

Enhanced hydrolysis resistance of biodegradable polymers and bio-composites

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ABSTRACT

This study investigated the hydrolysis of biodegradable polymers and bio-composites at 50 °C and 90% relative humidity (RH). With increasing hydrolysis time, the mechanical properties of the biodegradable polymers and bio-composites significantly decreased due to the easy hydrolytic degradation of the ester linkage of the biodegradable polymers. With increasing hydrolysis time, the tensile strength of the polybutylene succinate (PBS) treated with anti-hydrolysis agent or with trimethylolpropane triacrylate (TMPTA) significantly increased compared to the non-treated PBS. The same results were observed for the PBS-based bio-composites. This result was confirmed by the Fourier transform infrared-attenuated total reflectance (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS) spectra, which exhibited a less eroded surface, small cracks and fewer holes due to the reduced surface hydrolysis and erosion under high humidity condition.

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1. Introduction

In recent years, polyolefins such as polypropylene (PP), polyethylene (PE) and polystyrene (PS) have been widely used as synthetic polymers in the commercial plastic industry but their non-biodegradability and consequent waste disposal problems in the natural environment have caused various forms of environmental pollution [1,2]. Non-biodegradable plastic wastes can be reutilized by recycling to useful products rather than by burying them, but only a minor portion of the plastics is recyclable due to economic infeasibility and technical difficulty [3]. Thus, the demand for degradable and biocompatible polymers is rapidly increasing because of the growing recognition worldwide of the need to reduce the global environmental pollution resulting from non-biodegradable plastic waste [1,4]. Biodegradable polymers are leading candidates for substitution of non-biodegradable plastics because their hydrolytic and enzymatic degradation products, such as CO₂ and H₂O or CH₄ and H₂O, can be naturally metabolized into non-toxic substances as they are readily susceptible to biological attack in natural ecosystems such as active sludge, natural soil, lake and marine [1,5]. Most biodegradable synthetic polymers are mainly aliphatic polyesters produced microbiologically using enzymatic reactions and chemical synthesis such as polycondensation and ring-opening polymerization of natural, polymer-based products.

Recently, the incorporation of natural fiber and flour in biodegradable polymers, commonly called "Bio-Composites,

Bio-Plastic, Eco-Composites and Green-Composites" has received increasing attention from scientists for two main reasons: natural filler addition can reinforce the produced material and reduce the final product cost [6,7]. Compared to inorganic fillers, natural fillers offer various benefits such as environmental superiority, low cost, low density, lower manufacturing energy, low CO₂ emission, renewability and biodegradability. In this study, we used PBS as the matrix polymer and bamboo flour (BF) and wood flour (WF) as the reinforcing natural filler. PBS, a type of aliphatic polyester, is one of the most commercially available biodegradable polymers and can be efficiently synthesized through condensation polymerization from the starting materials of succinic acid and butan-1,4-diol. In addition, PBS has lower melting point of around 114–118 °C and excellent elongation at break compared to PP while other physical properties are similar to those of PP [8]. BF and WF have found wide use as completely biodegradable biomass materials and natural fillers. Especially, BF is an abundant natural resource in Asia, and it can be renewed much more rapidly than wood due to bamboo's more rapid growth than wood, which has resulted in its gradual invasion of wood forests and the reduction of the wood supply [9]. Due to its limited industrial applications, increasing the industrial applications of BF as an effective reinforcement for bio-composite materials will provide many benefits.

With the rising concern for environmental protection, biodegradable polymer and bio-composites have attracted much attention for increasing their application to automotive interior parts and other products. The main disadvantage of using biodegradable polymers in high strength application materials such as automotive interiors and electronic products is that they are easily degraded under high humidity condition. Due to the easy hydrolysis of

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biodegradable polymers under high humidity condition, the mechanical properties and thermal properties of biodegradable polymers and bio-composites are easily decreased. Because of these properties, biodegradable polymers and bio-composites are not widely used in this field. To expand the use of biodegradable polymer and bio-composites in automotive interiors and electronic products, the hydrolysis resistance property of these materials needs to be increased. In recent years, the biodegradability of biodegradable polymers and bio-composites has been mainly studied according to the biological activity in soil, compost soil, lake and marine, which is affected by microorganisms such as enzyme, fungi and bacteria [2,10]. Few studies have investigated the hydrolysis of biodegradable polymers and bio-composites under high humidity condition. Therefore, research on ways to evaluate and reduce the hydrolysis of biodegradable polymers and bio-composites under high humidity condition is very important for increasing the application of biodegradable polymers and bio-composites. This study employed a trifunctional monomer to induce crosslinking of biodegradable polymers and bio-composites during irradiation. Trifunctional monomers have been widely used as crosslinking agents for polyolefins and vinyl monomers [11].

In the present study, electron beam (EB) irradiation is applied to a trifunctional monomer to improve the hydrolysis and the influence of this treatment is investigated on the mechanical and thermal properties of the biodegradable polymers and bio-composites. Electron accelerators are widely used in printing companies, tire companies, automobile industries and cable factories for curing and crosslinking of polymeric materials [12]. The EB radiation method has been known to change the physical properties of polymers by macromolecule crosslinking (curing) and main chain scission (degraded) in high radiation energy and graft polymerization [13]. The advantages of using electron accelerators are short processing time, non-catalytic process, easy automation, unique process and environmentally friendly process [12].

The main objective of this study was to investigate the hydrolysis of biodegradable polymers and bio-composites at 50 °C and 90% relative humidity (RH). To reduce the hydrolysis of biodegradable polymers and bio-composites, we used an anti-hydrolysis agent and a trifunctional monomer. In addition, this study compared the mechanical and thermal properties, chemical analysis, surface hardness and morphological study of anti-hydrolysis agent-, trifunctional monomer- treated and non-treated biodegradable polymers and bio-composites. The study results suggested that appropriate selection of an anti-hydrolysis agent and trifunctional monomer content is important in reducing the hydrolysis of biodegradable polymers and bio-composites.

2. Experimental

2.1. Materials

2.1.1. Biodegradable polymer and natural flour

PP was supplied by LG Chem Co., Korea, with an MFI of 24 g/10 min (190 °C/2.160 g) and a density of 0.91 g/cm³. PBS and PBS-co-butylene adipate (PBAT) were prepared at Ire Chemical Ltd., South Korea. Their MFI were, respectively, 25 g/10 min and 2 g/10 min (test conditions 190 °C/2.160 g) and their densities respectively, 1.26 and 1.25 g/cm³. PBS adipate (PBSA) was supplied from SK Chemical Co., Korea, with an MFI of 15 g/10 min (190 °C/2.160 g) and a density of 1.22 g/cm³. PLA was supplied by Cargill-Dow Co., USA with an MFI of 15 g/10 min (190 °C/2.160 g) and a density of 1.22 g/cm³. The natural flours used as the reinforcing filler were BF and WF, supplied by Hangyang Advanced Materials Co., Korea. The particle size of BF and WF was 270–860 and 140 μm, respectively.

2.1.2. Anti-hydrolysis agent and trifunctional monomer

Anti-hydrolysis agent [Bis-(2,6-diisopropylphenyl) carbodiimide] was supplied by RheinChemie Co., Germany, with viscosity of 19 mPa s (80 °C) and a density of 0.94 g/cm³. Trimethylolpropane triacrylate (TMPTA, Miwon Commercial, Korea) was used as the trifunctional monomer. Fig. 1 shows the chemical structures of the anti-hydrolysis agent and trifunctional monomer.

2.2. Compounding and sample preparation

BF and WF were oven dried at 105 °C for 24 h to adjust the moisture content to 1–3% and then stored in sealed polyethylene bags before compounding. PBS was blended with BF, WF, anti-hydrolysis agent, and trifunctional monomer in a laboratory-sized, co-rotating, twin screw extruder using three general processes: melt blending, extrusion and pelletizing. The extruder barrel was divided into eight zones with the temperature in each zone being individually adjustable. Tables 1 and 2 show the content of anti-hydrolysis agent and trifunctional monomer which were used to reduce the hydrolysis of the biodegradable polymers and bio-composites. The temperature of the mixing zone in the barrel was maintained at 145 °C with a screw speed of 250 rpm. The extruded strand was cooled in a water bath and pelletized using a pelletizer. The extruded pellets were oven dried at 80 °C for 24 h, then stored in sealed polyethylene bags to avoid moisture infiltration. The extruded pellets were injection molded into tensile strength bars (ASTM D638), using an injection molding machine (Bau Technology, South Korea) at 145 °C with an injection pressure of 1200 psi and a device pressure of 1500 psi. After injection molding, the test bars were conditioned before testing at 50 ± 5% RH for at least 40 h according to ASTM D 618-99.

2.3. Electron beam (EB)-irradiated biodegradable polymer and bio-composites

TMPTA-treated and non-treated biodegradable polymers were irradiated with EB at radiation doses of 20 and 50 kGy using an EB accelerator at EB-TECH Co., South Korea. The EB-irradiated samples were tensile specimens. The irradiation was performed at room temperature (25 °C), humidity and in the presence of oxygen. EB

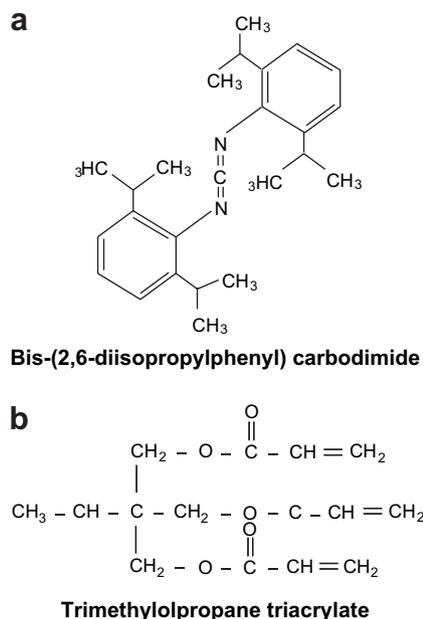


Fig. 1. Chemical structures of (a) anti-hydrolysis agent and (b) trifunctional monomer.

Table 1
Anti-hydrolysis agent content in PBS and bio-composites

	Content of anti-hydrolysis agent
PBS	1, 3, 5
PBS: natural flour (BF, WF) = 70:30	1, 3, 5

had an energy output of 1 MeV, beam current of 1 mA and velocity of 10 m/min.

2.4. Hydrolysis measurement of biodegradable polymer and bio-composites

The hydrolysis of non-biodegradable polymers such as PP and biodegradable polymers such as PLA, PBS, PBAT and PBSA was measured in a humidity chamber set at 50 °C and 90% RH for 30 days. The measurement was conducted under the same conditions for TMPTA-treated and non-treated PBS and bio-composites according to the content of TMPTA (3%). However, changes in the bio-composites and bio-composites treated with anti-hydrolysis agent, were characterized after storage in a humidity chamber set at 50 °C and 90% RH for 100 days according to the content of anti-hydrolysis agent (1, 3, 5%).

2.5. Mechanical property

2.5.1. Tensile strength

The tensile strength for the before and after hydrolysis specimens was conducted according to ASTM D 638-99 with a Universal Testing Machine (Zwick Co.) at a crosshead speed of 100 mm/min and a temperature of 24 ± 2 °C. Five measurements were conducted and averaged for the final result.

2.6. Gel content

The gel content of the crosslinked samples was estimated by measuring its insoluble part in dried sample after immersion in 1,2,4-trichlorobenzene (TCB) at 140 °C. The gel content was calculated as follows.

$$\text{Gel contents(\%)} = \frac{W_f}{W_i} \times 100$$

where W_i is the initial weight of the dried sample after EB irradiation and W_f the weight of the dried insoluble part of the sample after extraction with TCB.

2.7. Chemical structure analysis

2.7.1. Attenuated total reflectance spectroscopy (FTIR-ATR)

The infrared spectra in the FTIR-ATR spectra of the before and after hydrolysis specimens were obtained using a JASCO 6100 FTIR spectrophotometer from Japan. The specimens were analyzed over the range of 4000–600 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 30 scans. The analysis was performed at a point-to-point contact with a pressure device when analyzing the before and after hydrolysis specimens.

Table 2
TMPTA content in PBS and bio-composites

	Content of TMPTA
PBS	3
PBS:natural flour (BF, WF) = 70:30	3

2.7.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra (XPS) of the samples were obtained with a Sigma Probe (Thermo VG, U.K.) analyzer. The spectra were recorded using a monochromatic Al $K\alpha$ radiation X-ray source, operating at with 50 W and 10 kV voltage with a base pressure of 4×10^{-8} Torr in the sample chamber. XPS spectra were collected in the range of 0–1200 eV binding with a resolution of 1.0 eV and a pass energy of 50 eV. The XPS spectra were analyzed using a commercial, curve fitting software.

2.8. Surface hardness and morphological observation

2.8.1. Microhardness analysis

The microhardness of the samples was measured by a computer-controlled Fischerscope H100 XYp microhardness tester to monitor the surface hardness of the before and after hydrolysis specimens. The universal hardness (HU) and plastic hardness (HU_{pl}) measured by this equipment are defined by Eqs. (1) and (2), respectively.

$$HU = F_{\max}/26.43 \times (h_{\max})^2 \quad (1)$$

$$HU_{pl} = F_{\max}/26.43 \times (h_{\text{corr}})^2 \quad (2)$$

where F_{\max} is the indentation maximum force, h_{\max} the indentation maximum depth and h_{corr} the bounced back indentation depth. The mechanical work W_{total} expended during the indentation of the indenter is only partially consumed as plastic deformation work W_{plast} , while the remainder is released upon unloading as elastic recovery work W_{elast} . The microhardness was measured using a Vickers diamond indenter. The microhardness tests were performed at a maximum load of 10 mN and with a loading time of 20 s. This experiment is performed according to ISO 14577-1.

2.8.2. SEM observation

Scanning electron microscopy (SEM) was used to measure the before and after hydrolysis specimens using a SIRIOM scanning electron microscope (FEI Co.) from U.S.A. Prior to the measurement, the before and after hydrolysis specimens were coated with gold (purity, 99.99%) to prevent electrical discharge.

3. Results and discussion

3.1. Mechanical property

3.1.1. Effect of hydrolysis time of biodegradable polymer and bio-composites

The hydrolysis test was set at 90% RH and 50 °C to investigate the effect of high summer humidity on automotive interiors. Fig. 2 shows the tensile strength of PP and biodegradable polymers such as PBS, PBAT, PBSA and PLA as a function exposure time of up to 30 days to high humidity of 90% RH at 50 °C. The tensile strength of pure PP did not significantly change due to high hydrolysis resistance and non-biodegradability, whereas that of PBS and PBSA significantly decreased after 10 days. Polyolefin materials such as PP have several advantages such as excellent mechanical and thermal properties for use in various industrial fields but they cause environmental problems in the global environment [2]. The decreased tensile strength of biodegradable polymers is primarily due to the easy hydrolytic degradation of the ester linkage which occurs more randomly following the chain cleavage in the amorphous regions of the biodegradable polymer under high humidity condition [14,15]. However, the tensile strength of PBAT and PLA was slightly decreased after 10 days, although to a lower extent than

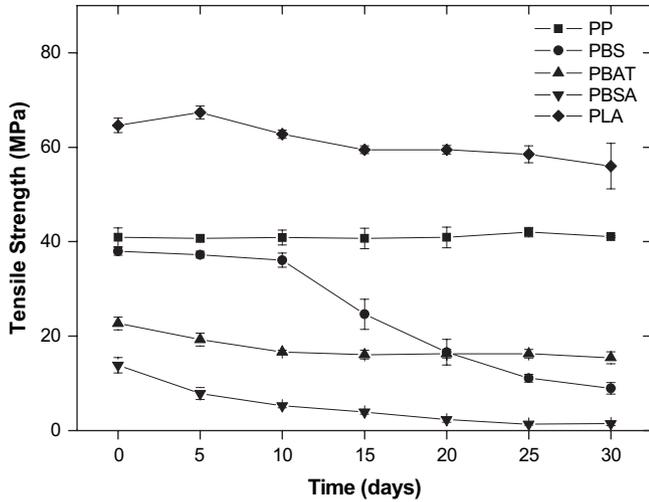


Fig. 2. Tensile strength of PP and biodegradable polymer as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

that for PBS and PBSA. This result arose due to the different chemical structures of these biodegradable polymers. Generally, the biodegradability and hydrolysis of biodegradable polymers depend mainly on their chemical structure and especially on the hydrolyzable ester bond in the main chain [2].

Fig. 3 shows the tensile strength of the PBS–BF and PBS–WF bio-composites as a function of high humidity exposure time at 50 °C and 90% RH for up to 30 days. The tensile strength of the PBS–BF and PBS–WF bio-composites was only measured because hydrolysis occurred more easily for PBS than for PBAT and PLA under high humidity condition. With increasing hydrolysis time, the tensile strength of the PBS–BF and PBS–WF bio-composites was significantly decreased, which was attributed to the increased hydrolysis of the ester group of the pure PBS. Furthermore, the influence of hydrolysis on the bio-composites was expected to be more dependent on the matrix polymer than on the natural flour.

3.1.2. Effect of anti-hydrolysis agent

The tensile strength of the anti-hydrolysis-treated and non-treated PBS is shown in Fig. 4. To reduce the PBS hydrolysis, an anti-hydrolysis agent is used under high humidity condition. With

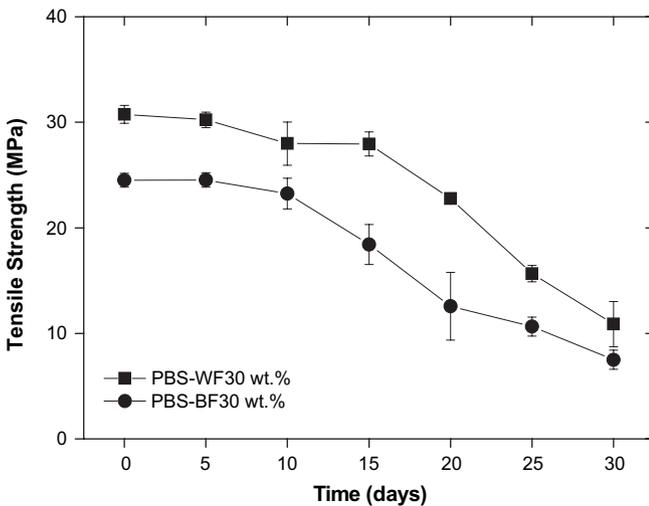


Fig. 3. Tensile strength of PBS–WF and PBS–BF bio-composites as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

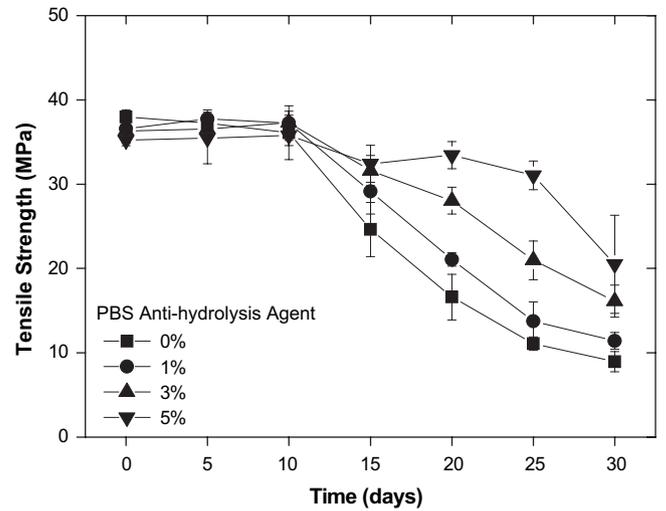


Fig. 4. Tensile strength of anti-hydrolysis agent-treated and non-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

increasing anti-hydrolysis agent content, the tensile strength of PBS was significantly increased compared to non-treated PBS at 30 days, indicating that the anti-hydrolysis agent-treated PBS exhibited increased resistance to hydrolysis of approximately 30% under

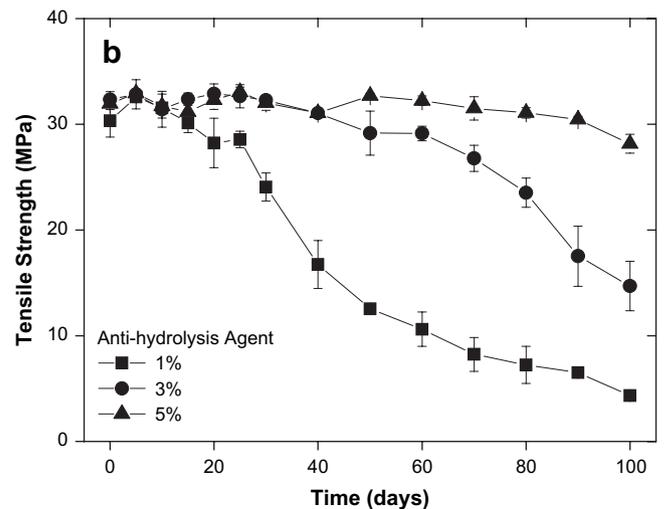
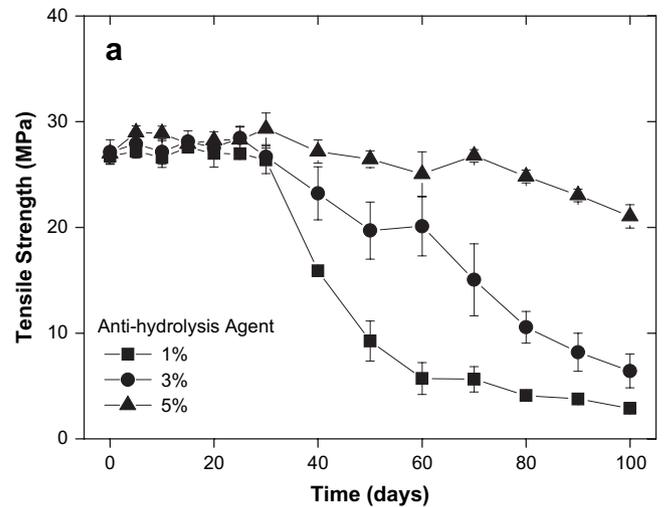


Fig. 5. Tensile strength of anti-hydrolysis agent-treated and non-treated (a) PBS–BF and (b) PBS–WF as a function of high humidity exposure time at 50 °C and 90% RH for 100 days.

high humidity condition. The increased hydrolysis resistance of the anti-hydrolysis agent-treated PBS indicated that the anti-hydrolysis agent increased the water absorption in the controlled humidity chamber. Initially, PBS hydrolysis begins with surface and core erosion due to water and then progresses to the inner bulk surface under high humidity condition. With increasing hydrolysis time, carbodiimide groups of the anti-hydrolysis agent in PBS may react with OH groups of water with a resulting reduction in the hydrolysis of the hydrolytic degradation of the PBS ester linkage. These results indicated that the anti-hydrolysis agent acted as a stabilizer against the hydrolytic degradation of the biodegradable polymer.

Fig. 5(a) and (b) shows the tensile strength of the anti-hydrolysis agent-treated and non-treated PBS-BF and PBS-WF bio-composites for 100 days. With increasing anti-hydrolysis content, the tensile strength of the PBS-BF and PBS-WF bio-composites significantly increased after 15 days, confirming the stronger hydrolysis resistance under high humidity condition of the anti-hydrolysis agent-treated bio-composites compared to the non-treated bio-composites. The anti-hydrolysis agent-treated PBS demonstrated improvement hydrolysis resistance under high humidity condition. After 30 days, the tensile strength of the anti-hydrolysis agent-treated bio-composites was significantly decreased at an anti-hydrolysis content of 1 and 3%. However, at an anti-hydrolysis content of 5%, the tensile strength of the PBS-WF and PBS-BF bio-composites was not significantly different from the control samples. These results indicated that a 5% anti-hydrolysis content is effective for reducing the hydrolysis of PBS and natural flour-filled, biodegradable polymer bio-composites.

3.1.3. The effect of trifunctional monomer

The tensile strength of EB-irradiated PBS at radiation doses of 20 and 50 kGy is shown in Fig. 6. The tensile strengths of PBS irradiated with EB and of PBS both irradiated with EB and treated with TMPTA (irradiation doses 20 and 50 kGy) were clearly higher than those of the non-irradiated control samples. Suhartini et al. [16] reported that EB irradiation of 3% trimethyl isocyanurate (TMAIC)-treated PBS up to a dose of 100 kGy did not change the gel content due to the increased formation of crosslinking of PBS up to a dose of 100 kGy. Therefore, this study selected EB irradiation doses of 20 and 50 kGy to increase the crosslinking of PBS and TMPTA-treated PBS, which was probably due to the sufficiently high amount of polymer radicals produced that react with monomers at these doses. The increased tensile strength of the

EB-irradiated PBS was due to the slightly increased crosslinking in the amorphous PBS region that resulted in the production of polymer radicals and hydrogen radicals [12–17]. Khan et al. [18] reported that the tensile strength of EB-irradiated PBS at low irradiation dose (20 and 50 kGy) slightly increased due to the formation of additional crosslinking in PBS from the production of mainly polymer radicals and hydrogen radicals. Also, the tensile strength of TMPTA-treated PBS was much higher than that of TMPTA non-treated PBS at the irradiation doses of 20 and 50 kGy. After 15 days of high humidity exposure, the tensile strength of the EB-irradiated PBS and EB-irradiated, TMPTA-treated PBS was significantly decreased at irradiation doses of 20 and 50 kGy. However, the tensile strength of the EB non-treated PBS was significantly decreased after 15 days of high humidity exposure. This result suggested that TMPTA has three functional groups (C=C) and a cyclic unit (acrylate) that achieves the formation of a three-dimensional network structure [11,19]. An EB radiation dose of 50 kGy on PBS and TMPTA-treated PBS gave the highest tensile strength and was, therefore, chosen as the proper radiation dose to reduce hydrolysis.

Fig. 7(a) and (b) shows the tensile strength of EB-irradiated, TMPTA-treated, PBS-BF and PBS-WF bio-composites at radiation doses of 20 and 50 kGy. With increasing hydrolysis time, the tensile strength of the TMPTA-treated, PBS-BF and PBS-WF bio-composites was decreased at radiation doses of 20 and 50 kGy. However,

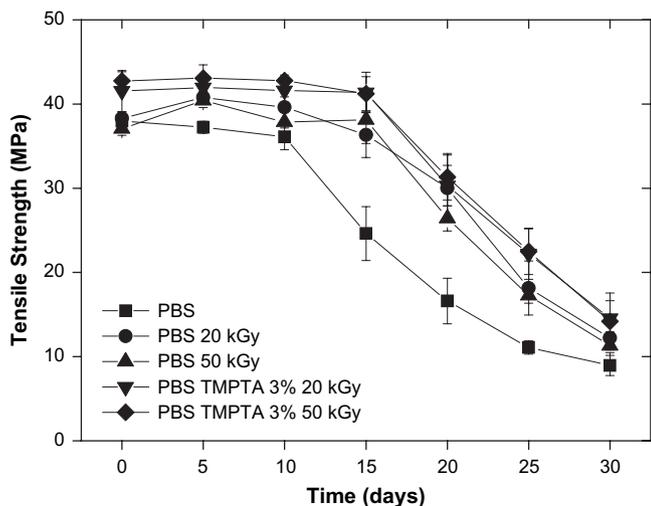


Fig. 6. Tensile strength of EB-irradiated PBS at irradiation dose of 20 and 50 kGy as a function of high humidity exposure time at 50 °C and 90% RH for 100 days.

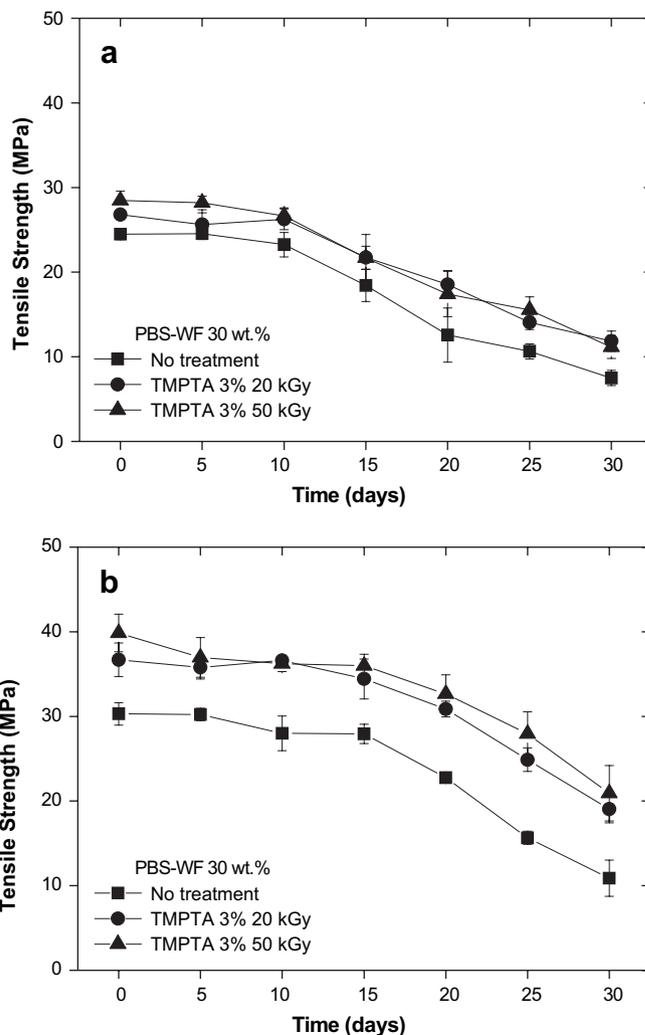


Fig. 7. Tensile strength of EB-irradiated (a) PBS-BF and (b) PBS-WF bio-composites with TMPTA at irradiation dose of 20 and 50 kGy as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

the tensile strength of the TMPTA-treated, PBS–BF and PBS–WF bio-composites was slightly higher than that of the non-treated bio-composites. At the higher tensile strength of the TMPTA-treated, bio-composites, it is clearly seen that the crosslinking reaction of the bio-composites by EB irradiation treatment can prevent the hydrolysis of the bio-composites. These results suggest that a TMPTA content of 3% and EB irradiation dose of 50 kGy are effective for reducing the hydrolysis of biodegradable polymers and natural-flour-filled, biodegradable polymer bio-composites.

3.2. Gel content

The gel contents of PBS in the presence of TMPTA versus the EB irradiation dose are shown in Fig. 8. No gels were formed in the irradiated pure PBS. However, the gel content was 53.6 and 66.8% in the 3% TMPTA-treated PBS at EB irradiation doses of 20 and 50 kGy, respectively. The increased gel content of the TMPTA-treated PBS was due to the formation of crosslinking when the TMPTA-treated PBS was irradiated at 20 and 50 kGy. The increased crosslinking of the PBS and bio-composites was caused by the improved mechanical properties of the PBS and bio-composites. Nagasawa et al. [11] reported that the optimum gel content was achieved with 3% triallyl isocyanurate (TAIC)-treated PLA at an EB dose of 50 kGy. Therefore, we assumed that PBS with a similar TMPTA content of 3% would maximize the PBS gel content at an EB dose of 50 kGy.

3.3. Chemical structure analysis

3.3.1. FTIR-ATR spectroscopy

Fig. 9 shows the FTIR-ATR spectra of PBS before and after the hydrolysis test under high humidity condition. With increasing hydrolysis time, the PBS specimens showed a significantly reduced absorption intensity of the C–C–O band, compared to before the hydrolysis test. The peak of 1266–1227 cm^{-1} resulted from C–C–O stretching for the functional groups in the ester linkage of PBS. The band in the 1715 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 hydrolysis test, mainly due to hydrolysis of the ester bonds, C–C–O and O–C–C, in the main chain. Furthermore, this figure shows new peaks at 1312–1332 cm^{-1} for PBS after the hydrolysis test. These peaks were attributed to carboxyl acid C–O stretching of the degradation products of PBS [2]. The intensity of the bending vibration of these peaks increased with increasing

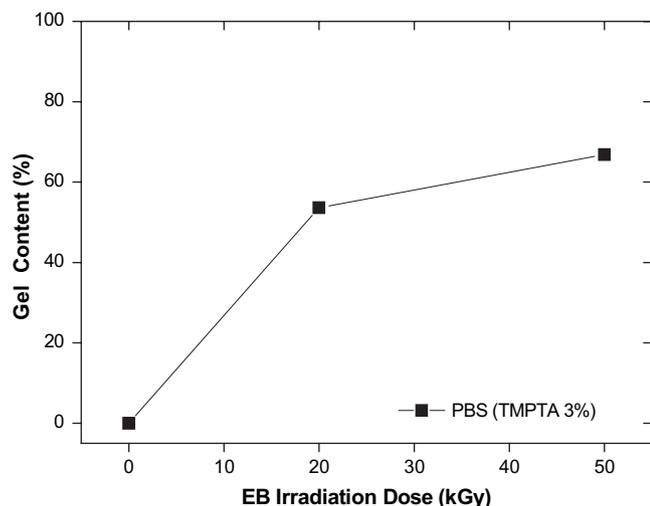


Fig. 8. Gel content of TMPTA-treated PBS at EB irradiation dose at 20 and 50 kGy.

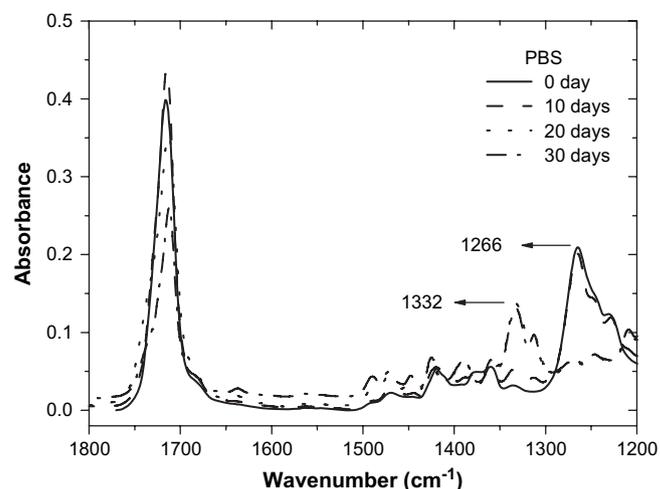


Fig. 9. FTIR-ATR spectra of PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

hydrolysis time. The FTIR-ATR spectra of the anti-hydrolysis agent-treated PBS under high humidity condition for 30 days are shown in Fig. 10. With increasing hydrolysis time, the absorption intensity of NH_2 (3316 cm^{-1}) and NH (1547 cm^{-1}) of the anti-hydrolysis agent-treated PBS increased, indicating that the carbodiimide group of the anti-hydrolysis agents was reacted under high humidity condition with the water which was increasingly converted from the amine and amide groups. This result suggested that the increase in this reaction of the anti-hydrolysis-treated PBS was prevented by the hydrolysis of the ester groups of the PBS main chain under humidity condition. This result further confirmed that the tensile strength of the anti-hydrolysis agent-treated PBS was higher than that of the non-treated PBS due to the reduced hydrolysis of PBS. Fig. 11 shows the FTIR-ATR spectra of the TMPTA-treated PBS under high humidity condition for 30 days. With increasing hydrolysis time, the absorption bands in the region 1240–1262 cm^{-1} (C–C–O) and the absorption band at 1716 cm^{-1} (C=O) of the TMPTA-treated PBS were decreased, due to the hydrolytic degradation of matrix polymer in the TMPTA-treated PBS.

3.3.2. XPS spectroscopy

Fig. 12 shows the XPS spectra of (a) PBS 0 day and (b) PBS 20 days before and after the hydrolysis test under high humidity

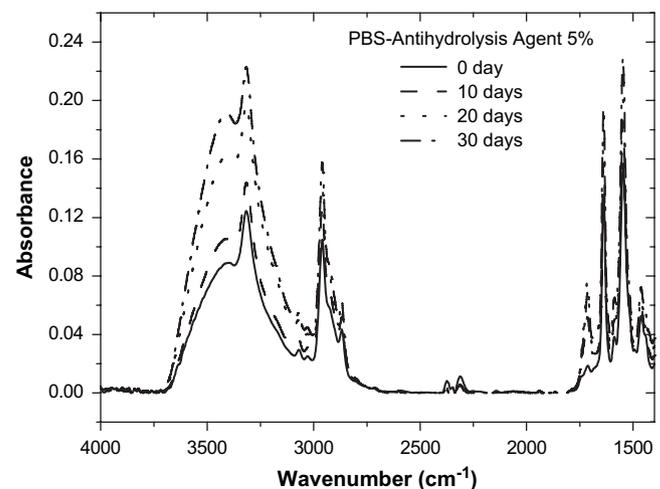


Fig. 10. FTIR-ATR spectra of anti-hydrolysis agent-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

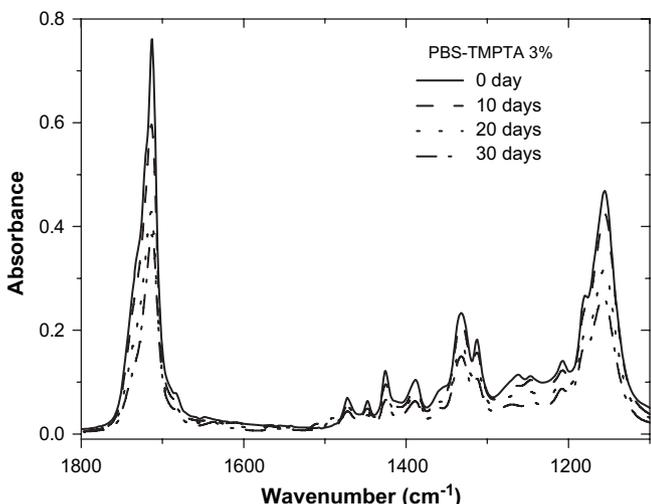


Fig. 11. FTIR-ATR spectra of TMPTA-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

condition. As seen in Fig. 12(b) and Table 3, pure PBS exhibited two new characteristic peaks of C1s (BE = 287.5 eV) and O1s (BE = 531.2 eV) after the hydrolysis test. The new C1s and O1s peaks were related to the degradation products of PBS such as C1s (C–O

Table 3
C1s and O1s peaks in the XPS spectra for PBS

Core level	Corresponding bond	Peak BE
PBS 0 day C1s	C–C, C–H	284.9
	C–O, C–O–C	286.4
	C–O=O	289.1
O1s	C–O–C/C–OH	532.2
	O=C–O	533.6
	PBS 20 days C1s	C–C, C–H
C–O, C–O–C		286.3
C–O, O–C–O		287.5
C–O=O		288.9
C=O		531.2
O=C–O		533.8

and O–C–O) and O1s (O=C) bonding types [12,20,21]. The new C1s (C–O and C–O–C) and O1s (O=C) peaks of pure PBS resulted from the hydrolysis and degradation of the ester groups of the PBS main chain under high humidity condition.

The XPS spectra of the 1% anti-hydrolysis agent-treated PBS (a) 0 day and (b) 20 days are shown in Fig. 13 and Table 4. In Fig. 13(a), the anti-hydrolysis agent-treated PBS showed the new characteristic peak of C1s (BE = 285.6 eV), which is also seen in Fig. 13(b). These peaks were due to the formation of the C=N functional

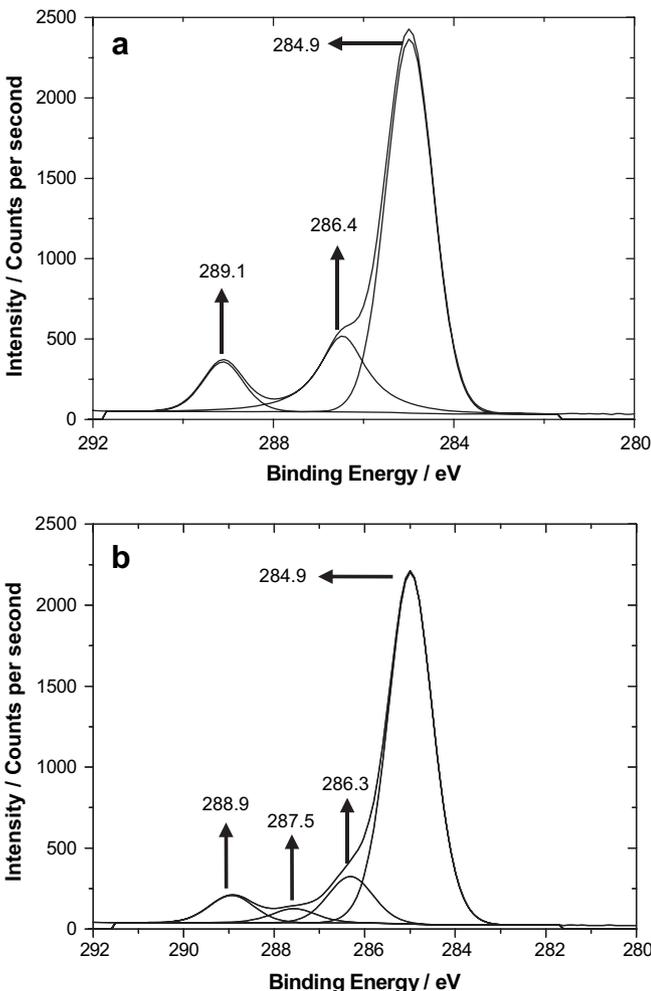


Fig. 12. XPS spectra of carbon peaks (C1s) of (a) PBS 0 day and (b) PBS 20 days.

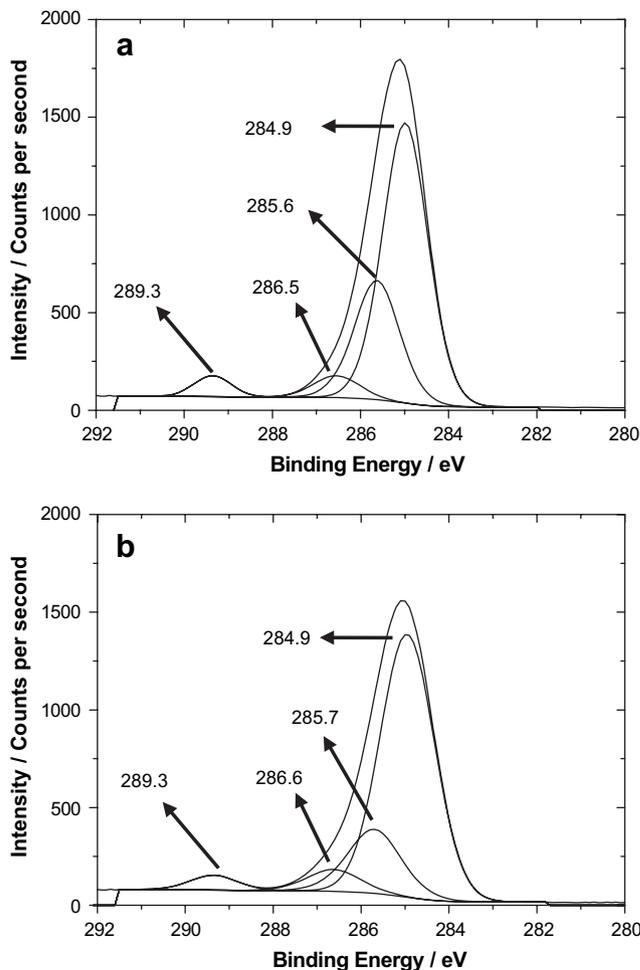


Fig. 13. XPS spectra of carbon peaks (C1s) of anti-hydrolysis agent-treated PBS (a) 0 day and (b) 20 days.

Table 4
C1s and O1s peaks in the XPS spectra for anti-hydrolysis agent-treated PBS

Core level	Corresponding bond	Peak BE
PBS (anti-hydrolysis agent) 0 day		
C1s	C–C, C–H	284.9
	C=N	285.6
	C–O, C–O–C	286.5
	C–O=O	289.3
O1s	C=O	531.4
	C–O–C/C–OH	532.4
	O=C–O	533.4
	O=C–N	534.3
PBS (anti-hydrolysis agent) 20 days		
C1s	C–C, C–H	284.9
	C=N	285.7
	C–O, C–O–C	286.6
	C–O=O	289.3
O1s	C=O	531.6
	C–O–C/C–OH	532.7
	O=C–O	533.4
	O=C–N	534.1

group of the anti-hydrolysis agent. In addition, the anti-hydrolysis agent-treated PBS did not show the degradation peak C1s (BE = 287.5 eV), indicating that the anti-hydrolysis agent reduced the hydrolysis of PBS. As seen in Table 4, the anti-hydrolysis agent-treated PBS before and after hydrolysis showed the new peaks of O1s (BE = 534.3 and 534.1 eV). These peaks may have been caused by the reaction of the anti-hydrolysis agents with the water which was converted from the O=C–N functional groups. This result was confirmed by the FTIR-ATR spectra of the anti-hydrolysis agent-treated PBS.

3.4. Surface hardness and morphological observation

3.4.1. Microhardness analysis

Fig. 14(a) and (b) shows the microhardness test of the anti-hydrolysis agent-treated and non-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days. With increasing hydrolysis time, the universal hardness and plastic hardness of the anti-hydrolysis agent-treated and non-treated PBS increased, indicating that the brittleness of the anti-hydrolysis agent-treated and non-treated PBS surface was increased because of the increasing surface erosion under high humidity condition. With increasing content of anti-hydrolysis agent, the universal hardness and plastic hardness of PBS slightly decreased, which was attributed to the lower

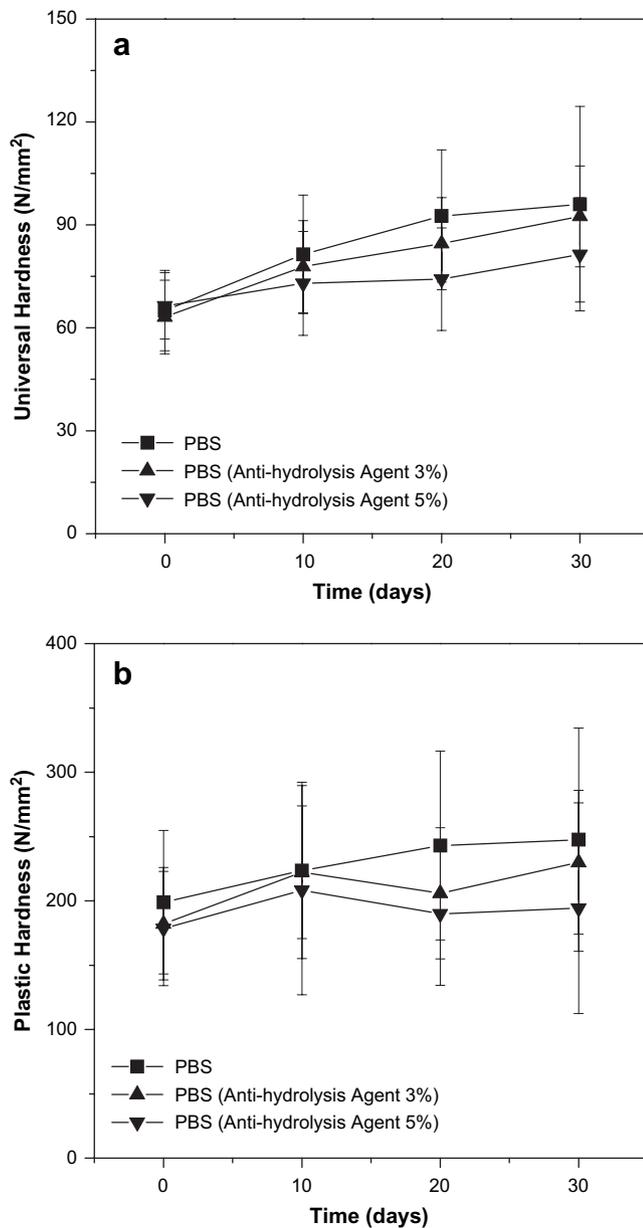


Fig. 14. Microhardness test of anti-hydrolysis agent-treated PBS and non-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

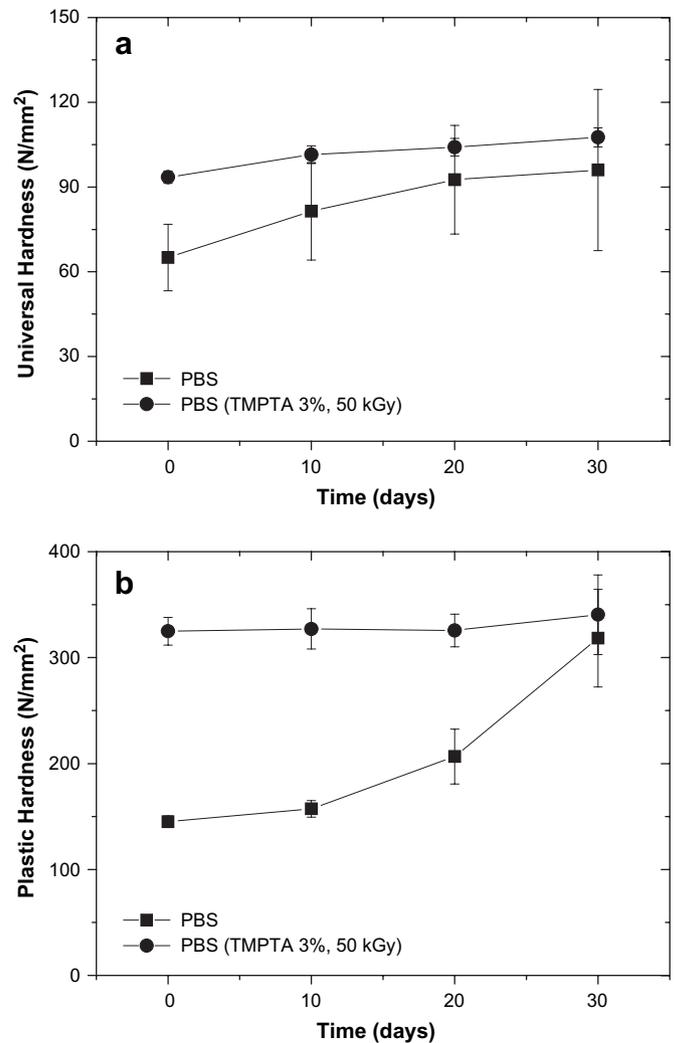


Fig. 15. Microhardness test of TMPTA-treated PBS and non-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days.

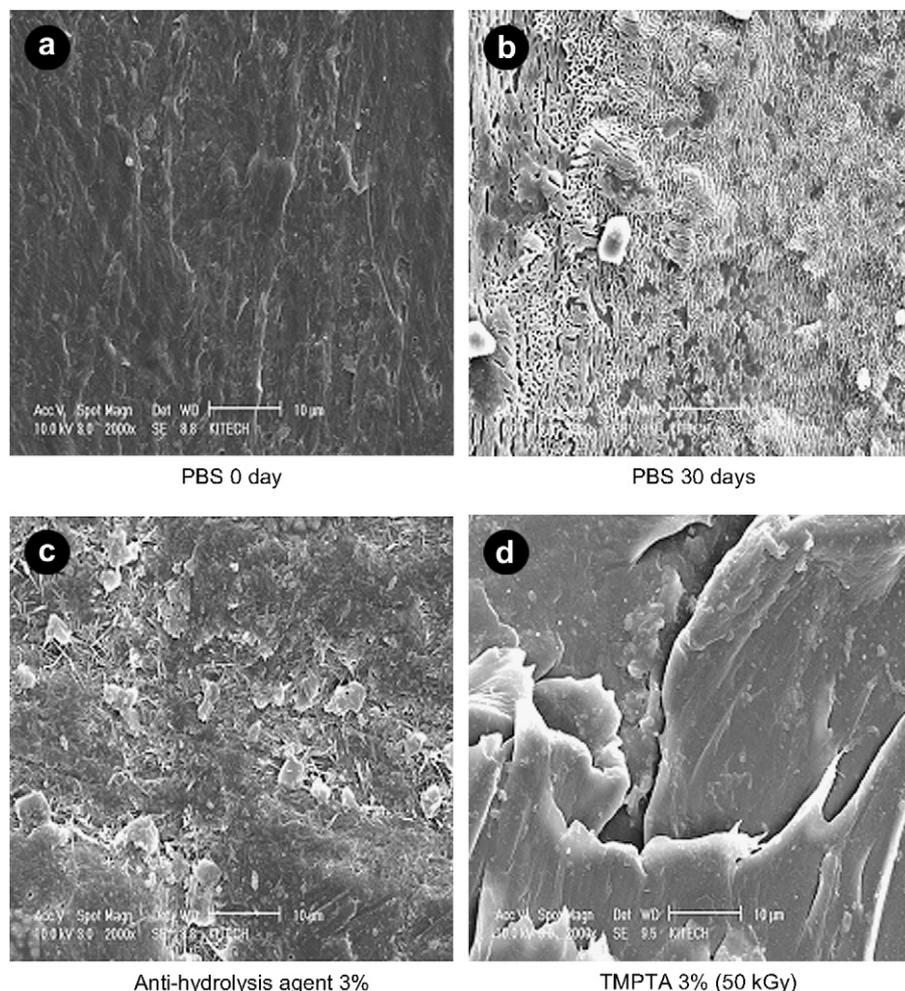


Fig. 16. SEM micrographs of pure PBS ($\times 2000$): (a) before hydrolysis, (b) non-treated, (c) anti-hydrolysis agent 3% and (d) TMPTA 3% (50 kGy) as a function of high humidity exposure time at 50 °C and 90% RH at 30 days.

surface hydrolysis of the anti-hydrolysis agent-treated PBS than that of the non-treated PBS. Therefore, this result suggested that the addition of anti-hydrolysis agent in the biodegradable polymer was an effective method for reducing the hydrolysis and brittleness of the surface of biodegradable polymers. Fig. 15(a) and (b) presents the microhardness test results of the TMPTA-treated and non-treated PBS as a function of high humidity exposure time at 50 °C and 90% RH for 30 days. The universal hardness and plastic hardness of the TMPTA-treated PBS was higher than that of the non-treated PBS, due to the increasing crosslinking density of the TMPTA-treated PBS by EB irradiation at a dose of 50 kGy. With increasing hydrolysis time, the decrease rate of the TMPTA-treated PBS was lower than that of the non-treated PBS, suggesting that the increased crosslinking of PBS was reduced by the hydrolysis and brittleness of the PBS surface under high humidity condition.

3.4.2. Morphological observation

Fig. 16(a) and (b) shows before and after SEM images of the degradation surface of the pure PBS under high humidity condition for 30 days. Before the hydrolysis test, the pure PBS presented a relative smooth and clear surface. However, with increasing hydrolysis time, the PBS surface underwent random degradation which increased the formation of cavities, a rough surface with large holes and the extension to many deep holes. This observation indicated that the pure PBS is easily degraded by water under high humidity condition. This degraded surface of PBS was caused

by the low mechanical properties. Also, Fig. 16 shows the SEM images of the degradation surface of the (b) non-treated PBS, (c) anti-hydrolysis agent-treated PBS and (d) TMPTA-treated PBS (50 kGy) at 30 days. The degradation surface of the anti-hydrolysis agent- and TMPTA (50 kGy)-treated PBS clearly exhibited less surface erosion, smaller cracks and fewer holes.

4. Conclusions

The tensile strength of pure PP did not significantly change due to its high hydrolysis resistance and non-biodegradability, whereas that of biodegradable polymers significantly decreased due to the easy hydrolytic degradation of the ester linkage of these biodegradable polymers after 10 days under high humidity condition. With increasing anti-hydrolysis agent content, the tensile strength of the anti-hydrolysis agent-treated PBS and bio-composites was significantly increased compared to the non-treated PBS and bio-composites under high humidity condition. In addition, the tensile strength of the TMPTA-treated PBS and bio-composites was much higher than that of the TMPTA non-treated PBS and bio-composites at the irradiation doses of 20 and 50 kGy. With increasing hydrolysis time, the PBS specimens showed a significantly reduced absorption intensity of the C–O band, compared to that before the hydrolysis test. However, with increasing hydrolysis time, the absorption intensity of NH_2 (3316 cm^{-1}) and NH (1547 cm^{-1}) of the anti-hydrolysis agent-treated PBS increased. This result indicated

that the carbodiimide group of the anti-hydrolysis agents was reacted under high humidity condition with the water which was increasingly converted from the amine and amide groups. The new C1s (C–O and C–O–C) and O1s (O=C) peaks of the pure PBS from the XPS spectra resulted from the hydrolysis and degradation of the ester groups of the PBS main chain under high humidity condition. After the hydrolysis test under high humidity condition, the universal hardness and plastic hardness of the anti-hydrolysis agent-treated and non-treated PBS increased due to the increasing surface erosion and brittleness of PBS, whereas those of the anti-hydrolysis agent- and TMPTA-treated PBS slightly decreased. With increasing hydrolysis time, the pure PBS surface underwent random degradation which increased the formation of cavities, a rough surface with large holes and the extension to many deep holes. However, the degradation surface of the anti-hydrolysis agent- and TMPTA (50 kGy)-treated PBS clearly exhibited less surface erosion, small cracks and fewer holes. These study results suggested that the addition of an anti-hydrolysis agent and TMPTA is an effective method for reducing the hydrolysis and degradation of biodegradable polymers and bio-composites under high humidity condition.

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