

Study on poly(butylene adipate-co-terephthalate)/starch composites with polymeric methylenediphenyl diisocyanate

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ABSTRACT: To lower the cost of poly(butylene adipate-co-terephthalate) or PBAT, starch was used as a filler in this study. To increase tensile strength of PBAT/starch composites, polymeric methylenediphenyl diisocyanate (pMDI) was used as a compatibilizer. PBAT was melt-mixed with starch in a kneader, and then the mixtures were compression-molded. The effects of starch and pMDI content on the tensile strength and elongation at break of PBAT/starch composites were examined. The morphology and biodegradability of the composites in soil were also studied. The tensile strength of PBAT and PBAT/starch composites increases with increasing content of pMDI. The increase of weight average molecular weight of PBAT and improved interaction between PBAT and starch were observed with increasing content of pMDI. The weight average molecular weights of buried PBAT and the composites in soil significantly decrease. Especially, the reduction of the weight average molecular weight of PBAT/starch (70/30) composite is the most significant. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41884.

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INTRODUCTION

Plastic waste has an adverse effect on the environment. Incineration can cause toxic air pollution, and landfill sites are limited. Legislative threats and increasing public concern surrounding plastic waste have generated much interest in biodegradable polymers. Especially, many studies have been done for the utilization of biodegradable polyesters as films, sheets, bottles, and injection molded products.

One of the commercialized biodegradable polyesters is poly(butylene adipate-co-terephthalate) or PBAT, which is an aliphatic-aromatic copolyester. PBAT is prepared by polycondensation reaction of 1,4-butanediol with both adipic and terephthalic acids. Even though PBAT has a higher elongation at break than most biodegradable polyesters, its extensive application is limited because of high cost.¹

Therefore, to overcome this drawback, several studies on the addition of low-cost, biodegradable natural fillers to PBAT have been conducted. Muniyasamy *et al.* reported the properties of PBAT/distillers dried grains with solubles (DDGS) composites.² It was found that an increase in DDGS content resulted in a decrease in tensile strength and elongation at break, but a significant improvement in tensile modulus.² Wu studied maleic anhydride-grafted PBAT (PBAT-g-MAH)/cellulose acetate (CA)

composites.³ With increasing content of CA, tensile strength of PBAT-g-MAH/CA composites increased.³

Starch is readily available, inexpensive and has a very fast biodegradability.⁴⁻⁸ Also, starch is obtained from renewable sources. Therefore, starch has been used as a low-cost, biodegradable natural filler for many polyesters.⁹⁻¹¹ However, there have been few studies about PBAT/starch composites.⁹ Even though their cost decreased with addition of starch to polyesters, tensile strength and elongation at break of the composites significantly decreased.¹²⁻¹⁵ This is due to the poor interfacial adhesion between the hydrophilic starch and the hydrophobic polyesters.

Therefore, compatibilizers are widely used to improve the compatibility between starch and polyesters. For example, methylenediphenyl diisocyanate (MDI) has been used as a compatibilizer to improve the interfacial adhesion between hydrophobic fillers and various polyesters.^{10,11,16-20} MDI has highly reactive isocyanate groups that might react with both carboxyl and hydroxyl end groups on polyesters and with the hydroxyl groups on starch.^{10,11,16-20} It was also reported that MDI can connect the end groups of poly(lactic acid) (PLA) to produce high molecular weight PLA, resulting in increase of tensile strength.²¹ The excess amount of the isocyanate group of MDI can lead to chain cross-linking of polyesters and starch.^{21,22}

Table I. Important Characteristics of the Materials used in this Study

Materials	Supplier	Characteristics
PBAT	S-EnPol Co., Korea	Melt flow index (2.16 kg, 190°C): 2.0–4.0 g/10 min. T_g : $-30 \sim -25^\circ\text{C}$ T_m : $127 \sim 132^\circ\text{C}$ Density: 1.12 g/mL
Corn starch	Samyang Genex Corp., Korea	Viscosity: 8–12 cps Specific gravity: 0.53
pMDI	BASF, Germany	Viscosity: 200 cps NCO content: 30–32 wt %

MDI was used as a co-compatibilizer for PLA/soy protein concentrate foams. Using MDI as a co-compatibilizer for the foams resulted in high-cell density and low-foam density when chemical blowing agent concentration was low.²³ MDI was also used to introduce NCO on both hydroxyl ends of polycaprolactone (PCL) to prepare starch-g-PCL.²⁴ The use of aliphatic isocyanates as a compatibilizer between biodegradable polymers and corn starch led to improved tensile properties of the composites.²⁵ Compatibilizers containing the isocyanate groups were used to improve compatibility in immiscible polymer blends.^{26–36} The effect of isocyanates on the water absorption of the biodegradable polymer blends was also studied.^{17,22} The water absorption of soy protein isolate/PCL(50/50) and PBS/CS blends with isocyanates was slower than that of the blends without isocyanates.^{17,22}

The main focus of this study is to increase tensile strength of PBAT/starch composites with addition of polymeric MDI (pMDI). Increasing biodegradation rate of PBAT with addition of starch is another aim of this study. PBAT was melt-mixed with starch in a kneader, and then the mixtures were compression-molded. The effects of starch content and pMDI content on the tensile strength and elongation at break of PBAT/starch composites were examined in detail. Morphology of the composites was also studied. In addition, biodegradability of PBAT/starch composites in soil was studied based on their change of weight average molecular weights and morphology of the composites.

EXPERIMENTAL

Materials and Composite Preparation

Important characteristics of the materials used in this study are summarized in Table I. Oxidized corn starch was obtained from Samyang Genex Co. (Seoul, Korea). According to the provider, the oxidized starch was produced by reaction of starch with hypochlorite, resulting in partial conversion of hydroxyl groups of starch to carboxyl groups. Polymeric MDI (pMDI) comprising 30–32 wt % NCO group was purchased from BASF.

PBAT and starch were dried in an oven at 50°C for 24 h before processing. PBAT and starch were melt-mixed with or without pMDI in a bench kneader (Irie Shokai, Japan) at 20 rpm for 10 min. Mixing temperature was fixed at 130°C . Mixing ratio of PBAT/starch composites was 90/10, 80/20, 70/30, and 60/40 wt %. Six levels of pMDI content in the PBAT/starch composites were selected: 0.1, 0.25, 0.5, 1, 1.5, and 2 wt %, based on the total weight of PBAT and starch. The obtained composites were

compression molded at 130°C for 5 min for the testing samples.

Testing

A Universal Testing Machine (Model 4466, Instron Co.) was used to obtain the tensile strength and elongation at break of the composites at room temperature. The crosshead speed was 500 mm/min. The tensile properties were measured according to ASTM D412. All measurements were performed for five replicates of specimens and averaged to get the final result.

The gel fraction of PBAT/starch composites was measured by extraction of the uncross-linked part of the samples in boiling chloroform for 72 hr using a Soxhlet extractor, until the sample attained a constant weight. The gel fraction was calculated using the following equation.

$$\text{Gel fraction (\%)} = (W_2 - W_3) / (W_1 - W_3) \times 100$$

W_1 = Initial weight of the sample, W_2 = Weight of the insoluble portion

W_3 = Initial weight of insoluble portion of starch

Most fractions of the oxidized corn starch used in this study were dissolved in boiling chloroform. However, some fractions of the oxidized corn starch were insoluble in boiling chloroform. The average insoluble weight fraction of oxidized corn starch was determined before the experiment of extraction of uncrosslinked part of PBAT/starch composites. On the basis of the average insoluble weight fraction of the oxidized corn starch, initial weight of insoluble portion of starch (W_3) in the equation was calculated.

To evaluate the soil biodegradation of the PBAT and PBAT/starch composites, film samples (thickness: 2 mm) were cut into 10 mm \times 10 mm pieces and buried in soil maintained at 50% water-holding capacity, and then incubated in a controlled environment chamber at $58 \pm 2^\circ\text{C}$. Soil used in the test was 1 : 1 (w/w) mixture of potting soil and sand. At predetermined time (60 days), each film was retrieved, and the film was cleaned and used for the measurement of molecular weight.

Molecular weights were determined by dissolving PBAT and PBAT/starch samples in chloroform (3 mg/mL) and injecting 100 μL of each sample solution into a gel permeation chromatograph (GPC). The GPC (Waters) was equipped with a Waters 515 pump, 2 columns (Shodex LF-804, 7.8×300 mm) and Waters 410 differential refractometer interface with Waters Empower software. A flow rate of 1.0 mL/min, a runtime of 35 min, and a temperature of 35°C were used.

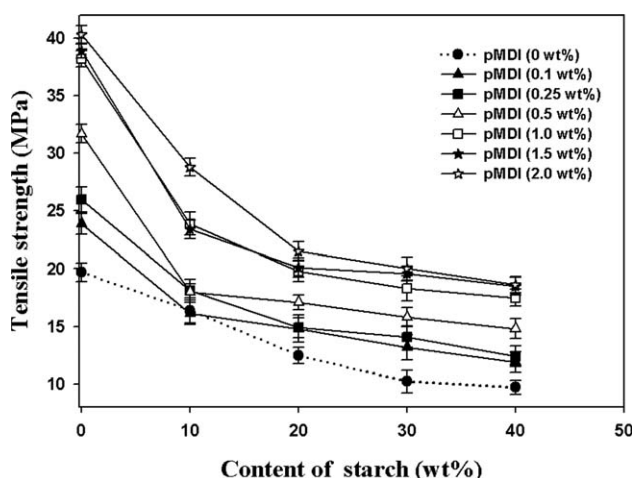


Figure 1. Effect of starch content on the tensile strength of PBAT/starch composites with different amount of pMDI content.

To investigate the morphology, the cryogenically fractured cross sections of the PBAT/starch composites were examined with field emission gun-Scanning Electron Microscope (SEM, FEI Quanta 200). Also, the surface of the PBAT/starch films with 1.5 wt % pMDI buried in soil for 60 days was investigated using SEM.

RESULTS AND DISCUSSION

Figure 1 shows the effect of starch content on the tensile strength of PBAT/starch composites with different amount of pMDI content. Tensile strength of PBAT increases with increasing content of pMDI. This may be due to the reactions between the isocyanate groups of pMDI and terminal hydroxyl or carboxyl groups of PBAT as shown in Figure 2. Therefore, a molecular chain-extended reaction of PBATs occurs with addition of pMDI, resulting in increase of the molecular weight of PBAT.

The effect of pMDI content on the weight average molecular weight and molecular weight distribution of PBAT is shown in Table II. The weight average molecular weight of PBAT increases with increasing content of pMDI as a result of a chain extended

Table II. Effect of pMDI Content on the Weight Average Molecular Weight and Molecular Weight Distribution of PBAT

Content of pMDI (wt %)	Weight average molecular weight of PBAT	Molecular weight distribution
0.0	107,268	3.08
0.25	144,572	3.18
0.5	193,211	3.52

reaction. Zhong *et al.* have reported that higher molecular weight poly(lactic acid) can be obtained through the chain-extended reaction of low molecular weight poly(lactic acid) with MDI.²¹ Also, the excess amounts of the isocyanate groups can lead to chain cross-linking of PBAT.²¹

The chain cross-linking could be the reason for the increasing molecular weight distribution with increasing content of pMDI shown in Table II. Because of formation of crosslinked gel fraction of PBAT at pMDI loading beyond 0.5%, molecular weight for such compositions could not be measured with GPC. In fact, the molecular weight reported for 0.5% loading of pMDI is the value of soluble fraction only.

The effect of pMDI content on the gel fractions of PBAT are shown in Table III. At 0.5 wt % pMDI content, the gel fraction of PBAT is 75%. With increasing pMDI content from 0.5 wt %, the gel fractions of PBAT increase. Therefore, based on GPC and gel fraction results, it can be concluded that the improvement of tensile strength of PBAT with addition of pMDI is due to the chain-extended reaction of PBAT including cross-linking.

As shown in Figure 1, the tensile strength of PBAT/starch composites decreases as starch content increases because of poor interfacial interaction between hydrophobic PBAT and hydrophilic starch. This result is in agreement with several previous studies.^{12–15} The tensile strength of PBAT/starch composites increases with increasing content of pMDI at the same content of starch. With increasing content of pMDI, tensile strength of PBAT/starch composites increases possibly due to the chain-

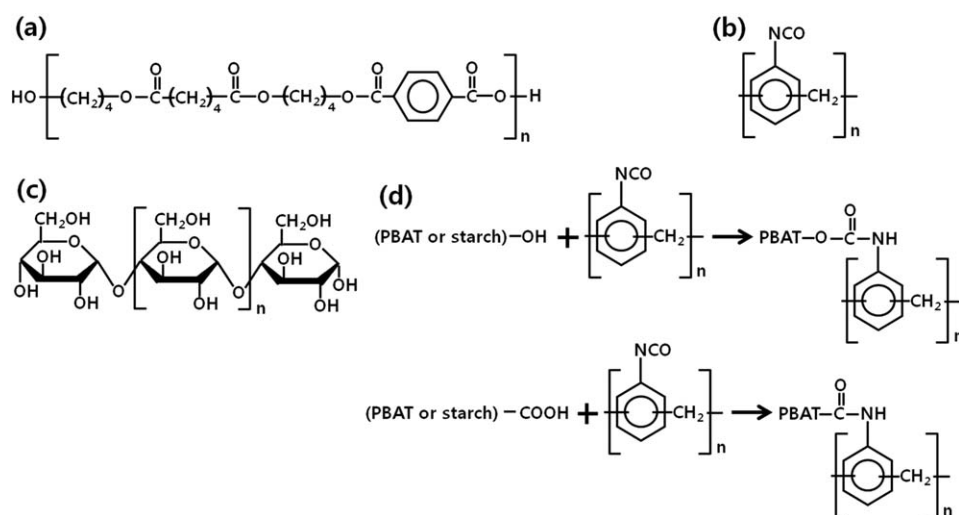


Figure 2. Chemical structures of (a) PBAT, (b) pMDI, (c) starch, and (d) their reactions.

Table III. Effect of pMDI Content on the Gel Fractions of PBAT and PBAT/Starch Composites

Content of pMDI (wt %)	PBAT (100)	PBAT/Starch (90/10)	PBAT/Starch (80/20)	PBAT/Starch (70/30)	PBAT/Starch (60/40)
0.0	0	0	0	0	0
0.1	0	0	0	0	0
0.25	0	0	0	0	0
0.5	75	75	74	74	73
1.0	80	80	80	78	78
1.5	99	99	99	99	99
2.0	99	99	99	99	99

extended reaction of PBAT including cross-linking and improved interaction between PBAT and starch.

Graft copolymers of PBAT and starch could be formed with addition of pMDI, improving the interaction between PBAT and starch. Polymeric MDI (pMDI) has highly reactive isocyanate groups that might react with both carboxyl and hydroxyl groups in PBAT and starch. The reactions could lead to the formation of graft copolymers of PBAT and starch. The improved interaction is confirmed by SEM micrographs as shown in Figure 3.

The effect of pMDI content on the gel fractions of PBAT/starch composites are shown in Table III. At 0.5 wt % pMDI content, the gel fractions of PBAT/starch composites are 73–75%. With increasing pMDI content from 0.5 wt %, the gel fractions of the composites increase. The gel fractions of samples obtained with the same pMDI content are not influenced by the PBAT/starch ratio. A possible explanation for the phenomenon is that the excess amount of the isocyanate group of pMDI could lead to chain cross-linking of starch as well as PBAT.^{21,22}

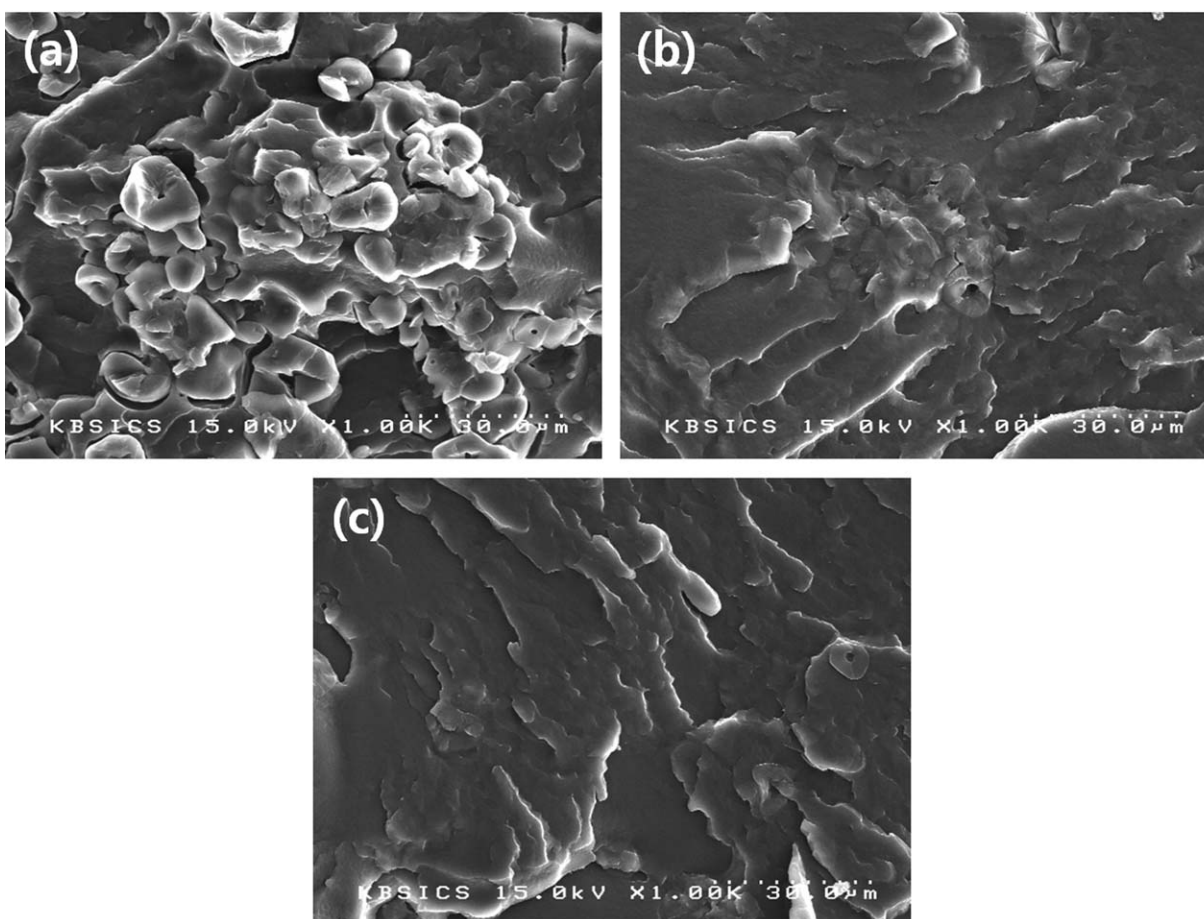


Figure 3. SEM micrographs of fractured surface of PBAT/starch (70/30) composites (a) without pMDI, (b) with 0.1 wt % pMDI, and (c) with 0.25 wt % pMDI.

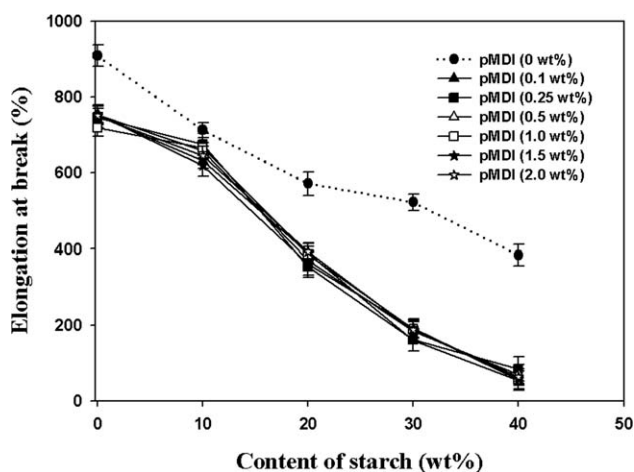


Figure 4. Effect of starch content on the elongation at break of PBAT/starch composites with different amount of pMDI content.

Figure 3(a) shows the SEM micrograph of the fractured surface of the PBAT/starch (70/30) composite without pMDI. Starch granules can be seen clearly, and gaps were observed between the PBAT matrix and the starch granules. This result indicates poor interfacial interaction between PBAT and starch. Figure 3(b,c) show the SEM micrographs of the fractured surface of the PBAT/starch (70/30) composites with 0.1 and 0.25 wt % pMDI, respectively. It is difficult to distinguish starch granules from PBAT matrix in Figure 3(b,c). The gaps observed in Figure 3(a) are not observed in Figure 3(b,c). Therefore, graft copolymers of PBAT and starch could be formed with addition of pMDI and function as a compatibilizer, improving the interfacial adhesion between PBAT and starch.

Figure 4 shows the effect of starch content on the elongation at break of PBAT/starch composites with different amount of pMDI content. With increasing content of starch, elongation at break of PBAT/starch composites decreases. The molecular mobility of PBAT could be restricted by rigid starch granules. This restriction could lead to the decrease of elongation at break of PBAT/starch composites. With increasing content of starch, the stiffness and the brittleness of the composites increase. With addition of 0.1 wt % pMDI, elongation at break of PBAT and PBAT/starch composites significantly decreases and then level off with further increase of pMDI content.

Table IV. Weight Average Molecular Weights (MW) of Original Samples (buried days: 0) and Buried Samples (buried days: 60) of PBAT/Starch Composites Without pMDI in Soil

	MW of Original Sample (buried days: 0)	MW of Buried Sample (buried days: 60)
PBAT(100)	107,268	7,849
PBAT/Starch(90/10)	107,035	8,615
PBAT/Starch(80/20)	112,439	7,786
PBAT/Starch(70/30)	110,922	4,330

To evaluate the soil biodegradation of the PBAT and PBAT/starch composites without pMDI, the weight average molecular weights of buried samples (buried days: 60) of PBAT and the composites in soil are investigated compared with the original samples (buried days: 0) as shown in Table IV. The weight average molecular weights of buried samples in soil significantly decrease. Especially, the reduction of the weight average molecular weight of PBAT/starch (70/30) composite is the most significant. This result indicates that 30 wt % addition of starch increases the biodegradation rate of PBAT.

Generally, biodegradation rate of biodegradable polymers increases with increasing water absorption because of increased hydrolytic degradation. Since starch is more hydrophilic than PBAT, the amount of water absorption could increase with increasing amount of starch in the composites. However, according to the previous study,¹⁰ the water absorption of the composites did not change significantly when the amount of starch was small, because the starch granules were well covered by the continuous poly (lactic acid) matrix. Similarly, the starch granules could be well covered by the continuous PBAT matrix for PBAT/starch (90/10) and (80/20) composites in this study. As a result, the biodegradation rate of PBAT/starch (90/10) and (80/20) composites does not change significantly compared with biodegradation rate of PBAT as shown in Table IV.

To evaluate the soil biodegradation of gel parts of the PBAT/starch composites with addition of pMDI, gel fractions of the buried samples (buried days: 60) of the composites with 1.5 wt % pMDI in soil were investigated compared with gel fractions of the original samples (Table V). Gel fractions of the original samples (buried days: 0) of PBAT/starch composites with 1.5 wt % pMDI content are 99%. However, gel fractions of the buried samples of the composites with 1.5 wt % pMDI content in soil are 9–10%. This result indicates that gel parts formed with addition of pMDI in PBAT/starch composites are also biodegradable.

Figure 5 shows SEM micrographs of the surface of the PBAT/starch films with 1.5 wt % pMDI buried in soil for 60 days. A relatively smooth surface is observed for PBAT/starch (90/10)

Table V. Gel Fractions of Original Samples (buried days: 0) and Buried Samples (buried days: 60) of PBAT/Starch Composites with 1.5 wt % pMDI in Soil

	Gel fraction (%) of original sample (buried days: 0)	Gel fraction (%) of buried sample (buried days: 60)
PBAT/Starch(90/10)/pMDI 1.5	99	10
PBAT/Starch(80/20)/pMDI 1.5	99	10
PBAT/Starch(70/30)/pMDI 1.5	99	9
PBAT/Starch(60/40)/pMDI 1.5	99	9

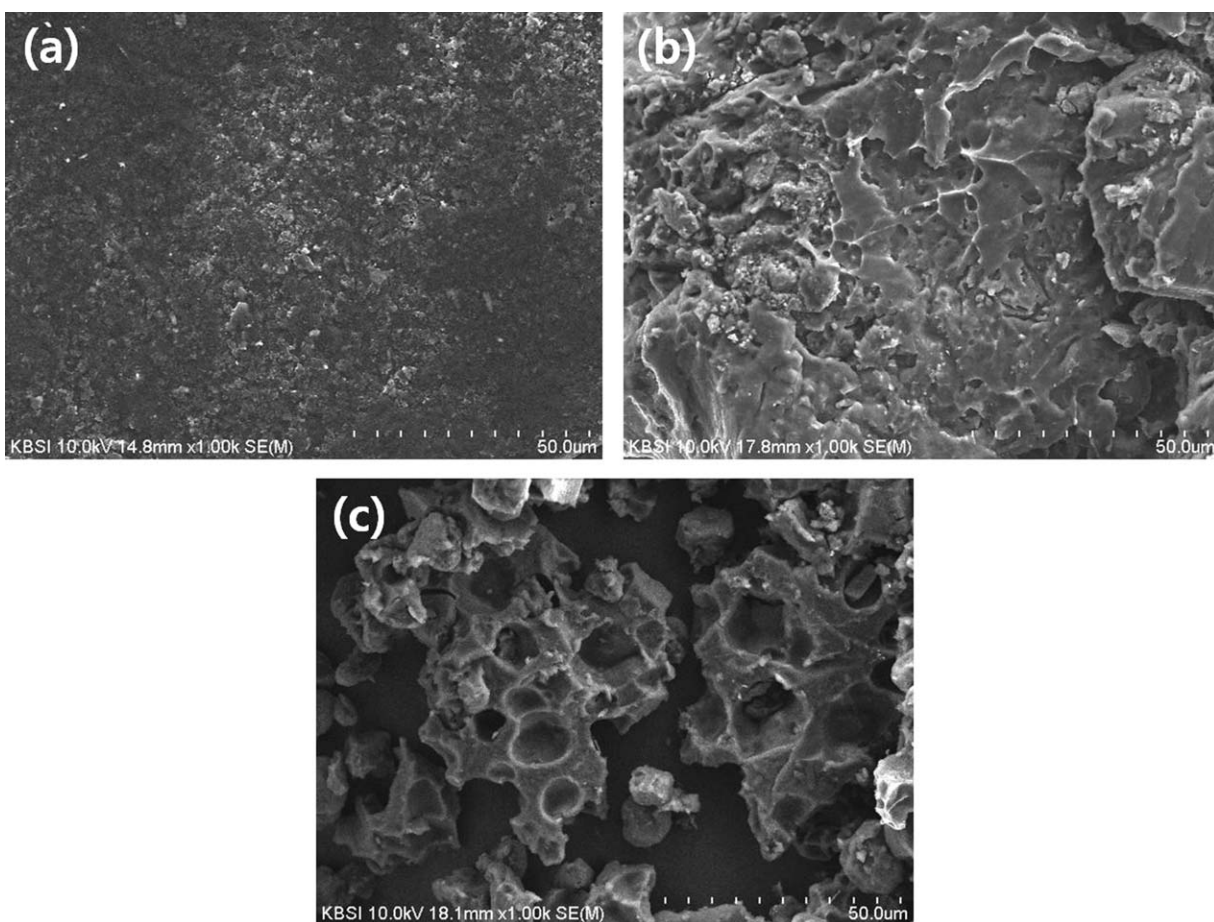


Figure 5. SEM micrographs of the surface of the PBAT/starch films with 1.5 wt % pMDI buried in soil for 60 days (a) PBAT/starch (90/10), (b) PBAT/starch (80/20), and (c) PBAT/starch (60/40).

film but the hollows of the surface are observed for PBAT/starch (80/20) film. And the erosion of the surface is more significant for PBAT/starch (60/40) film. This result indicates that the addition of starch increases the biodegradation rate of PBAT/starch composites.

Even though the PBAT/starch film with pMDI was recovered from the soil for SEM experiment after burial for 60 days, the recovery of the PBAT/starch films without pMDI was difficult because of the significant fragmentation. This may indicate the slower biodegradation of PBAT/starch composites with pMDI than that of the composites without pMDI because of cross-linking.

CONCLUSIONS

The tensile strength of PBAT increases with increasing content of pMDI. Based on GPC and gel fraction results, it can be concluded that increase of tensile strength is due to the increase of weight average molecular weight of PBAT as a result of a chain extended reaction of PBAT including cross-linking. The chain extended reaction of PBAT could be due to the reactions between the isocyanate groups of pMDI and terminal hydroxyl or carboxyl groups of PBAT. Also, the excess amounts of the isocyanate groups can lead to chain cross-linking of PBAT.

The tensile strength of PBAT/starch composites increases with increasing content of pMDI at the same content of starch. The increase of tensile strength of PBAT/starch composites with increasing content of pMDI is possibly due to the chain-extended reaction of PBAT including cross-linking and improved interaction between PBAT and starch. The improved interaction is confirmed by SEM micrographs.

Similar decrease is observed in the weight average molecular weights of buried PBAT, PBAT/starch (90/10) and (80/20) samples without pMDI in soil (buried days: 60) in this study. However, the reduction of the weight average molecular weight of PBAT/starch (70/30) composite without pMDI is the most significant. This result indicates that 30 wt % addition of starch increases the biodegradation rate of PBAT. Gel parts formed with addition of pMDI in PBAT/starch composites are also biodegradable, considering that gel fractions of the buried samples (buried days: 60) of the composites with 1.5 wt % pMDI in soil decrease compared with gel fractions of the original samples.

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