by the burial time. For example, samples at 24 weeks [Figure 11(a,b)] exhibited smaller curve inflection at the degradation temperature of starch (300–400°C) than samples at 6 weeks. Without starch, no curve inflection occurred in the temperature range of 300–400°C in the sample, as illustrated in Figure 9. The
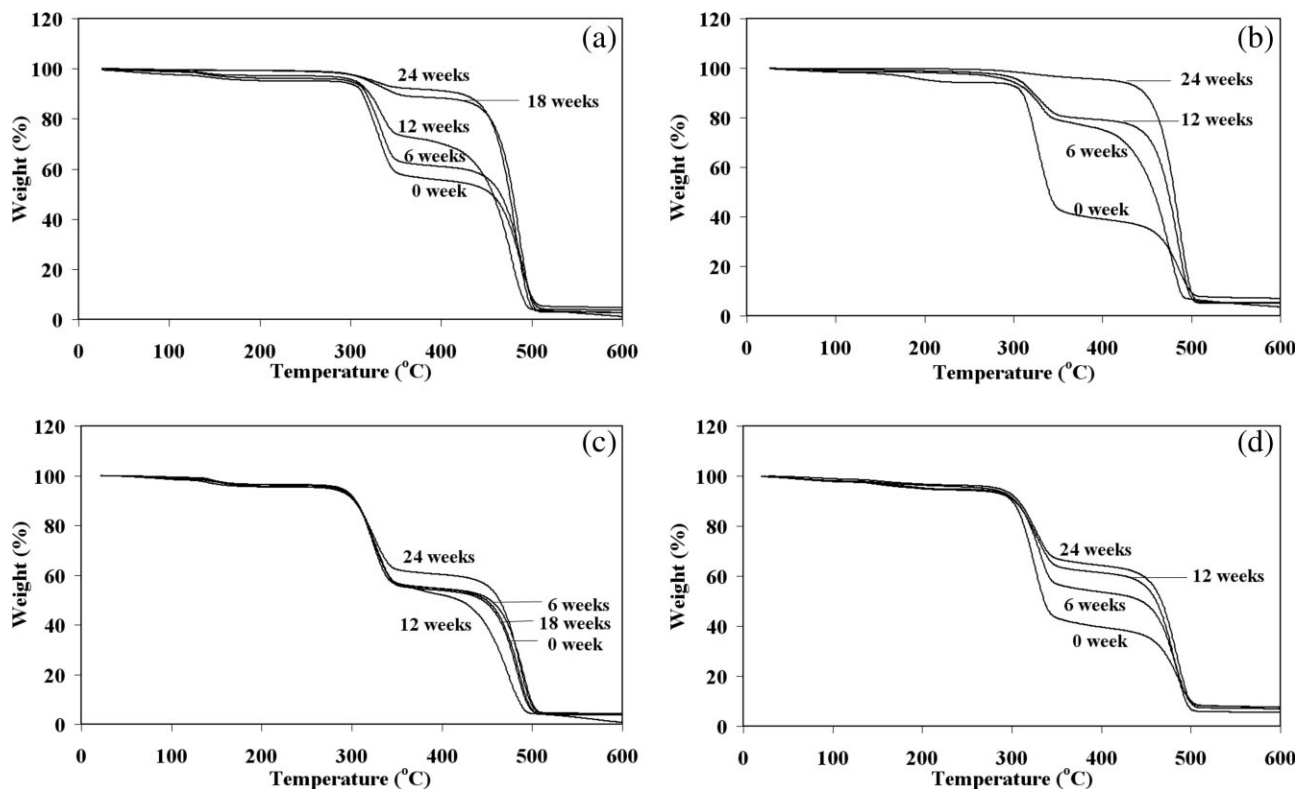

Figure 11 TGA thermograms of LDPE/starch blends after the soil burial test: (a) 50 wt % starch without initiators, (b) 70 wt % starch without initiators, (c) 50 wt % starch with initiators, and (d) 70 wt % starch with initiators.
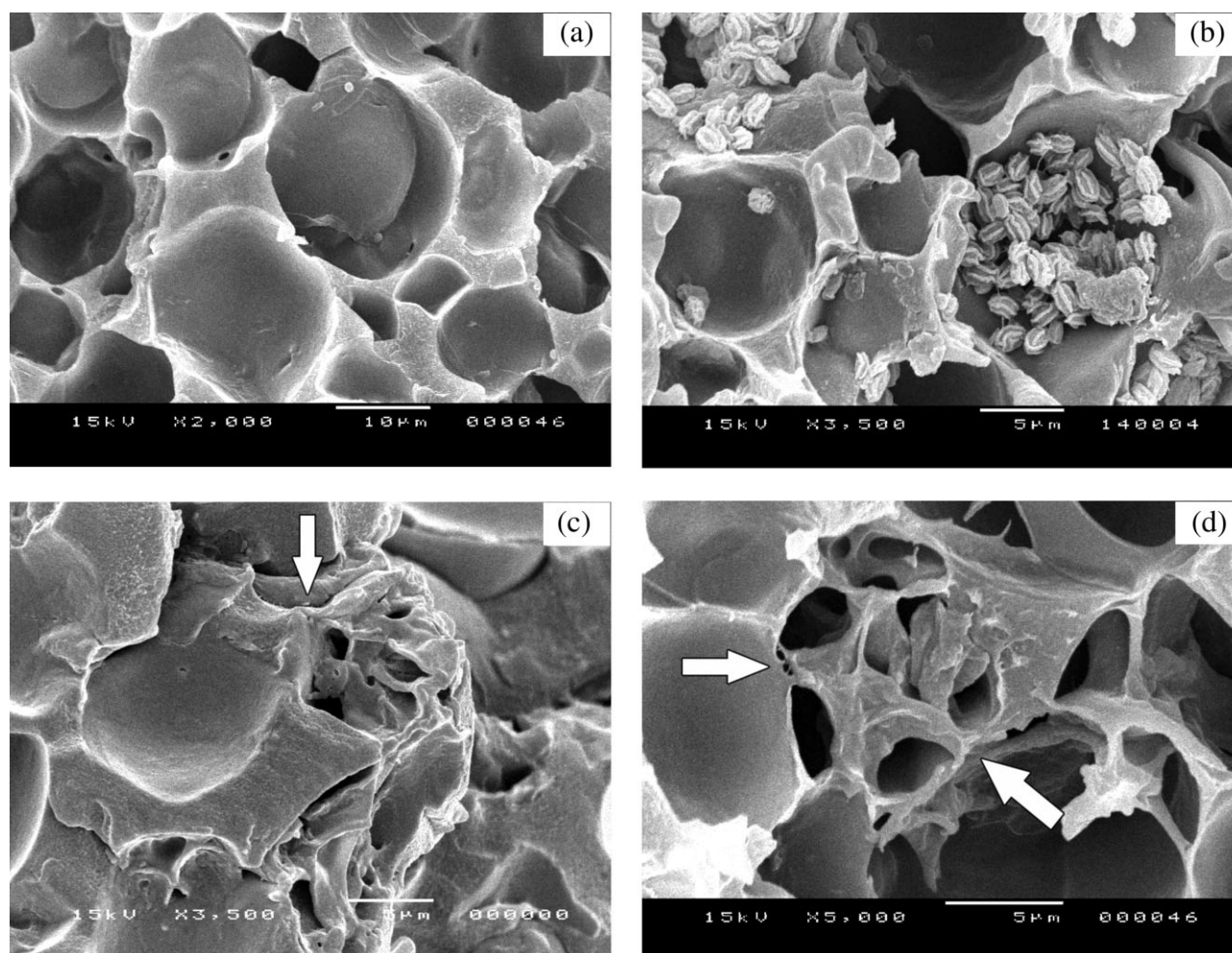
Figure 12 SEM micrographs of freeze-fractured surfaces of LDPE/starch blends containing 70 wt % starch with and without initiators after the soil burial test for 24 weeks: (a,b) without initiators and (c,d) with initiators.

depth of the curve inflection due to starch degradation in the samples containing initiators [Fig. 11(c,d)] was higher than that of the ones without initiators [Fig. 11(a,b)] with the same time interval for the soil burial test. This revealed that after soil burial testing, the blends containing initiators consisted of starch more than those without initiators. These TGA results also confirm the improvement of the interfacial adhesion of the blends due to the addition of initiators. These findings coincide with the results of weight loss after soil burial testing. Both the weight loss and the TGA test indicated that the biodegradation rate of starch in the samples decreased with the addition of initiators.

Freeze-fractured surfaces of blends containing 70 wt % starch were determined with SEM and are shown in Figure 12. Spores of microorganisms, as displayed in Figure 12(b), were observed in all samples. Figure 12(a,b) represents a sample without initiators, and no evidence of good adhesion between the starch granules and LDPE matrix can be seen. On the contrary, Figure 12(c,d) shows that the partly

biodegraded starch granule well adhered to the LDPE matrix, as indicated by the arrow. These SEM micrographs harmonize with the results obtained from weight-loss and TGA measurements explained earlier and also support the enhancement of the compatibilization of LDPE/starch blends due to the addition of PPS and BPO.

CONCLUSIONS

The compatibility of LDPE/starch blends was enhanced by the use of PPS and BPO as initiators for LDPE and starch during melt blending, and this was attributed to the formation of a graft copolymer between LDPE and starch on the surface of the starch granules. The formation of the graft copolymer increased the interfacial adhesion between the starch granules and LDPE. The formation of the graft copolymer and the enhancement of interfacial adhesion due to the addition of PPS and BPO were supported by the following phenomena: the increase in the modulus and tensile strength, the increase in

the α-relaxation temperature, the decrease in the water absorption of fresh samples, and the decrease in the weight loss of samples and the biodegradation rate of starch after the soil burial test. SEM micrographs also provided strong evidence of good adhesion between the starch granules and LDPE matrix before and after the soil burial test. On the basis of this study, it is essential to use both PPS and BPO as initiators to obtain optimum properties.

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