Biodegradation of Blends of Polyethylene-Octene Elastomer with Starches by Fungi

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Received 21 April 2008; accepted 18 June 2009
DOI 10.1002/app.30982
Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Five fungi including *Aspergillus niger, Penicilium pinophilum, Chaetoomium globsum, Gliocladium virens* and *Aureobasium pullulans* were used to investigate the biodegradation of starch-based elastomers: polyethylene-octene elastomer (POE)/starch and grafted POE-*g*-MAH/starch copolymer blends. The viability of the composite spore suspensions were measured before estimating the fungal growth on the surface of specimens. The weight loss, morphology and mechanical properties of the blended specimens were measured using scanning electron microscopy and a mechanical properties tester after 28 days of culturing. The spore suspension in the experiment showed good viability. Pure POE and POE-*g*-MAH did not allow significant fungal growth. Pure POE did not lose weight or have a change in tensile strength, but pure POE-*g*-MAH lost about 0.07% of its weight with a slight reduction in tensile strength during culture period. There was heavy growth on the surface of POE/starch and POE-*g*-MAH/starch blends after 28 days of culturing. The weight loss of POE/starch and POE-*g*-MAH/starch blends increased with increasing starch content. POE-*g*-MAH/starch blends tended to lose more weight than POE/starch blends. After biodegradation, the surface of POE/starch and POE-*g*-MAH/starch blends became rough with many holes and cracks, indicating that the films were eroded by the fungi. Tensile strength of POE/starch and POE-*g*-MAH/starch blends decreased after culturing because of microbial attack. On the contrary, elongation at break of POE-*g*-MAH/starch blends increased after biodegradation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3574–3584, 2009

Key words: polyethylene-octene elastomer; starch; blends; biodegradation; fungi

INTRODUCTION

Polyolefin materials, such as polyethylene, polypropylene, and polyethylene-octene elastomer (POE), have several advantages for use in various industrial fields but cause global environmental problems because of their nonbiodegradable nature.[1] Therefore, there is a need to find environment-friendly materials to replace them, which must be biodegradable while retaining the physical properties of the polyolefin polymers. Biobased polymers which include biocomposites and polymer blends with biodegradable components, are some of the materials that are able to solve the environmental pollution problem.[2–5]

Starch is a natural polymer, which is cheap, plentiful, renewable, and fully biodegradable. It can be blended with various polymers to produce biodegradable composites. In recent years, polymer/starch blends have been studied widely, including PE/starch,[6,7] LDPE/starch,[8–10] PVA/starch,[11,12] PVB/starch,[13] EVOH/starch,[14,15] polyester/starch,[16,17] PCL/starch,[18–20] PHB/starch,[21] and PLA/starch.[22,23] POE, which has the thermoplastic properties of plastic and crosslinking structure of rubber has received much attention. Unfortunately, POE does not naturally degrade, which makes it inconvenient to use. POE is blended with starch to overcome its shortages. This not only reduces the cost of POE, but also solves environmental pollution problem.

To develop degradable composites, it is very important to establish evaluation criteria for the material. Many methods are used to evaluate biodegradability, such as the soil burial method, direct microorganism growth method or enzyme decomposition method. Kim et al.[24] investigated the biodegradability of PBS biocomposite filled with rice-husk flour in natural and aerobic composted soil, and concluded that the use of biocomposites can reduce the environmental problems associated with waste pollution. Marqués-Calvo et al.[25] used two fungal lipases, two bacteria, and two filamentous fungi

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to investigate the enzymatic and microbial degradability of PET and PET copolyesters. Saroja et al.[26] studied the biodegradation of starch-*g*-polyacrylonitrile by *Bacillus cereus* isolated from soil.

In this study we investigated the biodegradation of POE/starch and POE-*g*-MAH/starch blends by fungi. The viability of composite spore suspension was measured at the beginning of experiment. The fungal growth on the surface of specimens was noted every week during the culturing. The weight loss, morphological changes, and mechanical properties of blended specimens before and after biodegradation were measured using scanning electron microscopy (SEM) and mechanical properties tester.

EXPERIMENTAL

Materials

POE (Type 8150) was supplied by Dow Chemical Corp. Gelatinized waxy corn starch was supplied by TianJin TingFung Starch Development Co. Maleic acid anhydride (MAH) was supplied by Shandong Zibo Qifeng Organic Chemical Limited Company. Dicumyl peroxide (DCP) was supplied by Shanghai Gaoqiao Chemical Company. POE-*g*-MAH copolymer was made in our laboratory with a grafting percentage of about 0.8%.

Sample preparation

POE-*g*-MAH copolymer

Grafting POE with MAH was conducted using a corotating intermeshing twin-screw extruder with a screw configuration adapted for grafting. 0.08–0.1 wt % DCP was used as the initiator, and the content of MAH was 2 wt %. POE, MAH, initiator, and caprolactam were blended uniformly with a little dispersant, and then, the mixtures were extruded with a twin screw extruder (TE-35). The temperature profile during the extrusion was 100/140/170/190/190/180°C, and the temperature of the handpiece was 180°C. The screw speed was 60 rpm, and the feeding speed was 300 rpm.[27]

Blend preparation

Before blending, POE and POE-*g*-MAH were dried for at least 3 h in vacuum at 40°C, while the starch was dried in an oven at 105°C for 24 h. For POE/starch and POE-*g*-MAH/starch blends, five different starch contents were used: 0, 10, 20, 30, and 40 wt %. During the extrusion, the temperature profile was 120/140/140/120°C (from feed zone to die). The screw speed was 50 rpm, and the blend time was 8 min. The blends were compression molded into 1.5 mm thick sheets in a plate vulcanizing press (XLB-D) at 140–150°C and 6–8 MPa for 3 min.

Microorganisms

The biodegradation of the samples was studied in microbiological environment according to the ASTM G21 standard, which is used to measure the resistance of synthetic polymeric materials to fungi. The fungi used in the growth test were *Aspergillus niger* ATCC 9642, *Penicilium pinophilum* ATCC 11,797, *Chaetoomium globsum* ATCC 6205, *Gliocladium virens* ATCC 9645, and *Aureobasium pullulans* ATCC 15,233, which were obtained from Guangzhou Institute of Microbiology. Maintained cultures of these fungi were inoculated separately on a potato dextrose agar medium. The stock cultures were kept at approximately 4°C for not more than 4 months. Used subcultures incubated at 28–30°C for 7 to 20 days in preparation of the spore suspension.

Nutrient-salts solution preparation

0.7 g K_2HPO_4, 0.7 g KH_2PO_4, 0.7 g MgSO4·7H_2O, 1.0 g NH_4NO_3, 0.005 g NaCl, 0.002 g FeSO4·7H_2O, 0.002 g $ZnSO_4$·7H_2O, and 0.001 g $MnSO_4$·H_2O were dissolved in 1000 mL of water. The pH of solution was adjusted to 6.0 by the addition of 0.01 mol/L NaOH solution. The solution was sterilized by autoclaving at 121°C for 20 min.

Nutrient-salts agar preparation

2% (v/v) agar was added into nutrient-salts solution and heated. The culture was sterilized by autoclaving at 121°C for 20 min.

Spore suspension preparation

A sterile 10 mL portion of the solution containing 0.05% of a nontoxic wetting agent was poured into a subculture of each fungus. The surface growth from the culture of the test organism was scraped gently with a nichrome inoculating wire. The spores were poured into a sterile 150 mL glass-stoppered Erlenmeyer flask containing 30 mL of sterile water and 10 solid glass beads, 5 mm in diameter. The flask was shaken vigorously to liberate the spores from the fruiting bodies and to break up the spore clumps. Mycelial fragments were removed through filtering the shaken suspension. The filtered spore suspension was centrifuged aseptically and the supernatant liquid was discarded. The residue was resuspended in 50 mL of sterile water and centrifuged. The spores obtained from each of the fungi were washed in this manner three times. The final washed residue was diluted with sterile nutrient-

TABLE I
Fungal Growth on the Surface of the Specimens

Sample	Microorganism growth on specimens			
	1st week	2nd week	3rd week	4th week
Pure POE	0	0	0	0
POE/starch 90/10	+ +	+ +	+ +	+ + +
POE/starch 80/20	+ + +	+ + +	+ + + +	+ + + +
POE/starch 70/30	+ + + +	+ + + +	+ + + +	+ + + +
POE/starch 60/40	+ + + +	+ + + +	+ + + +	+ + + +
Pure POE-*g*-MAH	0	0	0	0
POE-*g*-MAH/starch 90/10	+ +	+ +	+ + +	+ + + +
POE-*g*-MAH/starch 80/20	+ + +	+ + +	+ + + +	+ + + +
POE-*g*-MAH/starch 70/30	+ + + +	+ + + +	+ + + +	+ + + +
POE-*g*-MAH/starch 60/40	+ + + +	+ + + +	+ + + +	+ + + +

0, nil growth; +, traces of growth; + +, light growth; + + +, medium growth; + + + +, heavy growth.

salts solution in such a manner that the resultant spore suspension should contain 10^7 spores/ml as determined with a counting chamber. Each individual organism used in the test underwent this operation. Equal volumes of the resultant spore suspension were blended to obtain the final mixed spore suspension. The spore suspension was prepared fresh each day.

Sample sterilization

POE/starch and POE-*g*-MAH/starch blends were sterilized by immersion in a 70% (v/v) ethanol solution for 30 min. They were filtered and dried overnight at room temperature.

Biodegradation in an agar medium without a carbon source

Sufficient nutrient-salts agar solution was poured into suitable sterile dishes to provide a solidified agar layer. After the agar solidified, the specimens were placed on the surface of the agar. The surfaces of the specimens were sprayed with a sterilized atomizer using the composite spore suspension until the entire surface was moistened with the spore suspension. The inoculated test specimens were covered and incubated at 28 to 30°C and not less than 85% relative humidity for 28 days.

Characterization of the POE/starch and POE-*g*-MAH/starch blends

Viability was tested by inoculating sterilized filter paper with the spore suspension using the sterilized atomizer. The inoculated filter papers were incubated at 28 to 30°C at a relative humidity not less than 85% and examined after 14 days of incubation. After biodegradation, the growth of the fungus on specimens in the culture medium was judged, and the visual rating of fungal growth was decided. The rate of fungal growth was estimated in accordance to ASTM G21 where the recorded parameter (S) is the fraction of the surface covered by fungi [nil growth (0), $S < 10\%$ (+, traces of growth), $10 \leq S < 30\%$ (+ +, light growth), $30 \leq S < 60\%$ (+ + +, medium growth), and $S \geq 60\%$ (+ + + +, heavy growth)]. After biodegradation, the fungi were cleared and the specimens were washed, dried, and weighed. The weight loss of specimens (W) was measured according to the weight of specimens before (W_0) and after biodegradation (W_1).

$$W\ (\%) = \frac{W_0 - W_1}{W_0} \times 100\%$$

The surface microstructure of POE/starch and POE-*g*-MAH/starch blends were observed before and after biodegradation by using a JSM-6330F field emission SEM. The specimens were coated with a gold film in an automatic sputter coater (Polaron) to avoid charging under an electron beam. Each specimen's mechanical properties were tested before and after biodegradation by using a Hounsfield THE 10K-S Mechanical Properties Tester with a loading rate of 50 mm/min.

RESULTS AND DISCUSSION

Fungal growth

The effects of fungal growth on the starch-based specimens were observed and recorded in Table I. Figure 1(b–k) shows photographs of the Petri dishes

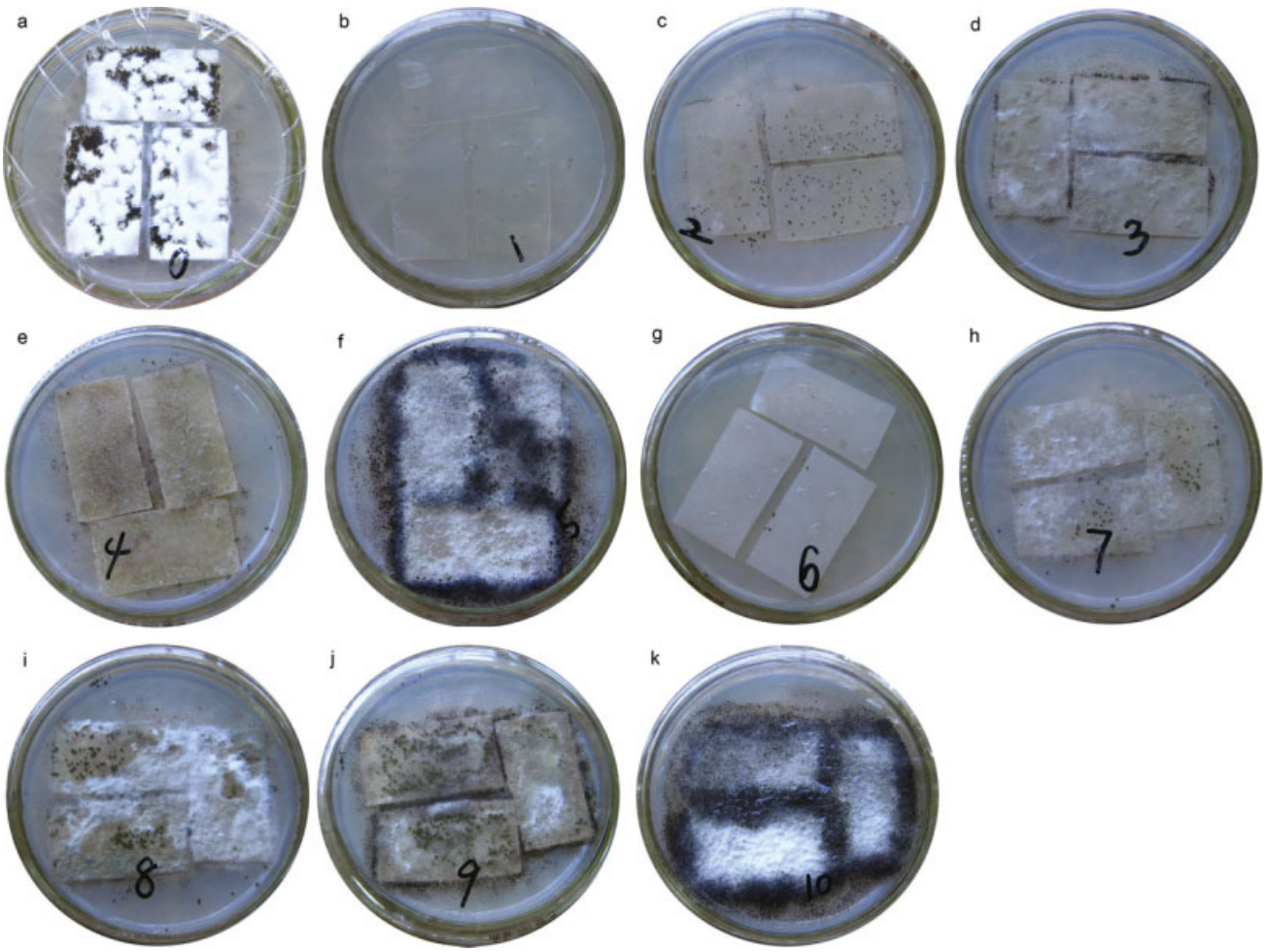

Figure 1 Photographs of Petri dishes with POE/starch and POE-*g*-MAH/starch blends after 28 days of culturing: (a) filter paper; (b) pure POE; (c) POE/starch 90/10; (d) POE/starch 80/20; (e) POE/starch 70/30; (f) POE/starch 60/40; (g) pure POE-*g*-MAH; (h) POE-*g*-MAH/starch 90/10; (i) POE-*g*-MAH/starch 80/20; (j) POE-*g*-MAH/starch 70/30; (k) POE-*g*-MAH/starch 60/40. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

with POE/starch and POE-*g*-MAH/starch blends after 28 days of culturing. Colonies of the fungi were observed for initial 7 days of incubation on the surface of POE/starch and POE-*g*-MAH/starch films. No significant growth was observed on the surface of pure POE and pure POE-*g*-MAH specimens by the end of the experiment. The viability of spore suspension was also measured before testing the specimens. Sterilized filter papers were placed on the surface of agar inoculated by spraying with spore suspension, and incubated at proper conditions. The viability results [Fig. 1(a)] showed that there was copious growth on all filter papers with more than 60% of its area covered with heavy growth. Therefore, the composite spore suspension had good viability and could be used to test specimens. As clearly seen from the Figure 1(b–k) photographs, there was evidence that fungal growth of specimens containing 10 and 20 wt % starch increased with culturing time. The covered area with fungi of specimens containing 30 and 40 wt % starch was more than 60% in just the first week, which is heavy growth. With increased culturing time, fungal growth became denser. We also found that the rate of fungal growth increased with the amount of starch in the blends. Because starch is a natural polymer it can be readily used as a carbon source by the fungus. As the starch content increases, the starch phase becomes more continuous, which can be more easily accessed by the microorganisms. When the starch content was low, the starch may remain encapsulated in the synthetic polymer matrix, which made it difficult for the microorganisms to access and use as a source of carbon.[28] In such a case, the fungal growth will be slow. The synthetic polymer did not serve as an efficient carbon source. So by blending the two, the starch component is degraded more readily by the fungal, leaving POE or POE-*g*-MAH almost unaffected. Fungal growth was faster in POE-*g*-MAH/

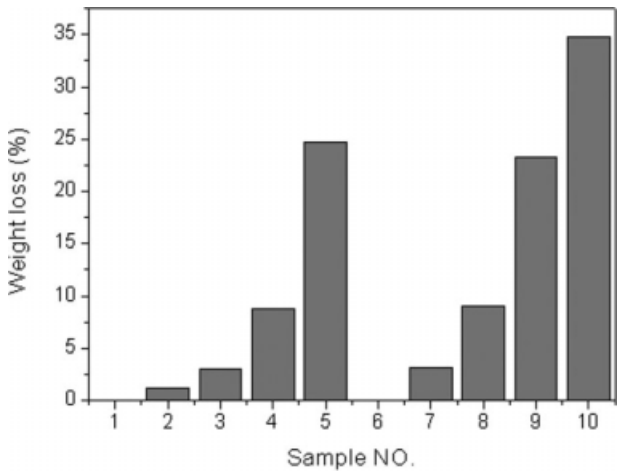

Figure 2 Weight loss of POE/starch and POE-*g*-MHA/starch blends after 28 days of culturing: 1. pure POE; 2. POE/starch 90/10; 3. POE/starch 80/20; 4. POE/starch 70/30; 5. POE/starch 60/40; 6. pure POE-*g*-MAH/starch; 7. POE-*g*-MAH/starch 90/10; 8. POE-*g*-MAH/starch 80/20; 9. POE-*g*-MAH/starch 70/30; 10. POE-*g*-MAH/starch 60/40.

starch blended specimens than in POE/starch blended specimens, therefore, POE-*g*-MAH/starch biodegraded more easily. This may be because of the acidic POE-*g*-MAH, which has anhydride groups, can react with the hydroxyl groups of starch forming ester groups that can be more readily accessed by the microorganisms.[29] The colonization of the specimens' surface because of microorganisms led to a dramatic decrease of the mechanical characteristics of the POE/starch and POE-*g*-MAH/starch films.[30]

Weight loss

The weight loss of POE/starch and POE-*g*-MAH/starch blends after 28 days is shown in Figure 2. Pure POE (No. 1) specimen lost the least weight, which is almost no weight loss. POE-*g*-MAH/starch 60/40 specimen (No. 10) lost the most weight at about 35%. Blends with 40 wt % starch content did not lose all their starch content during the culturing time. A possible explanation for this result is that starch inclusions in some area of blend are well protected and not easily accessible to fungal action.[31] The weight loss of POE/starch 90/10, 80/20, 70/30, and 60/40 blends were 1.14, 3.02, 8.82, and 24.73%, respectively. The increasing starch content helped to speed up the weight loss of POE/starch blends. This effect occurs because starch is the sole carbon source available to the microorganisms. Whereas when starch content was less than 30 wt %, the weight loss was less than 10%. Wool et al.[32] described the invasion of polymer/starch matrix by microorganisms in terms of a scalar percolation theory. They found that the minimum level of starch needed to achieve connectivity between starch domains, and therefore accessibility of the starch to biodegradation, is the percolation threshold. According to their simulation experiments, this level was found to be about 31% starch by volume. Below this level the theoretical analysis, as well as acid hydrolysis studies, showed less than 10% of the starch was accessible to hydrolysis. In our experiments, we found that the minimum level of starch needed to be accessible to biodegradation for POE/starch blends was 30% by weight.

The weight loss of pure POE-*g*-MAH specimen was 0.07%, and POE-*g*-MAH/starch 90/10, 80/20, 70/30, 60/40 blends were 3.09, 9.07, 23.28, and 34.79%, respectively. With increasing starch content, the weight loss of POE-*g*-MAH/starch blends also increased. Also, POE-*g*-MAH/starch specimens lost more weight than comparable POE/starch blends. This indicates that POE-*g*-MAH/starch blends degraded by fungi more easily, which agrees with earlier results. Starch components and ester reactants of POE-*g*-MAH/starch blends were both consumed.

Morphology

SEM photographs of the specimens after culturing are shown in Figures 3 and 4, which seems to corroborate the findings from the weight loss measurements. The surfaces of pure POE and POE-*g*-MAH specimens were flat and smooth, with no traces of biodegradation such as holes found. For the POE/starch and POE-*g*-MAH/starch blends with 10 wt % starch content, a few small holes were found on the surface of the specimens. This result is because of the limited accessibility of starch to the fungus, thus keeping the biodegradation relatively difficult. But for specimens containing 20 wt % starch, more and larger holes and cracks were observed on the surface compared with 10 wt % starch content. The film surface became rough due to starch consumption. There was significant fragmentation of the surface layers and large holes were clearly evident in specimens containing 30 and 40 wt % starch. In the micrograph shown in Figures 3(d,e) and 4(d,e), a few black droplets surrounded by some white traces were observed. Black droplets were pores created by microorganism and white spots were the sites with less thickness compared with the unaffected area of polymer films.[31] With increasing starch content, more and larger holes and cracks were found on the surface of specimens. This indicates that specimens with higher content of starch can be eroded by fungi more easily, and has better biodegradation. The degradation formed a very rough topography creating

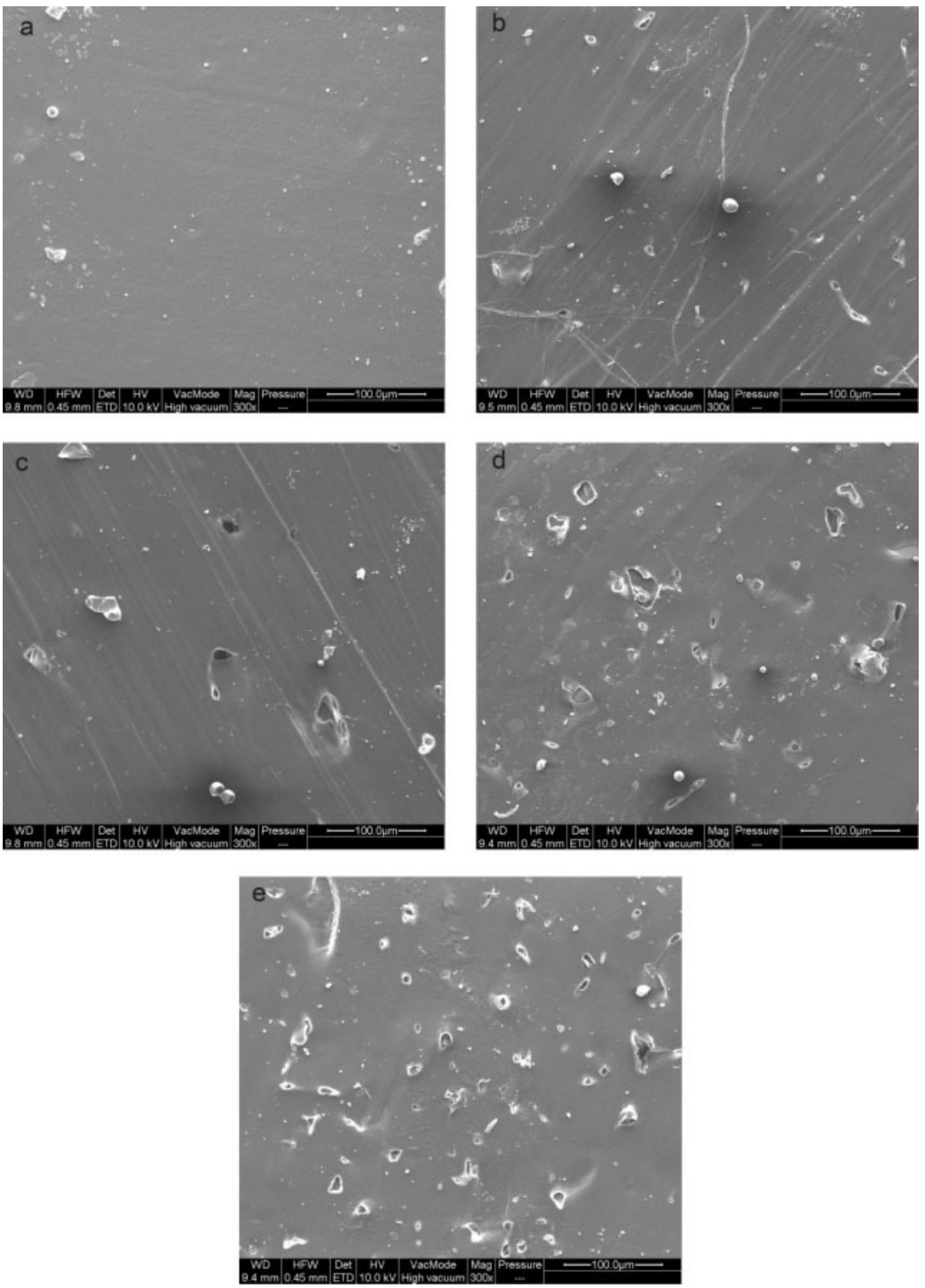

Figure 3 Scanning electron micrograph of POE/starch blends after 28 days culturing: (a) pure POE; (b) POE/starch 90/10; (c) POE/starch 80/20; (d) POE/starch 70/30; (e) POE/starch 60/40.

larger surface area, which helps fungi to colonize. The biodegradation of blended specimens is mostly due to starch consumption. As a sole carbon source, starch is an important agent facilitating the binding of fungal hyphae because it provides nucleating sites for the growth of fungal hyphae resulting in the degradation of POE/starch and POE-*g*-MAH/starch blends.[33] Also, highly relative humidity and appropriate temperature provide an advantaged environment for fungal growth, and the water absorption of specimens speeds up the biodegradation.

Before biodegradation, the surface of POE/starch 60/40 (in Fig. 5) and POE-*g*-MAH/starch 60/40 (in Fig. 6) blended specimens was smooth and flat. However, after culturing for 28 days, the surface of the specimens subjected to fungus was significantly

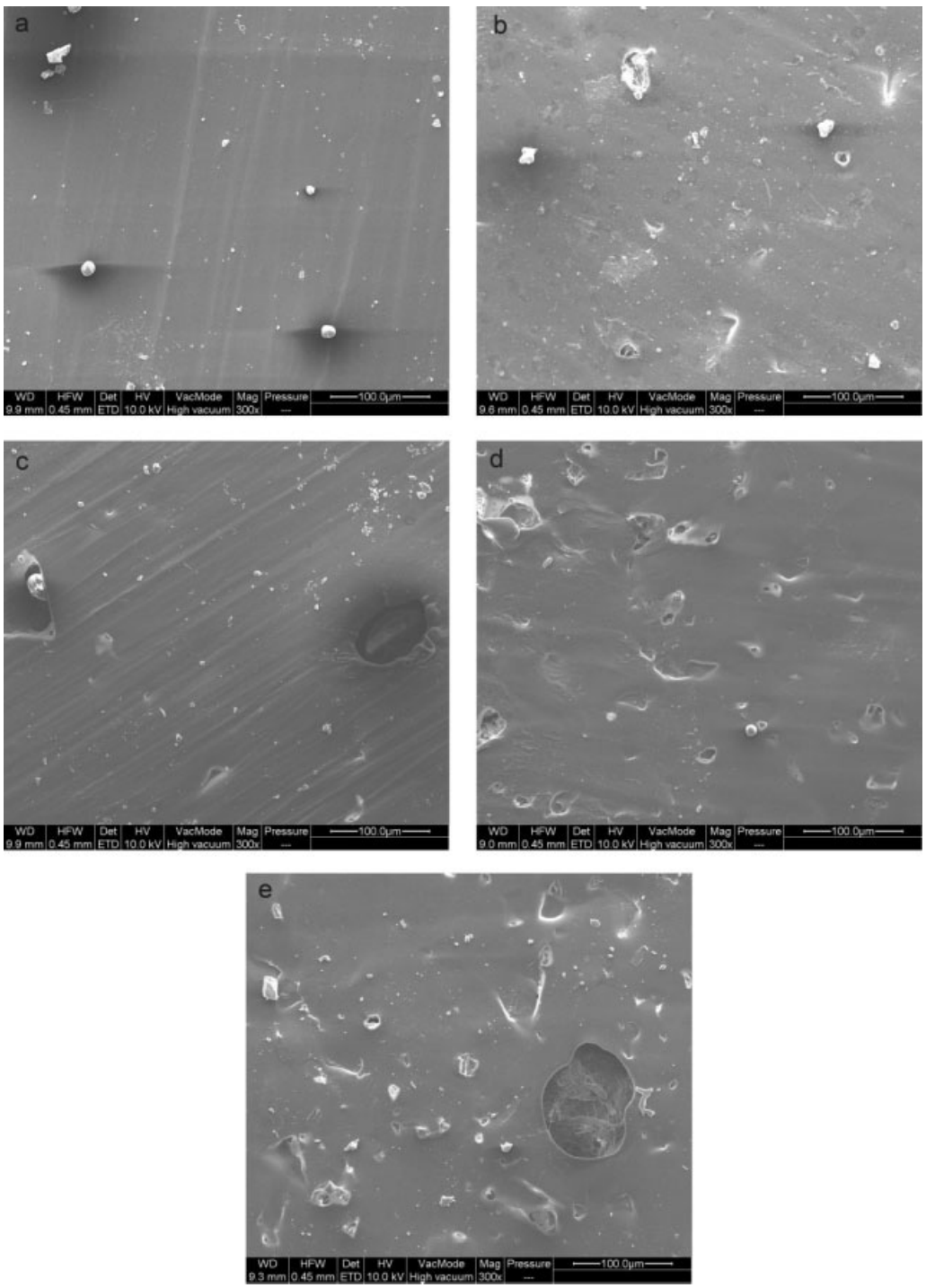

Figure 4 Scanning electron micrograph of POE-*g*-MAH/starch blends after 28 days culturing: (a) pure POE-*g*-MAH/starch; (b) POE-*g*-MAH/starch 90/10; (c) POE-*g*-MAH/starch 80/20; (d) POE-*g*-MAH/starch 70/30; (e) POE-*g*-MAH/starch 60/40.

eroded, with a lot of holes and cracks in various sizes were formed. The covered area of holes on the surface was extensive. This indicates that microorganisms present in the degraded starch analogous to the work of Nakamura et al.[10] There were very large holes on the surface of the specimens, even at low starch content that were deep and expanded around, showing that the specimens degraded completely. Inside of the holes, the film was destroyed and eroded by fungi little by little. Therefore, for 40 wt % starch content blend, the biodegradation is almost adequate, which agrees with its high weight loss. We also found that POE-*g*-MAH/starch blends had better biodegradation than POE/starch blends.

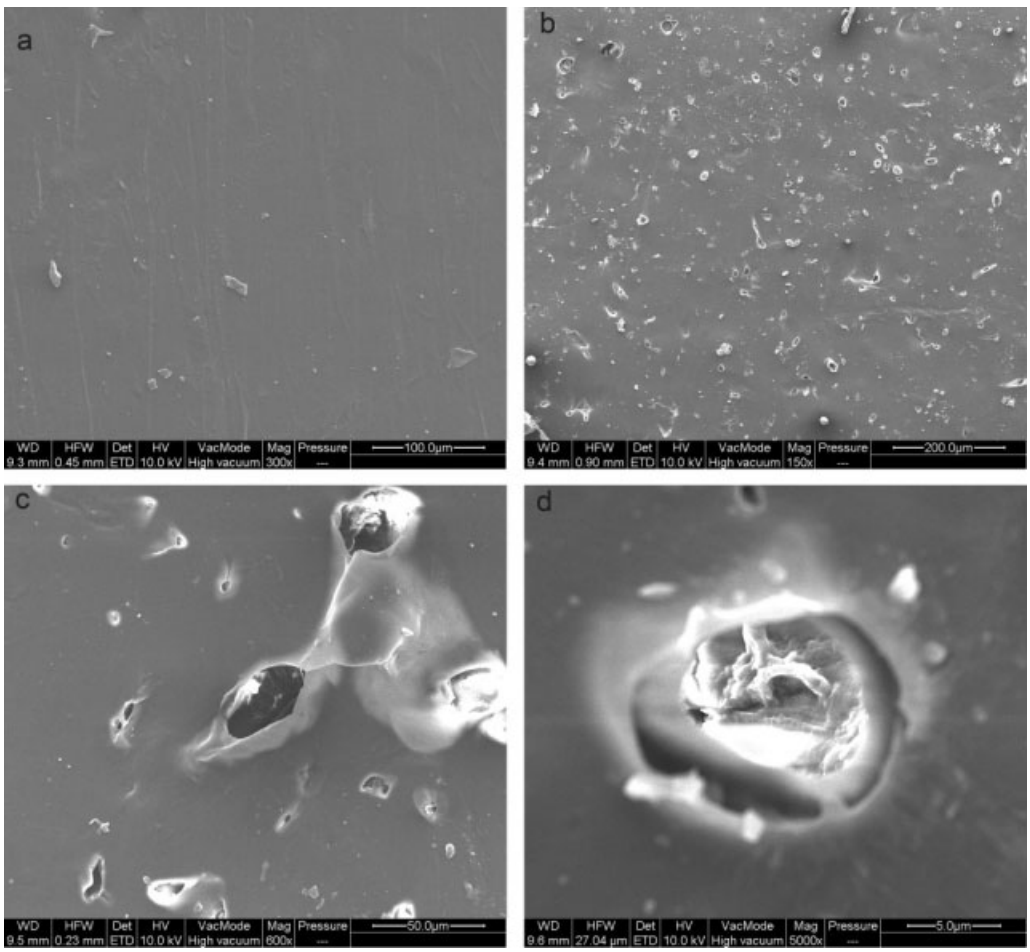

Figure 5 Scanning electron micrograph of POE/starch 60/40 blend: (a) before biodegradation; (b) degraded by fungus for 28 days (×150); (c) degraded by fungus for 28 days (×600); (d) degraded by fungus for 28 days (×5000).

POE-*g*-MAH/starch blends were equivalent to POE/starch blends with compatibilizer, where POE-*g*-MAH is used as compatibilizer usually. The anhydride groups of POE-*g*-MAH can react with the hydroxyl groups of starch and form ester groups, which may make specimens more susceptible to microbial attack. Singh et al.[34] observed SEM of PCL-starch blends with and without compatibilizer and found compatibilized compositions appeared rougher and more degraded. They thought that the surface of PCL-starch blend with compatibilizer was smoother might reflect a preferential consumption of starch granules to the detriment of the host matrix. Consequently POE-*g*-MAH/starch blends degrade more easily than POE/starch blends.

Mechanical properties

Tensile strength of POE/starch and POE-*g*-MAH/starch blends before and after biodegradation are shown in Figure 7. The tensile strength of pure POE almost did not change because it did not biodegrade. Pure POE-*g*-MAH had a slight reduction in tensile strength because it could be probably attacked slightly by fungi. With increasing starch content, tensile strength of POE/starch and POE-*g*-MAH/starch blends decreased. This is because of poor surface adhesion and compatibility between starch and polymer phase when starch content is high. After degraded by fungi, tensile strength of POE/starch and POE-*g*-MAH/starch blends decreased compared with the original specimens. Especially for POE/starch 90/10, 80/20 and POE-*g*-MAH/starch 60/40 blended specimens, tensile strength reduction of those was 27.58, 31.68, and 41.95% respectively. The decrease in tensile strength of POE/starch and POE-*g*-MAH/starch blends can be caused by the starch embedded in polymer matrix, which can be attacked by fungi. Furthermore, the starch portion can easily absorb more moisture from its surroundings and decrease the tensile property of the blends, leading to increased porosity and void formation.[35] POE-*g*-MAH/starch 60/40 decreases the most because anhydride groups of POE-*g*-MAH react with hydroxide groups of starch forming ester groups. These hydrophilic groups are

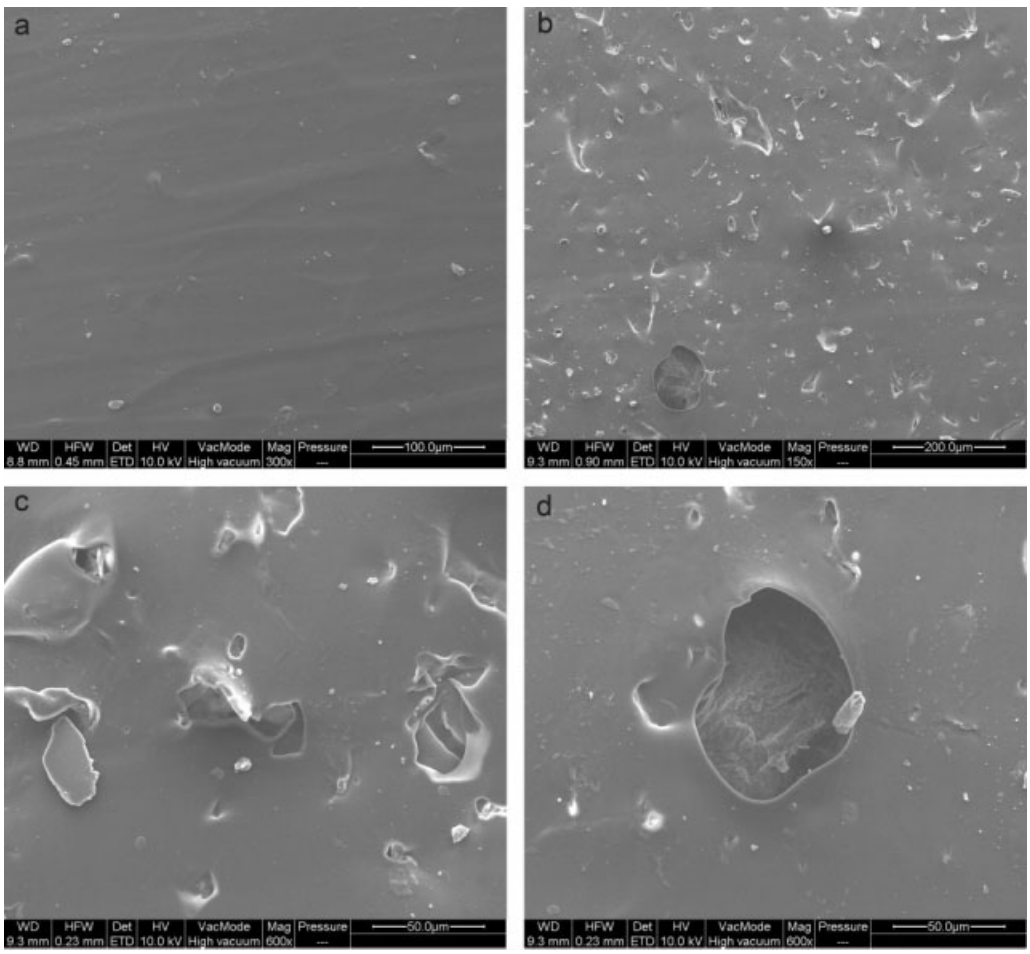

Figure 6 Scanning electron micrograph of POE-*g*-MAH/starch 60/40 blend: (a) before biodegradation; (b) degraded by fungus for 28 days (×150); (c) degraded by fungus for 28 days (×600); (d) degraded by fungus for 28 days (×600).

susceptible to microbial access. The ability of microorganisms to consume multiple food sources is critical for their survival in the environment because of intense competition for limited resources.[36] Consequently, not only starch but also esters are eroded by fungi. POE-*g*-MAH/starch 60/40 has more starch content, and ester groups formed, so it has the largest decrease in tensile strength.

Elongation at break of POE/starch and POE-*g*-MAH/starch blends (in Fig. 8) changed differently from tensile strength. Pure POE in elongation at break almost did not change, but pure POE-*g*-MAH/starch decreased slightly, which agreed with the tensile strength. After biodegraded by fungi, elongation at break of POE/starch 90/10 and 80/20 blends reduced 15.73% and 11.39% respectively. Elongation at break of POE/starch 70/30 and 60/40 blends changed slightly, only 0.79% and 3.18% respectively. But for POE-*g*-MAH/starch blends except POE-*g*-MAH/starch 90/10, elongation at break increased contrarily after biodegradation. POE-*g*-MAH/starch 80/20, 70/30, 60/40 blends in

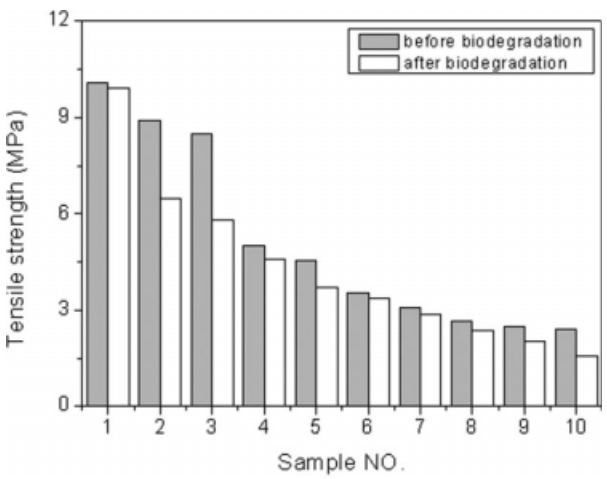

Figure 7 Tensile strength of POE/starch and POE-*g*-MAH/starch blends before biodegradation (■) and degraded by fungus for 28 days (□): 1. pure POE; 2. POE/starch 90/10; 3. POE/starch 80/20; 4. POE/starch 70/30; 5. POE/starch 60/40; 6. pure POE-*g*-MAH; 7. POE-*g*-MAH/starch 90/10; 8. POE-*g*-MAH/starch 80/20; 9. POE-*g*-MAH/starch 70/30; 10. POE-*g*-MAH/starch 60/40.

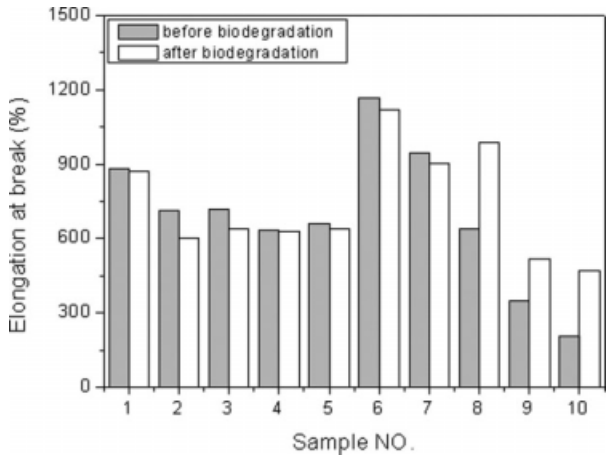

Figure 8 Elongation at break of POE/starch and POE-*g*-MAH/starch blends before biodegradation (■) and degraded by fungus for 28 days (□): 1. pure POE; 2. POE/starch 90/10; 3. POE/starch 80/20; 4. POE/starch 70/30; 5. POE/starch 60/40; 6. pure POE-*g*-MAH; 7. POE-*g*-MAH/starch 90/10; 8. POE-*g*-MAH/starch 80/20; 9. POE-*g*-MAH/starch 70/30; 10. POE-*g*-MAH/starch 60/40.

elongation at break increased 0.54, 0.48, 1.29 times respectively than original specimens. This may be probably because of the network structure of POE-*g*-MAH inside the composite after starch is consumed by fungi. According to Joseph et al.,[37] water molecules act as a plasticizing agent in the composite material, which leads to an increase of the maximum strain for the composites after absorption. Therefore, more starch can easily absorb water from its surroundings resulting in the increased elongation at break.

CONCLUSIONS

The biodegradation of two blend systems POE/starch and POE-*g*-MAH/starch blends by fungi was investigated. Heavy growth of fungus was experienced on specimens containing 30 wt % and 40 wt % starch. With increased culturing time and starch content, fungal growth became denser. This is because starch can be readily used as a carbon source by the fungi. Fungal growth of POE-*g*-MAH/starch blended specimens is faster than POE/starch blended specimens. This may be because of the anhydride groups of POE-*g*-MAH reacting with the hydroxyl groups of starch forming ester groups, which can be accessed by fungi. There is no weight loss of pure POE, but POE-*g*-MAH/starch 60/40 had the largest weight loss of nearly 35%. With increasing starch content, the weight loss of POE/starch and POE-*g*-MAH/starch blends also increases. POE-*g*-MAH/starch blends lost more weight than comparable POE/starch blends. This indicates that POE-*g*-MAH/starch blends are degraded by fungi more easily.

SEM photographs show that the surfaces of pure POE and POE-*g*-MAH specimens are flat and smooth, when no biodegradation happens. With increasing starch content, the film surface becomes rough with more and larger holes and cracks on the surface of specimens due to starch consumption. This indicates that the specimens with higher starch content can be eroded by fungi more easily, and has better biodegradation as well. After biodegradation, many large holes are found on the surface of specimens, expanding and rough, destroying the inside of the film as well. Starch is the sole carbon source providing nucleating sites for the growth of fungal hypha resulting in the degradation of POE/starch and POE-*g*-MAH/starch blends. Tensile strength of pure POE barely changed after biodegradation, which pure POE-*g*-MAH reduced slightly. Tensile strength of POE/starch and POE-*g*-MAH/starch blends decreased with increasing starch content, because of poor surface adhesion and compatibility. After degrading, tensile strength of blends decreases because starch is eroded by fungi. Elongation at break of POE/starch blends changes slightly, but POE-*g*-MAH/starch blends increase contrarily, which may be due to the network structure of POE-*g*-MAH inside the composite after starch is consumed by fungi.

The authors thank Mr. Jiashan Li, TianJin TingFung of the Starch Development Co. Ltd, for providing starch material. Xiaoya Shang thanks Dr. Lizhen Zhou for his help.

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