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THERMAL ANALYSIS OF HYDROLYSIS AND DEGRADATION OF BIODEGRADABLE POLYMER AND BIO-COMPOSITES

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The purpose of this study was to conduct a thermal analysis of the hydrolysis and degradation behavior of biodegradable polymers and bio-composites at 50°C and 90% relative humidity (RH). With increasing hydrolysis time, the thermal stability and degradation temperature of polybutylene succinate (PBS) slightly decreased. The glass transition temperature (T_g) and melting temperature (T_m) of PBS and the anti-hydrolysis agent treated PBS did not vary significantly with increasing hydrolysis time, whereas those of the trimethylolpropane triacrylate (TMPTA)-treated PBS slightly increased. With increasing hydrolysis time, the storage modulus (E') values of the bio-composites decreased, whereas those of the TMPTA treated bio-composites slightly increased. Also, the tanδ values of the anti-hydrolysis agent and TMPTA treated PBS–BF bio-composites were slightly lower than those of the non-treated bio-composites, due to the reduction in their degree of hydrolysis. The $\tan\delta_{max}$ peak temperature (T_g) of the anti-hydrolysis agent treated bio-composites was not significantly changed, whereas that of the TMPTA treated bio-composites was increased.

Keywords: *anti-hydrolysis agent, bio-composites, biodegradable polymer, hydrolysis, thermal analysis, TMPTA*

Introduction

In recent years, as a result of growing environmental awareness, there has been a global effort to develop biodegradable polymers and biodegradable bio-composites to meet the requirements of environmental concerns, legislation, scientific research and waste management. Currently, biodegradable polymers, bio-based materials and composites have become an area of focus for both industry and government [1]. Thermoplastic polymers based on petroleum-based synthetic resources, such as polypropylene (PP), polyethylene (PE: HDPE and LDPE) and polystyrene (PS), have generally been used in the plastic industries. However, these polymers do not degrade easily in the natural environment, resulting in various forms of environmental pollution in the eco-system [2]. The annual worldwide disposal of approximately 200 million tons of petrochemical plastics in commonly used commodities such as polyolefins in packagings, bottles and molding products is a significant environmental problem, especially with the continuously increasing production and consumption of these materials [3, 4]. Furthermore, plastic wastes are an undesired pollutant in soil, rivers and marine environments. Because of their resistance to microbial attack, they tend to accumulate in the natural environment [4]. To solve these problems, the use of environmentally friendly, degradable polymers and bio-based materials is being considered as an alternative to conventional plastic materials. During the last 50 years, considerable effort has been made to develop biodegradable polymers and bio-based materials that can be easily degraded by microorganisms, bacteria, enzymes and fungi in the natural environment [5]. Polybutylene succinate (PBS) is an aliphatic thermoplastic polyester with a range of desirable properties including biodegradability, melt processability and thermal and chemical resistance. PBS is produced through the condensation reaction of glycols such as 1,4-butanediol, and aliphatic dicarboxylic acids such as succinic acid are used as the principal raw materials [4].

In recent years, natural fibers and flours have been widely used as reinforcing fillers in non-biodegradable polymer and biodegradable polymer composite materials to provide positive environmental benefits with respect to their ultimate disposability and raw material utilization [5–8]. Bio-composites made using natural fibers and natural flour as reinforcing fillers offer various benefits, such as easy availability, low manufacturing energy, low CO_2 emission, low mass and cost, renewability, biodegradability and the absence of associated health hazards, as compared to inorganic fillers such as car-

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bon black, calcium carbonate, talc and zinc oxide [2]. Bamboo flour (BF) and wood flour (WF) have found wide use as completely biodegradable biomass materials and bio-fillers. 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 compared to wood, which has resulted in its gradual invasion of wood forests and the reduction of the wood supply [9]. RHF and WF have limited industrial applications. Therefore, increasing the industrial applications of RHF and BF as effective reinforcements for bio-composite materials would provide many benefits.

The main disadvantage of using biodegradable polymers in high strength application materials is that they are easily degraded under high humidity conditions. To expand the use of biodegradable polymers and bio-composites, the hydrolysis resistance properties of these materials needs to be increased. In recent years, the biodegradability of biodegradable polymers and bio-composites has mainly been studied in relation to the biological activity in soil, compost soil, lakes and marine environments, which is caused by microorganisms such as enzymes, fungi and bacteria [10]. However, few studies have been conducted to investigate the hydrolysis of biodegradable polymers and bio-composites under high humidity conditions. To reduce the hydrolysis of biodegradable polymers and bio-composites, this study employed an anti-hydrolysis agent and a trifunctional monomer to induce the cross-linking of the biodegradable polymers.

Thermal analysis (TA) is an experimental analytical technique which can be used to measure the thermal properties and the effects of degradation on the structure of biodegradable polymers and composite materials as function of temperature [11]. Among the various thermoanalytical techniques, thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been used to investigate the degradation of biodegradable polymers [12].

The main objective of this study was to conduct a thermal analysis of the hydrolysis and degradation of biodegradable polymers and bio-composites at 50°C and 90% relative humidity (RH). To reduce the hydrolysis of the biodegradable polymers and bio-composites, we used an anti-hydrolysis agent and a trifunctional monomer. In addition, this study compared the thermal stability, T_m, T_g and visco-elastic properties of the anti-hydrolysis agent-, trifunctional monomer-treated and non-treated biodegradable polymers and bio-composites.

Experimental

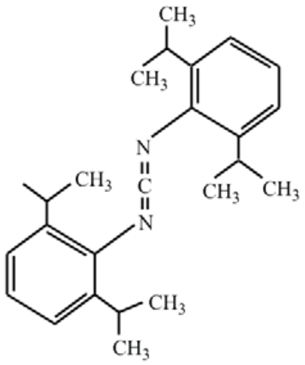
Materials

Matrix polymer and natural flour

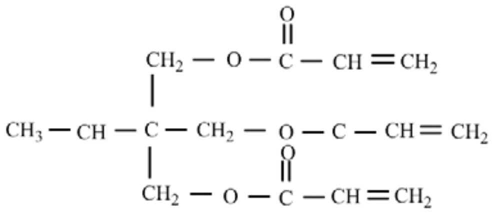
PBS was prepared at Ire Chemical Ltd., South Korea, with an MFI of 25 g/10 min (190°C/2, 160 g) and a density of 1.26 g cm^{-3}. The natural-flours used as the reinforcing filler were BF and WF, which were supplied by Hangyang Advanced Materials Co., South Korea. The particle sizes of BF and WF were 860 to 270 and 140 μm, respectively.

Anti-hydrolysis agent and trifunctional monomer

The anti-hydrolysis agent [*bis*-(2,6-diisopropylphenyl)carbodiimide] was supplied by Rhein-Chemie Co., Germany, with a viscosity of 19 mPa s (80°C) and a density of 0.94 g cm^{-3}. Trimethylolpropane triacrylate (TMPTA, Miwon Commercial, South Korea) was used as the trifunctional monomer. Figure 1 shows the chemical structures of the anti-hydrolysis agent and trifunctional monomer.



a – bis-(2,6-diisopropylphenyl)carbodiimide



b – trimethylolpropane triacrylate

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

Compounding and sample preparation

BF and WF were oven dried at 105°C for 24 h to adjust their moisture content to 1~3% and then stored in sealed polyethylene bags before compounding. PBS was blended with BF, WF, the anti-hydrolysis agent and trifunctional monomer in a laboratory-sized, co-ro-

Table 1 Content of anti-hydrolysis agent and TMPTA in PBS and bio-composites

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

tating, 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. Table 1 shows the content of the anti-hydrolysis agent and trifunctional monomer used to reduce the degree of hydrolysis of the biodegradable polymers and bio-composites. The temperature of the mixing zone in the barrel was maintained at 145°C while the barrel was rotated at 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 24h and stored in sealed polyethylene bags to avoid unwanted moisture infiltration.

Measurements

Hydrolysis measurement of biodegradable polymer and bio-composites

The hydrolysis of PBS 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 the anti-hydrolysis agent- and TMPTA-treated and non-treated PBS and bio-composites according to the content of the anti-hydrolysis agent (3%) and TMPTA (3%).

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

The TMPTA-treated and non-treated biodegradable polymers and bio-composites were irradiated with EB at radiation doses of 50 kGy using an EB accelerator at EB-TECH Co., South Korea. The irradiation was performed at room temperature (25°C), humidity and in the presence of oxygen. The EB had an energy output of 1 MeV, beam current of 1 mA and velocity of 10 m min^{-1}.

Thermogravimetric (TG) analysis

The TG measurements of the specimens before and after hydrolysis were carried out using a thermogravimetric analyzer (TA Instruments, TGA Q500) on samples of about 10~13 mg over the temperature range from 25 to 700°C at a heating rate of 20°C min^{-1} under a nitrogen flow of 40 mL min^{-1}. TG was performed with the biodegradable polymer placed in a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere to prevent unwanted oxidation.

Differential scanning calorimetry (DSC)

DSC analysis was carried out using a TA Instrument DSC Q 1000 with 3~5 mg of the specimens before and after hydrolysis at the designated time points. Each sample was scanned in dynamic mode as the temperature was raised from –80 to 200°C at a heating rate of 10°C min^{-1} and then cooled at the same rate under a nitrogen atmosphere. The glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures were determined from the second scan. T_m was taken as the maximum of the endothermic melting peak, T_c as the temperature at the top of the crystallization peak, and T_g as the deflection of the baseline from the cooling scan. The heats of fusion (ΔH_f) and crystallization (ΔH_c) were determined from the areas of the melting and crystallization peaks, respectively.

The specimens' relative percentage of crystallinity (X_c) was calculated according to the following equation:

$$X_c=(\Delta H_c/\Delta H_{100})\cdot 100\%$$

where ΔH is the heat of fusion of PBS and ΔH_{100} the heat of fusion for 100% crystalline PBS (ΔH_{100}= 110.3 J g^{-1}) [10].

Dynamic mechanical analysis (DMA)

The viscoelastic properties of the specimens before and after hydrolysis were measured using a dynamic mechanical analyzer (TA Instruments, DMA Q500). Rectangular specimens having a size of 35.0 mm×12.0 mm×3.0 mm were examined using the dual cantilever method. The measurements were performed at a frequency of 1 Hz and a strain rate of 0.1%. The temperature range was from –80 to 100°C at a scanning rate of 2° min^{-1}. The storage modulus (E'), loss modulus (E'') and loss factor (tanδ) of the specimens were measured as a function of temperature.

Results and discussion

Thermogravimetric (TG) analysis

Figure 2a shows the TG curves of PBS as a function of the exposure time to a high humidity environment at 50°C and 90% RH for 30 days. The thermal degradation of PBS showed a dramatic decrement of heat within the designated temperature range, suggesting that the polymer is composed of a series of interchained monomers. Thus, the temperature increase would promote the thermal degradation at the weak

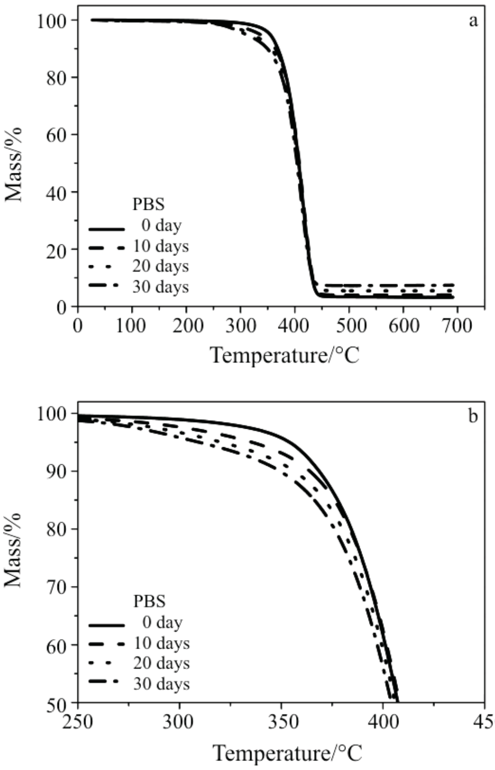


Fig. 2 TG curves of PBS in the temperature ranges of a – 24–700 and b – 250–450°C as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

sites of the polymer chains, thereby leading to the formation of oligomers or monomers [13]. With increasing hydrolysis time, the thermal stability and degradation temperature slightly decreased, as clearly shown in Fig. 2b, possibly due to the easy hydrolysis of the ester bonds in the PBS main-chain, which caused its random scission. Table 2 shows the 5% mass loss temperature and DTG_{max} temperatures for PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days. As the hydrolysis time increased, the 5% mass loss temperature and DTG_{max} temperatures of PBS decreased, due to its weak thermal stability resulting from the easy hydrolysis and degradation of its main-chain. At hydrolysis times of 20 and 30 days, PBS only shows the first peak of the DTG_{max} temperatures. It seemed that the first peak of the DTG_{max} temperatures was due to the hydrolysis and degradation of PBS. Figure 3 shows the TG curves of the PBS and anti-hydrolysis agent- and TMPTA-treated PBS at 30 days. The thermal stability and degradation temperature of the anti-hydrolysis agent-treated PBS were not significantly different from those of the untreated PBS. However, the 5% mass loss temperature of the anti-hydrolysis agent-treated PBS was lower than that of the non-treated PBS, as shown in Table 2. Also, the anti-hydrolysis agent-treated PBS only shows the first peak of the DTG_{max} temperatures, due to the degradation of the anti-hydrolysis agent itself. This was attributed to the fact that the thermal stability of the anti-hydrolysis agent was lower than that of PBS. The thermal stability and degradation temperature of the TMPTA-treated PBS were higher than those of the non-treated PBS, which was attributed to the increased cross-linking density of the former after being subjected to EB irradiation. The same tendency was also observed in the case of the 5% mass loss temperature and DTG_{max} temperatures of the TMPTA-treated PBS, as shown in Table 2.

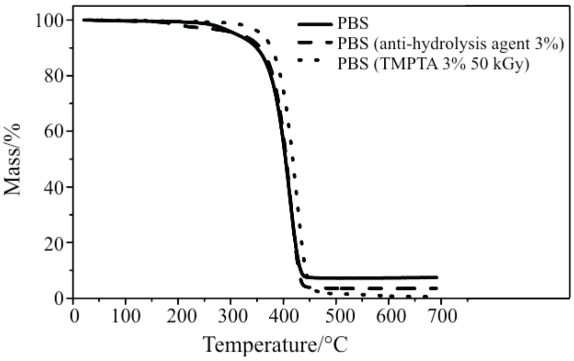


Fig. 3 TG curves of PBS, and the anti-hydrolysis agent and TMPTA-treated PBS at 30 days

Table 2 Summary of 5% mass loss temperatures and DTG_{max} degradation temperatures of PBS, and anti-hydrolysis agent and TMPTA treated PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

PBS	5 mass% loss temperature/°C	DTG_{max} temperature/°C	
		first peak	second peak
0 day	354.1	ND	416.7
10 days	355.6	ND	415.8
20 days	320.7	298.2	415.5
30 days	309.8	289.1	414.1
Anti-hydrolysis agent 3% (30 days)	314.9	202.3	414.5
TMPTA 3% (30 days)	358.2	ND	428.9

ND: not detected

Differential scanning calorimetry (DSC)

Figure 4 shows the DSC second heating curves of PBS maintained under high humidity conditions for 30 days. The T_m of PBS was taken as the maximum of the endothermic melting peak. Tables 3, 4 list the DSC test results of PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days. Table 3 presents the T_g and T_m of PBS before and after the hydrolysis test. With increasing hydrolysis time, the T_g and T_m of PBS were not significantly changed, indicating that they were not affected by its hydrolysis. These results demonstrated that DSC measurements could not be used to trace the hydrolysis of these aliphatic polyesters under high humidity conditions where their degradation precedes the surface erosion mechanism [14]. Tsuji *et al.* [14] reported that the changes in the T_g and T_m of aliphatic polyesters such as poly(ε-caprolactone: PCL) and poly[(R)-3-hydroxybutyrate] (R-PHB) were insignificant or very small in seawater maintained at 25°C for 10 weeks.

Table 3 lists the ΔH_f, ΔH_c and T_c of PBS before and after the hydrolysis test maintained under high humidity conditions for 30 days. With increasing hydrolysis time, the ΔH_m of PBS was slightly increased, but the T_m was not significantly changed. The shift in the ΔH_m and crystallinity of PBS are represented in Table 3. This result implies that the increase in the ΔH_f, ΔH_c and crystallinity of PBS after the hydrolysis test were related to the crystallization rate and extent of crystallinity [15, 16]. PBS is a semicrystalline polymer that consists of amorphous and crystalline regions formed from the main chains. Hence, the observed increases in the ΔH_f, ΔH_c and crystallinity values of PBS may have been caused by its crystallization and the effect of the resulting slightly decreased amorphous phase of PBS during its hydrolysis [14, 17, 18]. Table 4 lists the ΔH_f, ΔH_c and T_c values of the anti-hydrolysis agent-treated PBS before and after the hydrolysis test under high humidity conditions for 30 days. With increasing hydrolysis time, the ΔH_f, ΔH_c and crystallinity of the anti-hydrolysis agent-treated PBS slightly increased, but the T_g and T_m values were not significantly changed. The same result was also obtained in the case of the TMPTA-treated PBS (Table 5). These results showed that the anti-hydrolysis and non-TMPTA-treated PBS exhibited the same tendency. However, the T_g and T_m values of the TMPTA-treated PBS slightly increased, while its T_c decreased, possibly due to the increase in its cross-linking density caused by the EB irradiation [19].

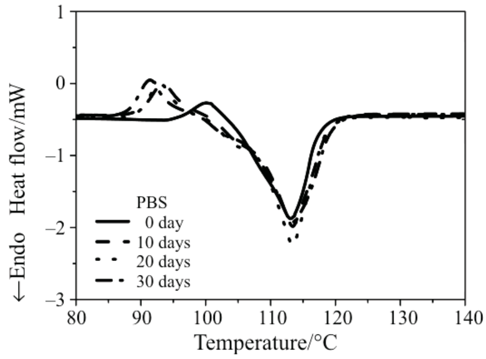


Fig. 4 DSC heating curves of PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

Dynamic mechanical analysis (DMA)

Dynamic mechanical test methods are widely used to examine the structures and visco-elastic behavior of composite materials. Figure 5 shows the temperature dependence of the dynamic storage modulus (E') of the PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days. With increasing hydrolysis time, the E' values of the PBS–BF bio-composites decreased, due to

Table 3 DSC test results of PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

Time/day	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}	Crystallinity/%
0	–34.4	113.1	64.8	72.8	69.9	57.1
10	–33.3	113.4	68.3	64.3	70.2	60.2
20	–34.5	113.5	72.6	64.2	75.1	64.0
30	–34.9	113.3	72.0	61.3	76.9	63.5

Table 4 DSC test results of 3% anti-hydrolysis agent-treated PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

Time/day	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}	Crystallinity/%
0	–31.4	113.4	67.1	70.3	74.3	60.8
10	–31.0	113.9	73.1	63.7	75.7	66.3
20	–28.8	113.8	76.2	67.2	78.2	69.1
30	–27.8	114.1	76.9	61.8	78.4	69.7

Table 5 DSC test results of 3% TMPTA-treated PBS as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

Time/day	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}	Crystallinity/%
0	–28.2	119.8	67.8	60.9	72.6	61.5
10	–28.4	118.7	68.8	64.5	74.1	62.4
20	–28.6	117.6	73.4	68.8	82.2	66.5
30	–27.3	116.4	73.2	72.2	84.2	66.3

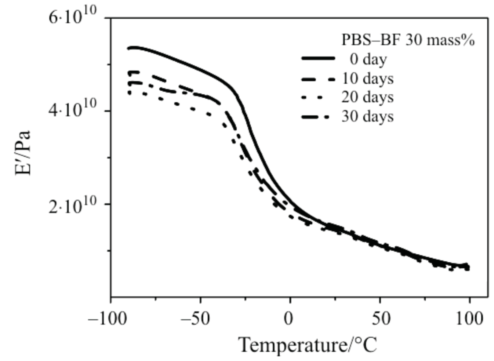


Fig. 5 Temperature dependence of the dynamic storage modulus (*E*') of the PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

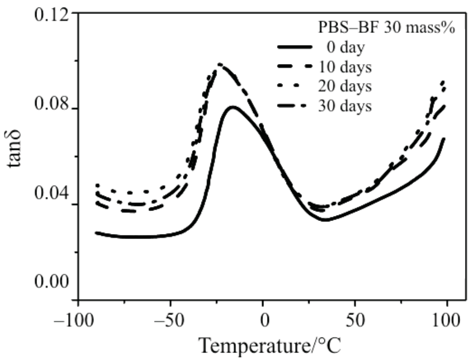


Fig. 6 Temperature dependence of the tanδ of the PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

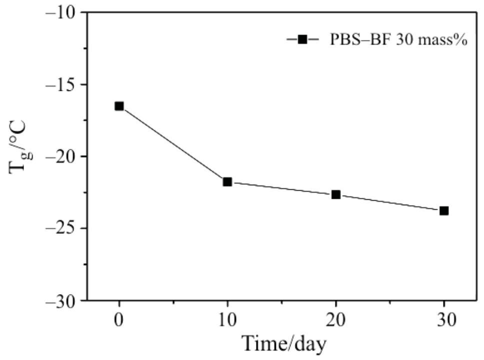


Fig. 7 Tanδ_{max} peak temperature (T_g) of PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days

the increase in the amount of hydrolytic degradation of the PBS main chain. At a hydrolysis time of 30 days, the *E*' values of the PBS–BF bio-composites were slightly higher than those at 20 days. This result suggests that the brittleness of the PBS–BF bio-composites was slightly increased at 30 days. Figure 6 shows the temperature dependence of the tanδ value of the PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days. The mechanical loss factor or tanδ, which is defined as the ratio of the loss modulus to the storage modulus, was measured [20]. The tanδ_{max} peak can also provide information on the T_g and energy dissipation of bio-composite materials. As the hydrolysis time increased, the tanδ values of the PBS–BF bio-composites increased, indicating that the energy dissipation of this bio-composite increased and the storage modulus decreased. The tanδ_{max} peak temperature (T_g) of the PBS–BF bio-composites as a function of the high humidity exposure time at 50°C and 90% RH for 30 days is shown in Fig. 7. With increasing hydrolysis time, the T_g of the PBS–BF bio-composites decreased. However, the T_g of PBS before and after the hydrolysis test was not significantly changed in the DSC measurements. This suggests that the measurement methods of DSC and DMA differ and that the hydrolysis of the bio-composites only occurred at the matrix surface. The decrease in the T_g of the PBS–BF bio-composites may be due to the fact that the water present penetrated the PBS chains and increased their mobility, causing random hydrolytic cleavage of the ester linkages to take place within the PBS surface [21].

Figure 8 shows the temperature dependence of the dynamic storage modulus (*E*') of the anti-hydrolysis agent and TMPTA treated and non-treated PBS–BF and PBS–WF bio-composites as a function of the high humidity exposure time at 20 days. We used the anti-hydrolysis agent and TMPTA to reduce the hydrolysis of the bio-composites. The *E*' values of the anti-hydrolysis agent treated bio-composites were not significantly changed, whereas those of the TMPTA treated bio-composites were slightly higher than those of the non-treated bio-composites. This was attributed

Table 6 tanδ_{max} peak temperature (T_g) of anti-hydrolysis agent and TMPTA treated and non-treated PBS–BF and PBS–WF bio-composites as a function of the high humidity exposure time at 20 days

Sample	tanδ_{max} peak temperature/°C
PBS–BF 30 mass%	–22.7
PBS–BF 30 mass% (anti-hydrolysis agent 3%)	–20.1
PBS–BF 30 mass% (TMPTA 3%)	–13.2
PBS–WF 30 mass%	–20.5
PBS–WF 30 mass% (anti-hydrolysis agent 3%)	–18.9
PBS–WF 30 mass% (TMPTA 3%)	–14.1

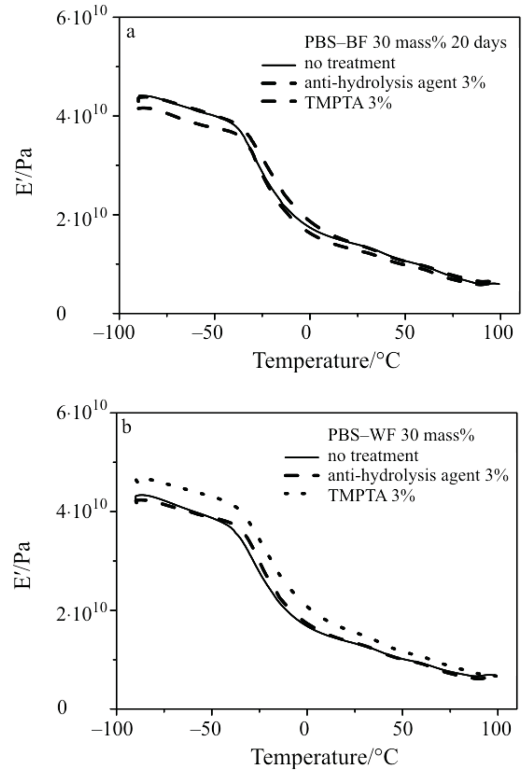


Fig. 8 Temperature dependence of the dynamic storage modulus (E') of the anti-hydrolysis agent and TMPTA-treated and non-treated a – PBS–BF and b – PBS–WF bio-composites as a function of the high humidity exposure time at 20 days

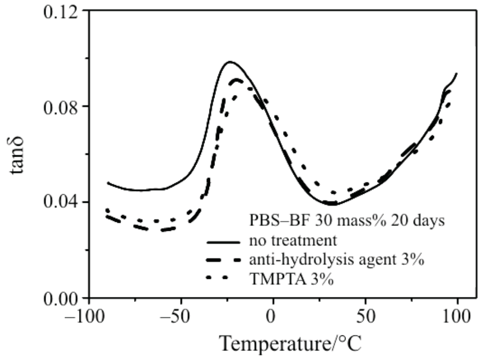


Fig. 9 Temperature dependence of the tanδ of the anti-hydrolysis agent and TMPTA treated and non-treated PBS–BF bio-composites as a function of the high humidity exposure time at 20 days

to the increase in the stiffness of the former with increasing TMPTA content. The enhanced stiffness of the PBS–BF bio-composites was due primarily to the three dimensional networks in the TMPTA treated bio-composites formed during the EB irradiation [22]. Figure 9 shows the temperature dependence of the tanδ value of the PBS–BF bio-composites as a function of the high humidity exposure time at 20 days. The tanδ values of the anti-hydrolysis agent and TMPTA treated PBS–BF bio-composites were slightly lower than those of the non-treated bio-composites. This result indicates that the energy dissipation of the anti-hydrolysis agent and TMPTA treated bio-composites decreased. This may be due to the reduction in their degree of hydrolysis. Kim *et al.* [23] reported that the tensile strength of anti-hydrolysis agent and TMPTA-treated bio-composites was significantly increased compared to that of the non-treated bio-composites. Table 6 shows the tanδ_{max} peak temperatures (T_g) of the PBS–BF and PBS–WF bio-composites. The T_g values of the anti-hydrolysis agent treated bio-composites were not significantly changed, whereas those of the TMPTA treated bio-composites were higher than those of the non-treated bio-composites, due to the increase in their cross-linking density caused by the EB irradiation. In a highly cross-linked material, the T_g values at the rubbery plateau are related to the cross-linking density [19].

Conclusions

The purpose of this study was to conduct a thermal analysis of the hydrolysis and degradation behavior of biodegradable polymers and bio-composites at 50°C and 90% relative humidity (RH). With increasing hydrolysis time, the thermal stability and degradation temperature of PBS slightly decreased due to the increasing hydrolysis of the ester groups of the PBS main chains. The T_g and T_m of PBS and the anti-hydrolysis agent treated PBS were not significantly changed, but their ΔH_f, ΔH_c and crystallinity values increased with increasing hydrolysis time in the DSC measurement. Also, the T_g and T_m of the TMPTA-treated PBS slightly increased, while its T_c decreased, possibly due to the increase in its cross-linking density caused by the EB irradiation. With increasing hydrolysis time, the *E*' values and tanδ_{max} peak temperatures (T_g) of the PBS–BF bio-composites decreased due to the increasing hydrolytic degradation of the PBS main chain. The *E*' values of the anti-hydrolysis agent treated bio-composites were not significantly changed, whereas those of the TMPTA treated bio-composites slightly increased. The tan δ values of the anti-hydrolysis agent and TMPTA treated PBS–BF bio-composites were slightly lower than those of the non-treated bio-composites due to the reduction in their degree of hydrolysis. The tanδ_{max} peak temperatures (T_g) of the anti-hydrolysis agent treated bio-composites were not significantly changed, whereas those of the TMPTA treated bio-composites increased. The results of this study suggest that the addition of an anti-hydrolysis agent and polyfunctional monomer (TMPTA) is an effective method of reducing the hydrolysis and degradation of biodegradable polymers and bio-composites under high humidity conditions.

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