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Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil

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Abstract

This study investigated the biodegradability of PBS and bio-flour, which is a poly(butylene succinate) (PBS) bio-composite filled with rice-husk flour (RHF) reinforcing, in natural and aerobic compost soil. The percentage weight loss and the reduction in mechanical properties of PBS and the bio-composites in the compost soil burial test were significantly greater than those in the natural soil burial test. These results were supported by degraded surface of PBS and bio-composites observed through morphological study and the total colony count of natural soil was lower than that of compost soil. The biodegradability of the bio-composites was enhanced with increasing bio-flour content because the bio-flour is easily attacked by microorganisms. As the biodegradability test progressed over time up to 80 days, the molecular weight of PBS decreased in the soil burial test. We confirmed by attenuated total reflectance (FTIR–ATR) analyser that the chemical structures of PBS and the bio-composites were changed after the compost burial test. The glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) of the natural and composted soil tested PBS were investigated using differential scanning calorimetry (DSC). From the results, we concluded that use of these bio-composites will reduce the environmental problems associated with waste pollution and the study findings support the predicted application of bio-composites as "green-composites" or "eco-materials". © 2005 Elsevier Ltd. All rights reserved.

Keywords: Bio-flour; Poly(butylene succinate); Biodegradability; Microbial counts; Bio-composites; Green-composites; Eco-materials; Compost soil

1. Introduction

In recent years, eco-friendly biodegradable polymers and plastics have gained increasing attention because of growing recognition worldwide of the need to reduce global environmental pollution [1-3]. These biodegradable materials can be completely degraded into natural ecosystems such as active sludge, natural soil, lake and marine. Accordingly, the biodegradability of biodegradable polymers corresponds to the ability to be chemically transformed by the action of biological enzymes or microorganisms [3,4]. Petroleum-based synthetic polymers are widely used in modern society. However, the annual worldwide disposal of approximately 150 million tons of petrochemical plastics in commonly used commodities such as polyolefin in packing, bottle and moulding products is a significant environmental problem, especially with the continuously increasing production and consumption of these materials [3,5]. Furthermore, plastic wastes are an undesired pollutant in soil, rivers and marine. Because of their resistance to microbial attack, they tend to

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accumulate in the natural environment. Although these biodegradable polymers can partially solve the problem of non-biodegradable plastic waste pollution, the majority of biodegradable polymers are not widely used because they are too expensive and the range of the material selection suitable for various end-use products is limited [5,6]. Poly(butylene succinate) (PBS) is one of the commercially used biodegradable polymers with a range of interesting properties including good mechanical properties, melt processing, biodegradability and compostability [6]. PBS is produced by the condensation reaction of the glycols 1,4-butanediol and aliphatic dicarboxylic acid, which is succinic acid [7]. Some studies have evaluated the biodegradability of biodegradable polymers in a compost soil environment [8,9]. Yang et al. [8] reported the biodegradability of biodegradable polymers in the mature compost soil and found that the biodegradability of PBS was slower than that of poly(butylene succinate-co-adipate) PBSA in compost soil [8].

Bio-composites are composed of a biodegradable polymer which is a matrix polymer and cellulosic materials which act as the reinforcing filler. There are many studies concerning the use of bio-fibre and bioflour as reinforcing in biodegradable polymer biocomposite systems. These reinforcing materials can be naturally degraded by microorganisms and play a significant role in degrading natural organic substances in the ecosystem [10,11]. We have investigated the application of rice-husk flour (RHF) as a reinforcing filler in the bio-composites. RHF is a surplus by-product of the rice production process that has limited industrial applications. Therefore, the use of RHF as reinforcement for bio-composites can represent the conversion to industrially useful biomass energy [12].

The object of this study was to investigate the biodegradability of bio-flour-filled PBS bio-composites in a natural soil burial environment and when exposed to simulated municipal solid waste (MSW) aerobic compost soil. We compared the biodegradability of conventional plastic, PBS and bio-composites. In order to compare the effects of the biodegradability of natural soil versus compost soil, microbial counts were performed using CFU (colony forming units) on NA (nutrient agar) and AIA (actinomycetes isolation agar) plate methods. In addition, molecular weight, chemical structure and morphological changes in PBS and the bio-composites were measured using attenuated total reflectance (FTIR-ATR), gel permeation chromatography (GPC) and scanning electron microscopy (SEM), respectively. Also, the melting (T_m) , crystallization (T_c) and glass transition (T_g) temperatures and the heat of fusion $(\Delta H_{\rm f})$ and heat of crystallization $(\Delta H_{\rm c})$ of the natural and composted soil tested PBS were analysed by DSC. From these results, we suggest the predicted applications of bio-composites that are considered an alternative to non-biodegradable plastic materials.

2. Experimental part

2.1. Materials

PBS was supplied by SK Chemical Co., South Korea. It has a melt flow index of 20 g/10 min (190 °C/2.160 g) and a density of 1.22 g/cm³. High-density polyethylene (HDPE) was supplied by LG Chem., Ltd., South Korea, in the form of homopolymer pellets with a density of 0.957 g/cm³ and a melt flow index of 15 g/10 min (230 °C/2.160 g). The bio-flour used as the reinforcing filler was RHF from Saron Filler Co., South Korea. The RHF particle size was 74 μ m.

2.2. Compounding and sample preparation

RHF was dried in an air dryer oven at 105 °C for 24 h to reduce moisture content to 1-3% and then stored in polyethylene bags until compounding. The compounding of RHF as the reinforcing filler with PBS as the matrix polymer was performed in a co-rotating twin screw extruder (laboratory-size) using three general processes: melt blending, extrusion and palletising. The temperature of the extruder barrel was divided into eight zones and the temperature in each zone was adjustable. The temperature feeding and mixing zone of the barrel were maintained at 120 °C and 140 °C, respectively, with a screw speed of 250 rpm. The extruded strand was cooled in water and pelletised using a pelletiser. Extruded pellets were dried at 80 °C for 24 h and stored in sealed polyethylene bags to avoid moisture infiltration. For measuring the biodegradability of the biocomposites, four levels of filler loadings were prepared: 10, 20, 30 and 40 wt.%.

Tensile strength (ASTM D 638) and Izod impact strength (ASTM D 256) test specimens were injection moulded using an injection moulding machine (Bau Technology, South Korea) at 140 °C with an injection pressure of 1200 psi. After moulding, the specimens were conditioned before testing at 50 \pm 5% RH for at least 40 h according to ASTM D 618-99.

2.3. Biodegradability test

2.3.1. Natural soil burial test and simulated municipal solid waste (MSW) aerobic compost test according to ASTM D 6003-96

The natural soil test of the PBS and bio-composites was conducted for 80 days [13]. The compost test method is used to determine the degree and rate of aerobic biodegradation of plastic materials exposed to a controlled composting environment. The test is designed to be applicable to all plastic materials that are not inhibitory to the bacteria and fungi present in the simulated MSW. The test was conducted with PBS and bio-composites. A controlled-environment chamber capable of maintaining a temperature of 30 ± 2 °C and reactor vessels of a size not greater than 4 l volume were used. The pH of the compost soil was maintained at 7 and the water content at 50–60%. The specimens underwent testing for tensile strength (ASTM D 638) and Izod impact strength (ASTM D 256). HDPE was used as the negative reference material. After each natural [13] and compost test of 10, 30, 40, 60 and 80 days duration, the buried specimens were dug out, removed from the soil and washed in distilled water. Finally, the specimens were dried in an air dried oven at 60 ± 2 °C for 24 h. Table 1 shows the constituents of

2.3.2. Mechanical property and weight loss tests after biodegradability

the simulated MSW aerobic compost [14].

After the biodegradability tests of PBS, HDPE and bio-composites at 10, 30, 40, 60 and 80 days, the tensile strength was obtained using a Universal Testing Machine (Zwick Co.) according to dog-bone shaped samples (ASTM D 638-99) at a crosshead speed of 100 mm/min and ambient temperature of 20 ± 2 °C. Notched Izod impact strength before and after the biodegradability test was measured using an Impact Tester (Dae Yeong Co.) by ASTM method D 256-97 at room temperature. Five measurements were conducted to determine the mechanical property which was the average of five samples. The percentage weight loss was determined by Eq. (1):

Weight loss (%) =
$$[(M_0 - M_d)/M_0] \times 100,$$
 (1)

where M_0 is the initial mass, and M_d is the degradation mass at each designated day. The percentage weight loss was taken from the average of five samples.

2.3.3. Microbial counts in natural and compost soil

The number of microorganisms in natural soil and compost soil was determined by a count of the growth colonies on NA and AIA plates. The NA medium consisted of 3 g bacto beef extract, 5 g bacto peptone, and 15 g bacto agar per litre of distilled water and was adjusted to pH 6.8. The AIA medium consisted of 2 g bacto casitone, 0.1 g asparagine, 4 g sodium propionate,

Table 1

Constituents of simulated municipal solid waste (MSW) aerobic compost soil

Category	Wet weight (%)	Wet weight of specific component (%)
Food waste	16.6	Solid wastes (16.6)
Garden waste	13.9	Leaves (6.9), grass (7.0)
Paper	58.5	Bleached (19.5), brown (19.5), cardboard (19.5)
Plastic	7.7	HDPE from milk bottles
Textiles	0.8	Cotton
Wood	2.5	Twigs

0.5 g KH₂PO₄, 0.1 g MgSO₄·7H₂O, 0.001 g FeS- $O_4 \cdot 7H_2O$, and 15 g bacto agar per liter of distilled water and was adjusted to pH 6.5. Three samples of NA and AIA plates were prepared for measuring microbial count in natural soil and compost soil. Each of the three NA and AIA plates were sterilized in an autoclave for 15 min at 121 °C, allowed to cool to 60 °C, and poured into Petri dishes. Natural and compost soil samples, each 1 g soil, were dissolved in 9 ml sterile water using a vortex mixer. They were each then diluted to 10^{-3} by adding 1 ml of the soil suspensions to 9 ml sterile water. From each of the 10^{-3} diluted solution samples, $100 \,\mu$ l were removed and spread onto NA and AIA plates, after which they were incubated at 30 °C for 24 and 48 h, respectively. After the incubation of each plate (NA and AIA), the number of colonies was measured by a colony counter. Three measurements were conducted and an average of the three samples was calculated.

2.3.4. Molecular weight after biodegradability

After the natural and compost soil burial tests of the PBS, each PBS specimen was eluted using 1,2,4trichlorobenzene (TCB) at 140 °C and filtered through a 0.2 µm polytetrafluoroethylene (PTFE) syringe filter. Molecular weights were measured by GPC at 145 °C using a PL-GPC 210 system (Polymer laboratories) equipped with refractive index (RI) detectors and a PL-gel 10 µm column (two mixed-B). TCB was used as an eluent solvent at a flow rate of 1 ml/min. The number-average (M_n) and weight-average (M_w) molecular weights were calculated using a calibration curve from polystyrene standards.

2.3.5. Differential scanning calorimetry (DSC) analysis

DSC analysis was carried out using a TA Instrument DSC Q 1000 (NICEM at Seoul National University) with 5–8 mg of PBS samples at the designated time points. Each sample was scanned as the temperature was raised from -80 to 200 °C at a heating rate of 10 °C/min and then cooled at the same rate under a nitrogen atmosphere. T_g , T_m , and T_c , were determined from the second scan. T_m was taken as the maximum of the endothermic melting peak from the heating scans and T_c was obtained from the temperature at the top of the peak on the crystallization peak from the cooling scans. T_g was considered to be a deflection of the base line from the areas of melting peaks and crystallization peaks, respectively.

2.3.6. FTIR-ATR analysis

The infrared spectra in the FTIR-ATR spectra of the compost soil burial tested PBS and bio-composite buried for 60 days were obtained using a Thermo Nicolet Nexus 870 FTIR spectrophotometer from the USA. A diamond was used as an ATR crystal. The specimens after the compost burial test were analysed over $525-4000 \text{ cm}^{-1}$ range and the resolution of the spectrum was 4 cm^{-1} . All spectra were averaged over 32 scans. This analysis was performed at point-to-point contact with a pressure device when analysing the solid specimens.

2.3.7. Morphological test

SEM was used to study the morphology of the surface degradation of PBS and bio-composites. Electron micrographs were obtained using a JEOL-5410 LV (JEOL, NICEM at Seoul National University) SEM microscope before and after the biodegradability tested specimens in natural and compost soil. Prior to the measurement, the specimens were coated with gold (purity, 99.99%) in order to prevent electrical discharge.

3. Results and discussion

3.1. Natural and compost soil burial test

The tensile strength of HDPE, PBS and RHF-filled PBS bio-composites as a function of compost soil burial time is shown in Fig. 1. This test is designed to determine the biodegradability of plastic materials, relative to that of a standard material, in an aerobic environment. Biodegradability aerobic experiments were carried out under a simulated MSW aerobic compost test [14]. The tensile strength of pure HDPE did not change, due to its non-biodegradability, whereas that of pure PBS slightly decreased after 10 days. Polyolefin materials such as HDPE have several advantages for use in various industrial fields but cause environmental problems in the global environment due to their nonbiodegradable nature [4]. Initially, the biodegradability of PBS begins with surface erosion due to the bacteria and fungi contained in the compost soil. This result was

confirmed by the SEM micrograph of the PBS degraded surface after the biodegradability test and is in line with the surface erosion mechanism reported by Tsuji and Suzuyoshi using polarizing microscope [15]. As the filler loading increased, the tensile strength and the notched Izod impact strength of PBS and the bio-composites decreased more rapidly during the compost soil burial test over 80 days (Fig. 2). This result indicated that the addition of RHF enhanced the biodegradability of PBS mainly because of the increased polymer surface created after RHF consumption by microorganisms [9]. Bio-flour is a complex material consisting of cellulose, hemicellulose and lignin. The major constituents of bio-flour can be degraded by many bacteria and fungi in the soil environment [16]. The chemical constituents of RHF are listed in Table 2. Cellulose and lignin are hydrophilic polymers consisting of glucose units linked by bonded β -1,4-glucosidic and phenolic compounds, respectively. The biodegradability of cellulose and lignin results from the hydrolytic depolymerisation of these materials to low molecular weight materials which then yield monomeric units [16]. We can expect that the biodegradability of cellulose mainly involves random chain scission of the bonded β -1,4-glucosidic and that of lignin involves cleavage of the side chains of the phenyl propane units [17]. Therefore, we can suggest that the biodegradability of PBS would be controlled by the bioflour content because it is more easily degradable than PBS in soil environment [4].

The percentage weight loss of HDPE, PBS and the bio-composites is shown in Fig. 3. With increasing RHF content, the percentage weight loss of the bio-composites decreased more rapidly. This result indicates that the degradation of RHF is faster than that of PBS matrix polymer because the cellulosic materials are easily attacked by microorganisms [18]. Fig. 4 compares the percentage weight loss of the bio-composites in natural and compost soil at 40 wt.% filler loading. Here



Fig. 1. Effect of compost soil burial duration up to 80 days on the tensile strength of HDPE, PBS and bio-composites.



Fig. 2. Effect of compost soil burial duration up to 80 days on the notched Izod impact strength of HDPE, PBS and bio-composites.

Table 2 Chemical constituents of WF and RHF

	Others (%)	Holocellulose (%)	Lignin (%)	Ash (%)	Total (%)
Rice-husk flour ^a	5.0	60.8	21.6	12.6	100
Wood flour ^a	10.9	62.5	26.2	0.4	100
Rice-husk flour ^b	6.3	59.9	20.6	13.2	100

^a Rice-husk and wood flours from Ref. [13].

^b Specification from Saron Filler Co.

too, the decrease in the percentage weight loss of biocomposites during the compost soil burial test occurred more rapidly than that during the natural soil burial test over 80 days. This is due to the enhanced biodegradation rate of bio-composites in a composting environment with the temperature and humidity maintained in the chamber [14]. From this result, we can expect that PBS and the bio-composites will degrade more easily under simulated MSW aerobic compost condition by microorganisms.

3.2. Microbial counts in natural and compost soil

Fig. 5 shows the total number of colonies on NA and AIA plates in natural and compost soil. Generally, NA and AIA plates are suitable for growing aerobic bacteria and actinomycetes in the soil environment [19]. We were able to see that the total colony count of natural soil was lower than that of compost soil. This result was confirmed by the growth of colonies on NA plates which can be seen in Fig. 6. This indicates that the microorganisms present in compost soil are more numerous than those found in natural soil because of the additional nourishment provided in a compost environment. It may also be seen that the metabolism rate of microorganisms in controlled compost soil was much higher than that of natural soil. From the above results, we can expect that the PBS and bio-composites in a compost soil burial test

100

95

90

85

80

HDPE 100% PBS 100%

PBS-RHF 10% PBS-RHF 20%

PBS-RHF 30%

PBS-RHF 40%

20

Veight Loss (%)



40

Time (days)

60

80



Fig. 4. Comparison of the percentage weight loss of PBS and biocomposites at 40 wt.% filler loading in natural and compost soil. *PBS and PBS-RHF 40 wt.% in natural soil test from reference [13].

are more easily biodegraded than those in a natural soil burial test, as many more microorganisms exist in compost soil. This result supports the theory that the biodegradability of biodegradable plastic and biocomposite materials in compost soil is superior to that in a natural soil environment.

3.3. Molecular weight analysis

Fig. 7 shows M_w and M_n of PBS before and after the biodegradability test in natural and compost soil test for 80 days. With increasing biodegradability time, M_w and M_n of PBS decreased in both the natural and compost test environments. It can be seen that the biodegradability of PBS initially commences with surface erosion, followed by random chain scission of the PBS main chain from the attached soil microbes [15]. The decreased molecular weight of PBS may be attributed to the hydrolysis of the aliphatic ester linkage of PBS, as well as to the changed low molecular weight materials such as



Fig. 5. The number of colonies grown on an NA plate for 24 h and an AIA plate for 48 h in natural and compost soil environments at 30 $^{\circ}$ C.



Natural soil



Compost soil

Fig. 6. The photographs of growth colonies of (a) natural soil and (b) compost soil on NA plates.

oligomer and monomer [10,20]. The rate of decrease of $M_{\rm w}$ and $M_{\rm n}$ of PBS was more accelerated in the compost soil test. The compost soil conditions are suitable for microorganism growth due to the high humidity, proper temperature of 30 °C and pH of 7. In addition, this result confirmed that the weight loss of PBS decreased more rapidly in the compost soil burial test.

3.4. DSC analysis

Fig. 8 shows the DSC second thermograms of PBS in the natural and compost soil tests for 80 days. It can be



Fig. 7. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of PBS in natural and compost soil.

seen that there are endothermic T_g and T_m peaks in the DSC thermograms. The T_g of PBS was indicated by a deflection of the base line and T_m was taken by the maximum of the endothermic melting peak [21]. Table 3



Fig. 8. DSC cooling and heating curves of PBS in compost burial test for 80 days.

Table 3 DSC test results of PBS before and after biodegradability test in natural and compost soil for 80 days

Day	$T_{\rm g}$ (°C)	$T_{\rm m}$ (°C)	$\Delta H_{\rm m}~({\rm J/g})$	$T_{\rm c}$ (°C)	$\Delta H_{\rm c} ~({\rm J/g})$
Compo	ost soil tested	d sample			
0	-33.8	112.2	99.2	50.7	78.4
30	-29.1	112.0	110.2	57.6	89.6
60	-28.8	112.1	114.6	58.4	96.2
80	-27.2	111.2	116.7	59.5	99.0
Natura	al soil tested	sample			
30	-32.8	112.3	106.5	60.9	84.6
60	-31.1	112.4	109.6	62.3	87.3
80	-29.7	112.3	110.4	63.3	95.0

presents Tg and Tm of PBS before and after the biodegradability test. As biodegradability time increased, $T_{\rm g}$ of PBS slightly shifted to higher temperature, whereas $T_{\rm m}$ of PBS remained constant. PBS is a semicrystalline polymer that consists of amorphous and crystalline regions formed from the main chain. After the biodegradability test, the increased $T_{\rm g}$ of PBS may have resulted from the decreasing amorphous regions of the PBS structure. From this result, we can expect that the biodegradability of PBS will initially occur in the amorphous regions and finally in the crystalline regions [10,15]. Ratto et al. [10] confirmed using DSC and GPC that the biodegradability of poly(butylene succinate-coadipate) PBSA occurs first in the amorphous zones. As the biodegradability progressed, the amorphous zones of PBS decreased which increased T_g with increasing crystallinity of the polymer chain arrangement. Table 3 shows that the decreased rate of T_{g} for PBS in compost soil was larger than that of PBS in natural soil. This may indicate that the biodegradability and degradation of the amorphous and crystalline regions of the natural soil tested PBS occurred more slowly than those of the compost soil tested PBS. This result was also indicated by the $M_{\rm w}$ and $M_{\rm n}$ values of PBS.

Table 3 illustrates $\Delta H_{\rm f}$, $\Delta H_{\rm c}$ and $T_{\rm c}$ of PBS before and after the biodegradability test in the natural and compost soil for 80 days. As the biodegradation time increased, $\Delta H_{\rm f}$ of PBS increased but $T_{\rm m}$ was not significantly changed. Furthermore, the shift in $\Delta H_{\rm f}$ and $T_{\rm c}$ of PBS is represented in Table 3. This implies that after the biodegradability test, the increased $\Delta H_{\rm f}$, $\Delta H_{\rm c}$ and $T_{\rm c}$ of PBS were related to the crystallization rate and extent of crystallinity [21,22]. Hence, the observed increases in $\Delta H_{\rm f}$, $\Delta H_{\rm c}$ and $T_{\rm c}$ values of PBS may have been caused by the effect of the decreased amorphous phase of PBS on the increased crystallinity of PBS in the soil burial test by soil microbes [10,22,23]. The increased rates of $\Delta H_{\rm f}$, $\Delta H_{\rm c}$ and $T_{\rm c}$, of PBS in the compost soil were higher than those of natural soil, because of the increased biodegradability of PBS in compost soil by activated microorganisms.



Fig. 9. Overlapping FTIR-ATR spectra of compost soil burial tested PBS.

3.5. FTIR–ATR analysis

Fig. 9 shows the FTIR-ATR spectra of PBS before and after the biodegradability test in the compost soil. It can be seen that the PBS specimens tested in the compost soil burial showed a significantly reduced absorption intensity of C-C-O and O-C-C bands, compared to before the biodegradability test. The peak of $1228-1264 \text{ cm}^{-1}$ may have resulted from C-C-O stretching for the functional groups in the ester linkage of PBS. The bands at the 1044 cm⁻¹ region were assigned to O-C-C stretching vibrations of PBS [24,25]. The band at the 1712 cm^{-1} region, also seen in this figure, was attributed to C=O stretching vibrations of the ester group in PBS. These results confirm that the chemical structures of PBS were changed after the compost burial test, mainly due to hydrolysis of the ester bonds, C–C–O and O–C–C, in the main chain [19,24]. Furthermore, this figure shows new peaks at 1314- 1330 cm^{-1} for PBS after the biodegradability test. These



Fig. 10. Overlapping FTIR-ATR spectra of compost soil burial tested bio-composites at 40 wt.% filler loading.

peaks were considered to be due to carboxyl acid C–O stretching of the degradation products of PBS [26]. Fig. 10 presents FTIR–ATR spectra of the biocomposites before and after the biodegradability test in compost soil at 40 wt.% filler loading. The peaks at 1156 and 1047 cm⁻¹ were due to the C–O–C and C–O stretching of cellulose in RHF, respectively [27]. The absorption band of a doublet at 1312 and 1334 cm⁻¹ may be attributable to the contents of crystalline and amorphous cellulose in RHF [28]. As biodegradability time increased, the absorption intensity of these peaks significantly decreased. This may have been due to the chain scission of the C–O–C and C–O bonds of the main chain and the degradation of crystalline and amorphous cellulose by bacteria and fungi in the compost soil [16,17]. These FTIR–ATR spectra results supported the biodegradability of PBS and bio-flour-filled PBS bio-composites.

3.6. Morphological test

Fig. 11 shows before and after images of the degradation surface of pure PBS in natural and compost soil for 80 days. Before the biodegradability test, the



Before biodegradation

Natural soil



Compost soil

Fig. 11. SEM micrographs of pure PBS (350×): (a) before biodegradability, (b) in natural soil, and (c) in compost soil for 80 days.

pure PBS sample exhibited a relative smooth and clear surface. However, at 80 days in the natural soil, there were a number of large holes in the PBS surface, indicating that the biodegradability surface of PBS was attacked by the microorganism under soil environment [13]. The degradation surface after the compost soil test presented many large holes and more cracks than that of the natural soil test. The biodegradability of PBS in the compost soil test was enhanced relative to that of the natural soil test due to the slow rate of hydrolysis at low temperature in natural soil. Fig. 12 shows before and after images of the degradation surface of the RHF-filled PBS bio-composites at 40 wt.% filler loading in natural and compost soil for 80 days. Larger holes and more numerous surface irregularities of bio-composites can be seen following the addition of RHF at 40 wt.% filler loading to the PBS, compared to that of pure PBS in the soil burial test. This is because the biodegradability of the PBS was enhanced by the incorporation of the bio-flour in the soil burial test [10].



Before biodegradation

Natural soil



Compost soil

Fig. 12. SEM micrographs of bio-composites $(350 \times)$: (a) before biodegradability, (b) in natural soil, and (c) in compost soil for 80 days at 40 wt.% filler loading.

4. Conclusions

The tensile strength, Izod impact strength and percentage weight loss of pure HDPE did not change, because of its non-biodegradability, whereas those of pure PBS were significantly decreased in the compost soil test. The reduction in the mechanical properties and percentage weight loss of PBS and the bio-composites in the natural soil burial test were significantly lower than that in the compost soil test because of the increased temperature and humidity conditions in the chamber. These results were confirmed using SEM observations by the presence of many large holes and more cracks in the degradation surface morphology of the compost soil tested PBS and bio-composites, compared to that of the natural soil test. Also, these results prove that the total number of colonies which grew on NA and AIA plates from a solution made with natural soil was lower than that observed from a solution made with compost soil.

After the biodegradability test in natural and compost soil, the decreased $M_{\rm w}$ and $M_{\rm n}$ of PBS were attributed to the hydrolysis of the aliphatic ester linkage and the changed low molecular weight materials. The degradation rate of $M_{\rm w}$ and $M_{\rm n}$ of PBS in the compost soil test was higher than that in the natural soil test due to the activated microorganisms in the controlledenvironment chamber. FTIR-ATR spectra proved that the chemical structures of PBS and the bio-composites were changed after the compost burial test, mainly due to hydrolysis of the ester bonds in the PBS main chain. In the case of the bio-composites, the biodegradability may have resulted from the chain scission of the C-O-C and C-O bonds of the cellulose main chain in RHF and the degradation of crystalline and amorphous cellulose by bacteria and fungi in the compost soil. As biodegradability time increased, T_g of PBS slightly shifted to a higher temperature but $T_{\rm m}$ of PBS was not significantly changed. As the biodegradability test progressed, the increased $\Delta H_{\rm f}$, $\Delta H_{\rm c}$ and $T_{\rm c}$ values of PBS were caused by the effect of the decreased amorphous phase of PBS on the increased crystallinity of PBS in the compost soil test. These results support the role of PBS and bio-composites as "green-composites" or "eco-materials" with potential as alternatives to non-biodegradable plastic materials for applications such as packing, injection moulded and disposable products.

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