

Hydrolytic degradation of biodegradable polyesters under simulated environmental conditions

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ABSTRACT: In this study, the durability of poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT), and PBS/PBAT blend was assessed by exposure to 50°C and 90% relative humidity for a duration of up to 30 days. Due to the easy hydrolysis of esters, the mechanical properties of PBS and PBAT were significantly affected with increasing conditioning time. The PBS, PBAT, and PBS/PBAT showed an increase in modulus as well as a decrease in tensile strength and elongation at break with increased exposure time. Furthermore, the impact strength of PBAT remains unaffected up to 30 days of exposure. However, it was clearly observed that the fracture mode of PBS/PBAT changed from ductile to brittle after being exposed to high heat and humid conditions. This may be attributed to the hydrolysis products of PBS accelerating the degradation of PBAT in the PBS/PBAT blend. The differential scanning calorimetry results suggested that the crystallinity of the samples increased after being exposed to elevated temperature and humidity. This phenomenon was attributed to the induced crystallization from low molecular weight polymer chains that occurred during hydrolysis. Therefore, low molecular weight polymer chains are often favored to the crystallinity enhancement. The increase in crystallinity eventually increased the modulus of the conditioned samples. The enhanced crystallinity was further confirmed by polarizing optical microscopy analysis. Moreover, the hydrolysis of the polyesters was evaluated by scanning electron microscopy, rheology, and Fourier transform infrared spectroscopy analysis. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42189.

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INTRODUCTION

During the past decade, biodegradable polymers and their blends have gained great attention in wide range of applications due to their low environmental footprint. Among the biodegradable polymers, poly(butylene succinate) (PBS) is a promising aliphatic polyester, made from fossil fuel based 1,4-butanediol and succinic acid precursors, which can also be derived from biobased succinic acid. PBS has many desirable properties including good toughness and melt processability. The mechanical properties of the PBS fall between polyolefins with a wide processing window.^{1,2} In addition, the mechanical and thermal properties of the PBS depend on the degree of crystallinity and the spherulite morphology.³ Degradability of the PBS has been widely studied under different environmental conditions.^{4–8} These studies claimed that the PBS is susceptible to hydrolysis in the presence of moisture/water. The main route of hydrolytic degradation occurs through cleavage of ester linkages and leads to lower molecular weight compounds.

Solely aromatic polyesters are resistant to biological degradation. Therefore, an attempt has been made to introduce aliphatic moieties into aromatic polyesters in order to enhance the hydrolytic degradation.⁹ For example, poly(butylene adipate-co-terephthalate) (PBAT) is a commercialized biodegradable aliphatic–aromatic copolyester.¹⁰ The PBAT exhibits good thermal and mechanical properties with a terephthalic acid concentration above 35 mol %.¹¹ At the same time, PBAT possesses good biodegradability with an aromatic moiety concentration below 55 mol %. The properties of PBAT can be compared with that of low density polyethylene with regards to its tensile properties. Nowadays, PBS and PBAT are widely used for many applications because of their inherent properties in addition to biodegradability. The only shortcomings of PBS are its insufficient impact strength and gas barrier properties for certain applications. This could be overcome by physical blending with a highly flexible PBAT while maintaining biodegradability.

The application of the polymeric materials depends on their durability and performance under different environments. The

durability of the polymers and composites is strongly related to the degradation mechanism. The degradation mechanism is a key factor for the lifetime prediction of polymeric materials.^{12,13} If the polymeric materials maintain their required mechanical performance at least 60 weeks at elevated temperature (50°C) and humidity (90%) it may be used for 10 year durable applications.¹⁴ The biodegradable polymers are sensitive to hydrolysis under high temperature and humidity and thus limit their durability as well as long-term performance under these conditions. In order to incorporate more widespread semicrystalline biodegradable polymers in durable applications, including automobiles and electronics, the performance of the polymers must be maintained throughout their life time. It is well-known that the amorphous regions are more susceptible to degradation than crystalline regions in a semicrystalline polymer. This can be explained by the rate of moisture penetration being higher in the amorphous regions than in the crystalline regions.¹⁵ These drawbacks could be overcome by blending or alloying polymers while tailoring the material's overall performance and cost.¹⁴ With this regard, we have extensively studied the PBS/PBAT blend in our previous research.¹⁶ However, it is very important to understand the durability behaviors of the PBS, PBAT, and PBS/PBAT blend in order to diversify as well as in predicting their applications. Such understanding will help to find out new areas in improving the required durability of these polymeric systems in different applications.

Only limited research works have been reported on the long term durability behaviours of biodegradable polymers under simulated environmental conditions.^{13,14,17–19} For instance, the long term durability of polylactide (PLA) samples has been studied by few researchers.^{13,14,20} These studies showed that the mechanical performance of the PLA was significantly affected after exposure to elevated temperature and moisture levels. Therefore, PLA is still an underperforming biopolymer for long-term durable applications such as automotive parts. In addition, Harris and Lee¹³ have studied the hydrolytic degradation of PLA and a PLA/polycarbonate (PC) blend exposed to elevated temperature and humidity for 28 days. They have noticed a reduction in the mechanical performance of PLA and PLA/PC blend with increasing conditioning time. Therefore, the author concludes that the PLA accelerated the degradation of PC in the PLA/PC blend under these conditions. However, PLA/PC blend exhibits superior flexural strength than neat PLA during the entire conditioning period. Another study by Kim and Kim¹⁷ showed that polypropylene (PP) has a more hydrolytic resistant behaviour than biodegradable polymers (PBS, PBAT, and PLA) because of its inherent non-biodegradability character.

To the best of our knowledge, there have not been many studies available in literature on the durability of PBS, PBAT, and their blends at elevated temperature and humidity. Considering the above, in the present study, our attention was to investigate the durability of PBS, PBAT, and PBS/PBAT blend at an elevated temperature and humidity level. In this sense, the present study was aimed to investigate the effect of mechanical and physico-mechanical properties of PBS, PBAT, and PBS/PBAT blend at 50°C with 90% relative humidity for duration of up to 30 days.

The samples were evaluated before conditioning and after 6, 12, 24, and 30 days of continuous conditioning. The hydrolytic degradation of the polyesters was examined by using various analytical techniques.

MATERIALS AND METHODOLOGY

Materials

For this study, commercially available PBAT pellets were supplied by Zhejiang Hangzhou Xinfu Pharmaceutical Co., Ltd, China, under the trade name of Biocosafe 2003F with a melting point of 117°C. PBS pellets were supplied by the same company under the trade name of Biocosafe 1903F with a melting point of 115°C. PP-1350N homopolymer was procured from Pinnacle Polymers (Garyville, LA). According to manufacturer information, the density and melt flow index of the PP-1350N are 0.9 g/cm³ and 55 g/10 min, respectively. Neat PBS and PBAT were dried in an oven for 6 h at 80°C to remove the moisture prior to melt processing.

Sample Preparation and Conditioning

Neat PP, PBS, PBAT, and blend of PBS/PBAT (60/40 wt %) were extruded in a Leistritz extruder with a screw speed of 100 rpm. The extruder was equipped with co-rotating twin-screws with a screw diameter of 27 mm and L/D ratio of 48. Prior to the injection molding, the extrudates were pelletized and dried in an oven at 80°C for 12 h. The dried extruded pellets were injection molded in an ARBURG allrounder 370C (Model No: 370 S 700-290/70, Germany) injection molding machine to obtain desired test specimens. The injection moulding machine had a maximum injection pressure of 2000 bar and a screw diameter of 35 mm. The extrusion and injection molding process was carried out with a processing temperature of 140°C for PBS, PBAT, and PBS/PBAT and 180°C for PP.

In the literature, the durability of polymers, polymer blends, and their composites was studied at different accelerated environmental conditions,^{21–23} in vehicle and in-field conditions.^{13,14} Furthermore, long-term durability of the polymeric material has been studied in the presence of Xenon light, UV light, metal halide, and carbon arc lamps by many researchers.^{24,25} However, in order to model the PBS, PBAT, and PBS/PBAT blend for automotive interior applications; all the moulded samples were conditioned under simulated temperature (50°C) and relative humidity (90%).¹⁸ These conditions were simulated using an environmental chamber, Envirotronics Endurance C340. The samples were tested initially before and after 6, 12, 24, and 30 days continuous conditioning at 50°C and 90% relative humidity (RH). Except moisture absorption analysis, all other characterizations were performed after drying the test samples at 80°C for 24 h in order to avoid plasticization effect of excess moisture in the specimens.

Moisture Absorption

Before performing moisture absorption test, all the samples were dried at 80°C till a constant weight is reached. The moisture absorption of the samples was calculated by taking out the samples at required time interval for the set environmental exposure conditions (50°C and 90% RH). The percentage of moisture uptake was calculated by using the equation:

$$\text{Moisture uptake (\%)} = \frac{W_a - W_b}{W_b} \times 100 \quad (1)$$

where W_a and W_b are weight of the samples after and before moisture exposure. The reported moisture absorption values are an average of three samples.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed in a Thermo Scientific Nicolet 6700 at room temperature with a Smart Orbit attachment. FTIR spectrum was recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 36 readings.

Mechanical Properties

Tensile and flexural tests were performed in an Instron Universal Testing Machine (Model 3382) according to ASTM D638 and D790, respectively. The cross-head movement speeds of 14 mm/min for flexural test and 50 mm/min for tensile test were used as recommended by the respective standards. The tensile tests were performed until the conditioned samples broke at the grip region as a consequence of embrittlement. After 30 days, conditioned PBS samples became more fragile and would rupture during handling. Therefore, the experiment was conducted only up to 30 days. Notched Izod impact strength was assessed with an impact test machine from TMI 43-02, The United States, complying with ASTM D256. The results are reported as an average of five samples for each formulation.

Differential Scanning Calorimetry

The DSC analysis was performed in a TA-Q200 instrument with a heating and cooling rate of 10°C/min and 5°C/min, respectively. The samples were heated under a nitrogen flow rate of 50 mL/min. The melting enthalpy was calculated by measuring area under the curves using TA analysis software. The first heating cycle was considered in order to measure sample crystallinity before and after conditioning. The percentage crystallinity of the PBS and PBAT was calculated by using the following formula:

$$\% \text{ Crystallinity } (\chi_c) = \frac{\Delta H_m}{\Delta H_{m100}} \times 100\% \quad (2)$$

where ΔH_{m100} is the theoretical enthalpy of melting for 100% crystalline PBS (110.3 J/g)⁸ and PBAT (114 J/g).²⁶ ΔH_m is the measured enthalpy of melting. The PBS crystallinity in the PBS/PBAT blend was calculated as follows:

$$\chi_c = \frac{\Delta H_m}{\Delta H_{m100(1-w_f)}} \times 100\% \quad (3)$$

where w_f is the weight fraction of the PBAT in the PBS/PBAT blend.

Dynamic Mechanical Analysis

DMA analysis was performed using TA Instrument (DMA Q800), The United States. The experiments were conducted from -60°C to 100°C. The selected temperature range was based on the glass transition temperature and melting temperature of the samples. The scans were performed at a constant rate of heating (3°C/min) with oscillating amplitude of 15 μm and a frequency of 1 Hz in a dual cantilever clamp mode.

Rheological Properties

Rheological properties were obtained in an Anton Paar Rheometer MCR302. The experiments were carried out in parallel

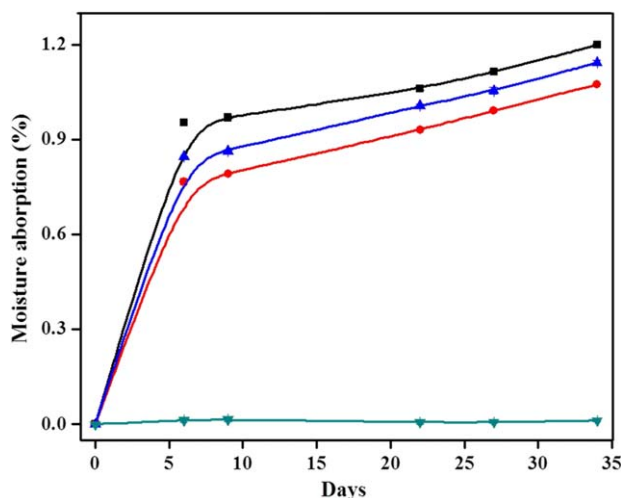


Figure 1. Moisture absorption curves as a function of conditioning time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plates with a gap of 1 mm and a diameter of 25 mm. In order to avoid degradation of the samples during the experiments, all the samples were vacuum dried at 80°C for 4 h before performing the experiments. The shear viscosity values of the samples both before and after conditioning were measured at 140°C from 300 to 0.01 rad/s.

Optical Polarizing Microscopy

Spherulite morphology of the samples was observed by using optical polarizing microscope (Nikon Eclipse LV100) equipped with a Linkam LTS 420 hot stage. Thin films of the samples were made by heating the sample between two transparent microscope glass slides. All the samples were heated to 150°C for 60 sec followed by the samples being quickly transferred to 90°C in the microscope hot stage. Subsequently, the samples were kept at close to crystallization temperature (90°C) and the spherulite growth was recorded using a Nikon camera.

Morphological Analysis

The specimens were prepared by sputtering gold particles in order to avoid electrical charging during examination. A scanning electron microscope, Inspect S 50, FEI Netherlands, was utilized to examine the fracture surface morphology of the specimens. The surface morphology of the specimens was examined at an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

Moisture Absorption

Moisture absorption of all the samples was investigated as a function of exposure time. Figure 1 shows the moisture absorption curves in percent of the PP, PBS, PBAT, and PBS/PBAT blend up to 34 days. Generally, more or less; all the polymers tend to absorb moisture in a humid atmosphere. Usually, polymers with strong polar functionality such as carbonyl (>C=O) groups and amine groups are able to absorb moisture by hydrogen bonds.²⁷ Therefore, it is expected that the polyesters can absorb more moisture than the relatively non-polar polymers such as PP. It can be seen that the PP absorbed a very small

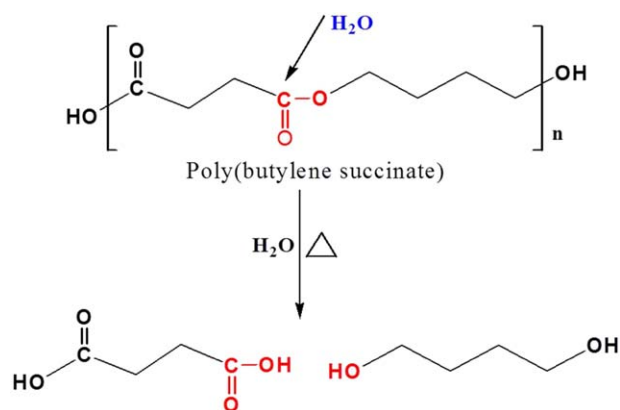


Figure 2. Hydrolysis reaction of PBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount ($0.011\% \pm 0.004\%$) of moisture and the moisture absorption curve has reached a typical Fickian behavior. It has been reported that the PP is resistant to moisture absorption even at elevated temperatures.²⁸ On the contrary, moisture absorption of PBS, PBAT, and their blend was monotonically increased with increasing exposure time up to 34 days. After 34 days exposure, the PBS showed a maximum moisture absorption ($1.11\% \pm 0.002\%$) followed by PBS/PBAT ($1.05\% \pm 0.01\%$) and PBAT ($0.99\% \pm 0.003\%$). The observed moisture absorption difference between the PBS and PBAT may be due to polarity differences between the polymers.²⁹ Due to the moisture absorption, it can be expected that the PBS and PBAT can undergo hydrolytic degradation at elevated temperature and humidity. Normally, higher moisture absorption of polyesters causes undesirable losses in mechanical performances.^{13,30}

Hydrolytic Degradation Mechanism of PBS and PBAT

It is known that the ester linkages of PBS and PBAT are more sensitive to elevated temperature and moisture.^{17,19} Therefore, in the presence of moisture, the PBS and PBAT primarily can undergo hydrolytic degradation through cleavage of ester linkages on the polymer backbone. In addition, the hydrolysis reaction may occur in the form of depolymerization process and random chain scission mechanism.³⁰ The possible hydrolytic degradation of PBS and PBAT under elevated humidity and temperature is depicted in Figures 2 and 3, respectively. The chain scission is frequently terminated by carboxylic acid end

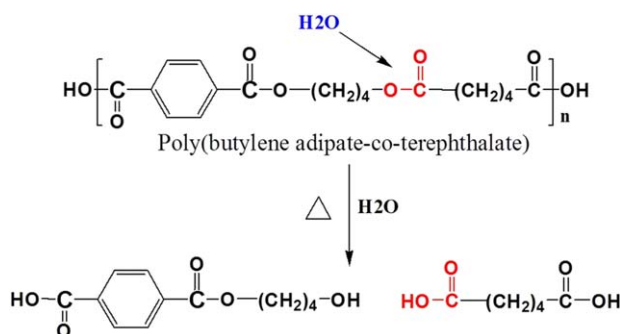


Figure 3. Hydrolysis reaction of PBAT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups^{13,30,31} and hydroxyl end groups.³² A similar type of hydrolytic degradation mechanism was proposed for PLA,¹³ PBS,^{8,33} and poly(ethylene terephthalate) (PET).³⁰ When PBS is exposed to high temperature and humidity environment, the surrounding moisture can interact with ester functionality of PBS and thus can create the low molecular weight PBS through hydrolytic degradation mechanism.³³

The hydrolytic degradation of PBS, PBAT and their blend was further confirmed by FTIR analysis. Figure 4 shows FTIR spectrum of PBS, PBAT and PBS/PBAT before and after 30 days of being exposed to elevated humidity and temperature. In PBS, the band at 917 cm^{-1} was corresponding to the $\text{C}-\text{OH}$ bending vibration of the carboxylic acid groups. The peak at 1045 cm^{-1} was attributed to the $\text{O}-\text{C}-\text{C}$ stretching vibration and the peak in the range 1151 cm^{-1} was due to the $\text{C}-\text{O}-\text{C}$ groups in the ester linkage of PBS.⁸ The band at 1325 cm^{-1} resulted from the asymmetric stretching of the CH_2 group in the PBS backbone. The band at 1712 cm^{-1} resulted from the $\text{C}=\text{O}$ stretching vibration of the ester group in PBS.¹⁷ After 30 days hydrolysis of PBS, a remarkable decrease of $\text{C}-\text{O}-\text{C}$ and $\text{C}=\text{O}$ absorption intensity was observed. These reductions in absorption intensity were due to lowering of the molecular weight and deterioration of the chemical structure by hydrolysis after being exposed to moisture and heat.^{8,18,34}

The characteristic peaks of the PBAT can be described as follows: a sharp peak at 1710 cm^{-1} represents the $\text{C}=\text{O}$ functionality of the ester linkage; the band at around 1267 cm^{-1} assigned to the $\text{C}-\text{O}$ group in the ester linkage; the peak at 727 cm^{-1} resulted from four or more adjacent CH_2 groups in the PBAT backbone. The peaks in the range of $700\text{--}900\text{ cm}^{-1}$ were attributed to benzene substitutes.³⁵ After 30 days of exposure to moisture and heat, there is no significant change observed in the FTIR spectra of PBAT. This is possibly due to the partial aromatic structure of PBAT. On the contrary, the FTIR spectra of PBS/PBAT showed a remarkable decrease in the characteristic peak intensity. This phenomenon may be

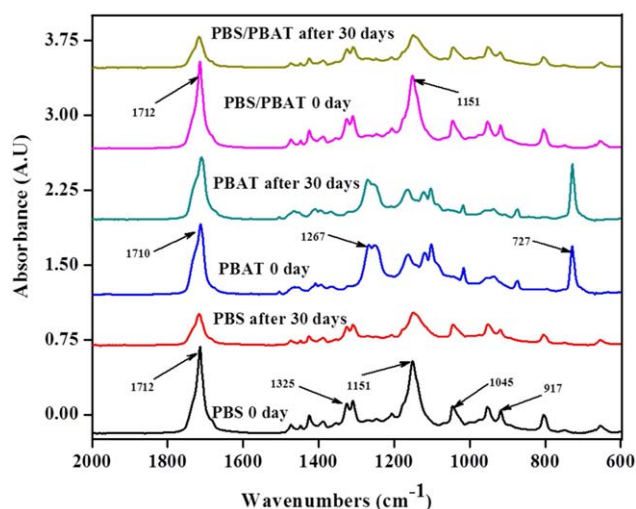


Figure 4. FTIR spectra of PBS, PBAT, and PBS/PBAT before and after 30 days exposed to 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

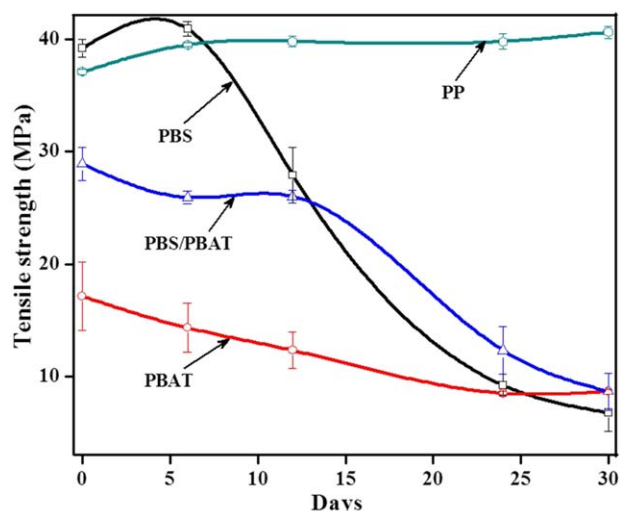


Figure 5. Tensile strength of PP, PBS, PBAT, and PBS/PBAT as a function of exposure time at 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

attributed to the hydrolysis product of PBS accelerating the degradation of PBAT in the PBS/PBAT blend.³¹

Changes in Mechanical Properties

Mechanical properties are the main indicators in order to evaluate the durability of the polymeric materials. The influence of moisture and heat on the mechanical properties was measured by tensile and flexural properties as well as impact strength. The mechanical properties of neat PBS, PBAT, PBS/PBAT blend, and PP are provided in our previous study.¹⁹ Figure 5 shows the tensile strength of PBS, PBAT, PBS/PBAT, and PP before and

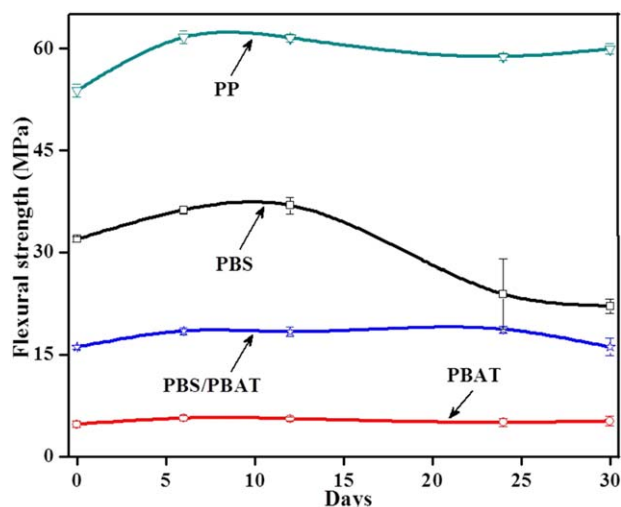


Figure 6. Flexural strength of PP, PBS, PBAT, and PBS/PBAT as a function of exposure time at 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after exposure at 50°C with 90% RH up to 30 days. In general, the mechanical properties of semicrystalline polymers are dependent on their molecular weight, crystal size, and percentage of crystallinity.³⁶ The tensile strength of PBS and PP showed slight enhancement after 6 days of exposure to 50°C and 90% RH. This can be attributed to the post crystallization of the samples after being exposed to elevated humidity and temperature. A similar result has been found for PLA,¹³ poly(hydroxybutyrate-co-valerate) (PHBV),³⁷ and homo polypropylene³⁸ specimens when exposed to different environmental conditions. However, after 6 days of exposure; PBAT as well as PBS/PBAT

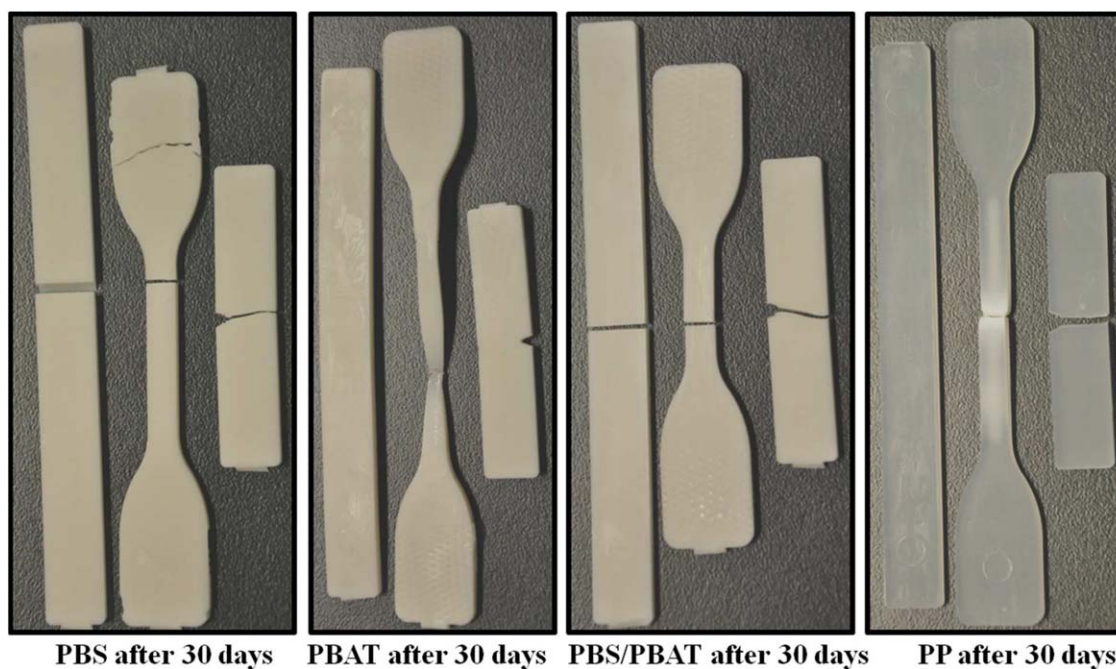


Figure 7. Testing failure mode of PBS, PBAT, PBS/PBAT, and PP after 30 days exposed to 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

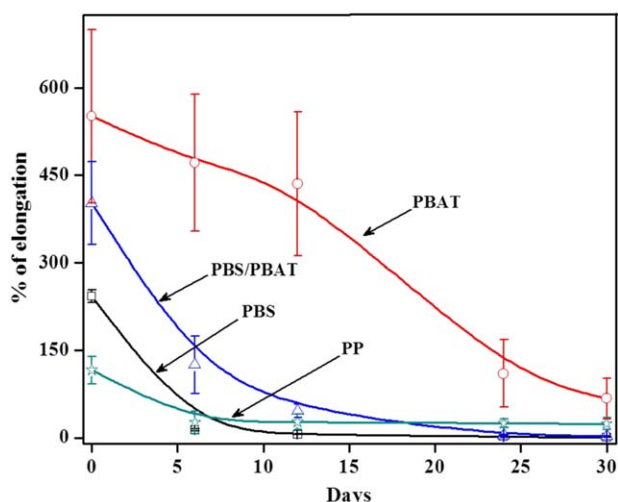


Figure 8. Percentage elongation of PP, PBS, PBAT, and PBS/PBAT as a function of exposure time at 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blend showed a slight reduction in tensile strength. This could be due to the plasticization effect of hydrolytically degraded amorphous region in the PBAT. It can be observed that the tensile strength of PBS, PBAT, and PBS/PBAT blend decreased significantly with increasing hydrolysis time. For example, after 12 days exposure time, the tensile strength of PBS, PBAT, and PBS/PBAT blend was reduced by 40%, 39%, and 11%, respectively. The reduced tensile strength may be attributed to the combined effect of hydrolytic degradation and molecular weight reduction after being exposed to the raised humidity and temperature.³³ Generally, the hydrolytic degradation of the biodegradable polymers is higher in the amorphous regions than crystalline regions under high humidity.³⁹ A similar type of observation has been made in PBS, PBAT, PBS/PBAT, and PP after being exposure to 18 days of elevated humidity and heat.¹⁹ However, after 30 days of conditioning, the tensile strength of the PBS and PBS/PBAT

blend exhibited extreme degradation in contrast to PBAT. This is possibly due to the accelerated degradation of PBS with the increased time at elevated temperature and humidity.¹⁵ Our finding had good agreement with the recent study by Kim and Kim.¹⁷ Usually, the hydrolytic degradation and biodegradability of the polymers mainly depend on the easily hydrolysable ester functionality in the polymer backbone. In the present study, PP did not show any significant reduction in the tensile strength up to 30 days conditioning, which is due to the non-polar as well as its hydrophobicity type of characteristic. Figure 6 demonstrates the flexural strength of the PBS, PBAT, PBS/PBAT, and PP after and before exposure to elevated temperature and humidity. After 6 days of conditioning, the PBAT did not show any significant improvement in the flexural strength which may be due to PBAT possessing a high entanglement density. Interestingly, the flexural strength of PBS, PBS/PBAT blend, and PP were increased 13%, 15%, and 15%, respectively, with increasing exposure time up to 6 days. After 18 days of continuous conditioning at 50°C with 90% RH, the flexural strength of PBS, PBS/PBAT, and PP samples was found to increase slightly.¹⁹ The increased flexural strength is probably due to the increased crystallinity of the samples after being exposed to elevated temperature.⁴⁰ However, it is important to note that the PBS and PBS/PBAT blend samples became more brittle after 30 days conditioning and leading to premature failure during flexural test, as shown in Figure 7. Harris and Lee¹³ found that the PLA and PLA/PC blend underwent severe flexural strength reduction because of the hydrolytic degradation under the exposed elevated temperature (70°C) and humidity (90% RH). On the other hand, they have noticed that the PC/ABS blend did not show any significant changes in the flexural strength up to 30 days conditioning because of the resistance to the hydrolysis.

Figure 8 represents the elongation at break of the samples with respect to exposure time. Except PBAT, all the samples showed drastic reduction in the elongation at break from early exposure time. The PP, PBS, and PBS/PBAT blend showed a drastic

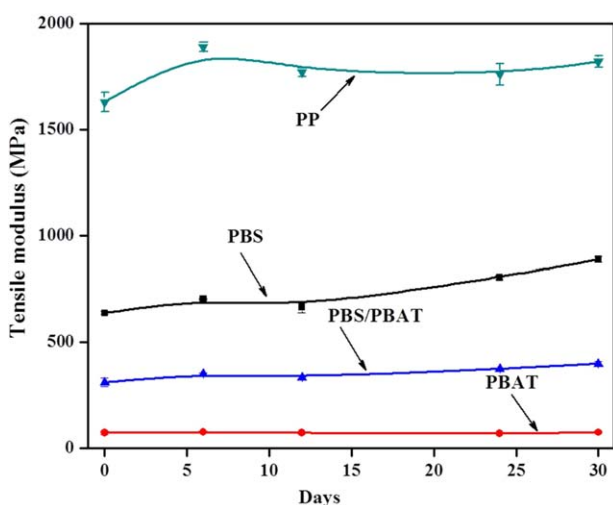


Figure 9. Tensile modulus of PP, PBS, PBAT, and PBS/PBAT as a function of exposure time at 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

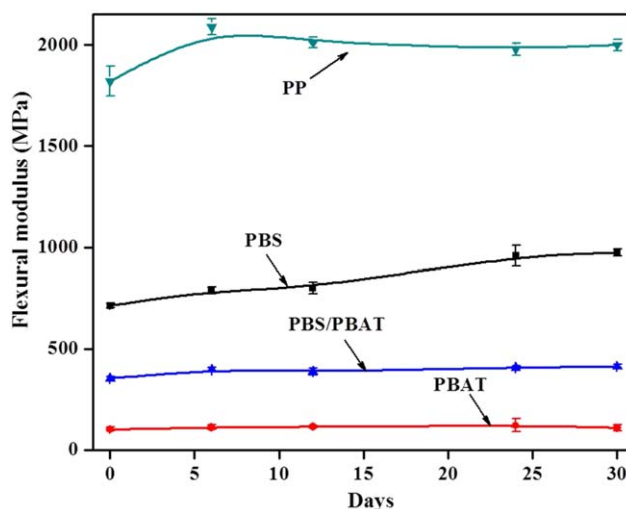


Figure 10. Flexural modulus of PP, PBS, PBAT, and PBS/PBAT as a function of exposure time at 50°C with 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Notched Izod Impact Strength of the Samples Before and After Conditioned at 50°C with 90% RH

Samples	Before conditioning	After 6 days conditioning	After 12 days conditioning	After 24 days conditioning	After 30 days conditioning
PBS	24.80 ± 6.55	12.54 ± 6.20	13.19 ± 1.91	12.90 ± 1.003	12.41 ± 1.07
PBAT	Non-break (210.55 ± 10.37)	Non-break (211.62 ± 46.54)	Non-break (209.09 ± 27.01)	Non-break (203.97 ± 25.22)	Non-break (193.16 ± 35.47)
PBS/ PBAT	Non-break (226.77 ± 43.95)	56.22 ± 4.24	52.24 ± 14.24	11.36 ± 1.92	13.04 ± 2.69
PP	30.40 ± 7.08	21.77 ± 0.79	24.47 ± 2.33	19.74 ± 0.79	20.97 ± 0.90

decrease in the percent elongation after 6 days conditioning. Therefore, it is clear that the toughness is more sensitive than the strength after being exposed to raised humidity and temperature. A similar trend has been reported in the literature for PP,⁴¹ high density polyethylene (HDPE),⁴² and PHBV.³⁷ After conditioning, PBS showed lower elongation than PP during the entire exposure time. This implies that the PBS is more moisture sensitive than the PBAT and the PP. Toughness of the polymer is mainly dependent on the tie molecules and entanglement of the polymer chains.^{42–44} When, the entanglement density decreased in the polymers it led to a reduction in the toughness of the resultant materials. Apparently, PBAT is more ductile and less crystalline than PBS due to the higher degree of chain entanglements. Therefore, PBAT maintains its elongation up to 12 days conditioning even after extensive chain scission occurred. Interestingly, the PBS/PBAT blend has higher elongation than PBS and PP up to 12 days due to the PBAT chain entanglements. After 12 days of conditioning, the PBS/PBAT blend experienced severe loss in elongation because of heavy chain scission of PBS leading to hydrolysis of the PBAT phase in the blend system.³¹

Figures 9 and 10 show the tensile and flexural modulus of the PP, PBS, PBAT, and PBS/PBAT as a function of conditioning

time. Both tensile and flexural modulus of the PP, PBS, and PBS/PBAT gradually increased with increasing conditioning time, whereas PBAT remains constant throughout the entire conditioning period. More specifically, the tensile and flexural modulus of PP and PBS was improved by ca. 200 MPa after 30 days conditioning period. This could be related to the increased crystallinity and subsequently increase in modulus.^{45,46} A number of researchers have observed a similar tendency in the modulus after exposure to different weathering conditions.^{12,37,42} These studies were concluded that the modulus improvement of the conditioned samples is associated with structural relaxation, increase in crystallinity, crystal perfection, and increase of lamella thickness. In addition, the brittleness of the PBS and PBS/PBAT blend sample was also improved with increasing conditioning time up to 30 days, accounting for the reduction in impact toughness.

Among the mechanical properties, impact energy is more sensitive to the environmental exposure. Table I shows the impact strength of PBS, PBAT, PBS/PBAT, and PP after and before conditioning at 50°C and 90% RH. Before conditioning, the PBAT showed non-break impact strength of 211 J/m while PBS and PP showed complete break with impact strength of 25 and 30 J/m, respectively. The impact energy of the PBS and PP decreased

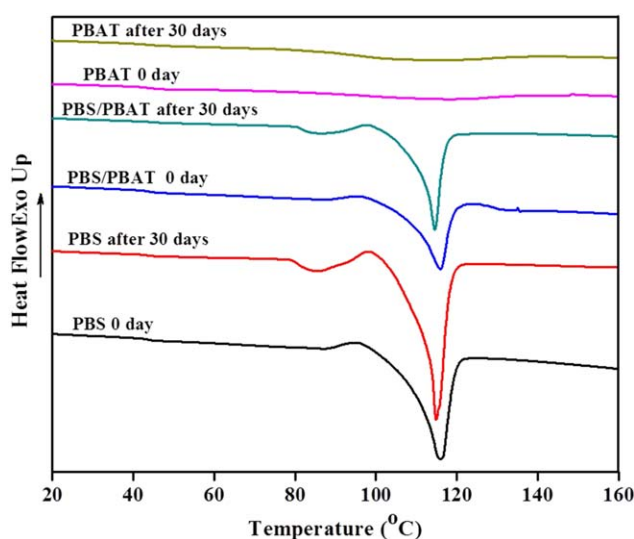


Figure 11. DSC heating cycles for PBS, PBAT, and PBS/PBAT before and after exposed to 50°C with 90% RH for 30 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

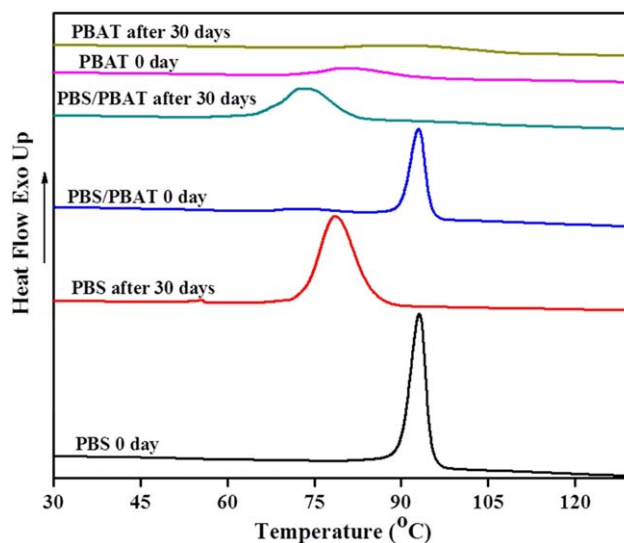


Figure 12. DSC cooling curves for PBS, PBAT, and PBS/PBAT before and after exposed to 50°C with 90% RH for 30 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. DSC Results for PBS, PBAT, and Their Blend Before and After 30 Days Conditioned at 50°C with 90% RH

Samples	T_m (°C)	ΔH_m (J/g)	T_c (°C)	χ_c (%)	T_g^a (°C)
PBS before	115.2	68.26	91.98	61.88	-16.72
PBS after	114.8	84.41	77.15	76.52	-14.24
PBAT before	117.11	9.29	81.11	8.14	-20.27
PBAT after	114.30	16.51	96.50	14.48	-25.00
PBS/PBAT before	114.97	41.04	93.91	62.01	-19.04
PBS/PBAT after	114.39	43.44	71.32	65.63	-20.71

^a T_g obtained from $\tan \delta$ peaks.

for the first 6 days of conditioning. This reduction is probably due to the inadequate degree of entanglement between amorphous and crystalline phase after exposed to 50°C and 90% RH.⁴⁵ The notched Izod impact strength of PBS, PBAT, PBS/PBAT blend, and PP samples after conditioning for 18 days is explained elsewhere.¹⁹ With increased exposure time (from 6 to 30 days), the impact energies of both PBS and PP were not significantly affected. In contrast, the impact energy of the PBAT remains unchanged up to 30 days of conditioning at elevated temperature and humidity. This may be due to the PBAT having sufficient molecular weight to form a significant degree of entanglement up to 30 days of hydrolysis environments.^{14,31} Furthermore, the impact strength of PBS/PBAT changed from a ductile to brittle fracture with increasing conditioning time, as shown in Figure 7. This could be due to the accelerated degradation of PBS with the increased exposure time. Moreover, except PBAT, all the samples exhibit brittle failure with increasing conditioning time. This observation corroborated with the modulus improvements.

Differential Scanning Calorimetry

After exposing the polymers to raised humidity and temperature, it is expected that the spherulitic growth rates, lamellar thickness, and crystal interphase are modified due to the free energy changes in the crystals formation. DSC traces of the samples before and after conditioning are shown in Figures 11 and 12. The thermal properties of PBS, PBAT, and PBS/PBAT blends are summarized in Table II. Melting enthalpy (ΔH_m) of the sample was calculated by measuring the area under the melting peak while crystallization enthalpy (ΔH_c) was the measured area under the crystallization peak. Before conditioning; all the samples showed a single melting temperature (T_m). In the heating cycles (Figure 11), a small exothermic peak was also observed for PBS and PBS/PBAT prior to melting peak. This resulted from the melt-recrystallization of PBS while heating.⁴⁷ However, after 30 days exposure, PBS and PBS/PBAT samples displayed a bimodal melting peak, as shown in Figure 11. These observed double endothermic peaks are attributed to the different crystal lamella thickness formation.⁸ In addition, the T_m of PBAT shifted to low temperature after 30 days conditioning. Either the change in amorphous-crystal surface energy or a decreased in the lamellar thickness was responsible for the T_m

decrease of a polyester after exposure to elevated temperature and humidity.³⁰ For both PBS and PBS/PBAT, no change was observed in the melting temperature ($\sim 115^\circ\text{C}$) after 30 days of exposure time.

In a semi-crystalline polymer, initially the amorphous regions are more susceptible for hydrolysis.⁶ From the DSC analysis, it was clearly observed that the ΔH_m and ΔH_c of the PBS, PBAT and PBS/PBAT increased after 30 days of conditioning, indicating that degradation mainly occurred in the amorphous regions. In addition, this phenomenon may be due to induced crystallization from low molecular weight polymer chains that occurs during conditioning.¹³ Therefore, low molecular weight polymer chains are often favored to the crystallinity enhancement. Our findings have good agreement with previous studies.¹⁴ According to these studies, the chain scission leads to reduced entanglement density and tie molecules of the semi crystalline polymers. The small molecular chains have potential to rearrange into the crystalline region which is called chemi-crystallization. This behavior has been observed in most of the semicrystalline aliphatic biodegradable polymers including PBS.⁴⁶ The increased crystallinity (χ_c) further accounts for the enhanced modulus as well as stiffness. The crystallization temperature (T_c) of the PBS and PBS/PBAT significantly reduced after 30 days of conditioning. This is attributed to the low molecular weight polymer chains leading to slow crystallization. A similar crystallization behavior for PBS has been reported after exposure to raised humidity and temperature.⁸ Contrary, the crystallization temperature of PBAT was shifted to higher temperature. This is probably due to the nucleation effect which is caused by oligomers.⁴⁸

Dynamic Mechanical Analysis

Figure 13 shows the temperature dependence dynamic modulus of PBS, PBAT, and their blend. It can be seen that the PBS had higher storage modulus than PBAT and PBS/PBAT. Similar occurrence has been observed in the tensile and flexural modulus. However, the storage modulus of all the samples gradually

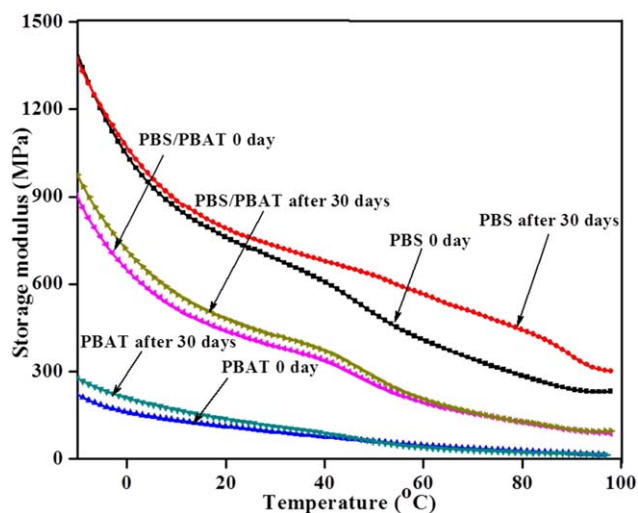


Figure 13. Storage modulus of PBS, PBAT, and PBS/PBAT before and after exposed to 50°C with 90% RH for 30 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

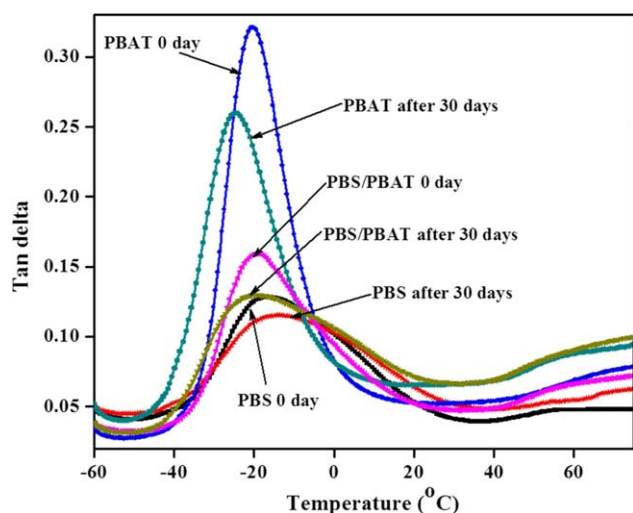


Figure 14. Loss factor peak ($\tan \delta$) of PBS, PBAT, and PBS/PBAT before and after 30 days exposed to 50°C with a RH of 90%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased with increasing temperature. This is attributed to the enhanced polymer chain mobility with increasing temperatures.¹⁶ As reported by Van der wal *et al.*⁴⁹ above the glass transition temperature, storage modulus is dependent to the degree of crystallinity. Below glass transition temperature, the modulus of crystalline as well as amorphous phase is almost identical. Interestingly, after 30 days of conditioning, the storage modulus of PBS, PBAT, and their blend samples was found to increase slightly. This is because the samples become stiffer, as evidenced by the increase in crystallinity after conditioning at elevated temperature and humidity.

Figure 14 shows the $\tan \delta$ (loss factor) curves with respect to temperatures. In fact, the peak temperature of the $\tan \delta$ represents the glass transition temperature (T_g). The T_g values of PBS, PBAT, and PBS/PBAT blends are summarized in Table II.

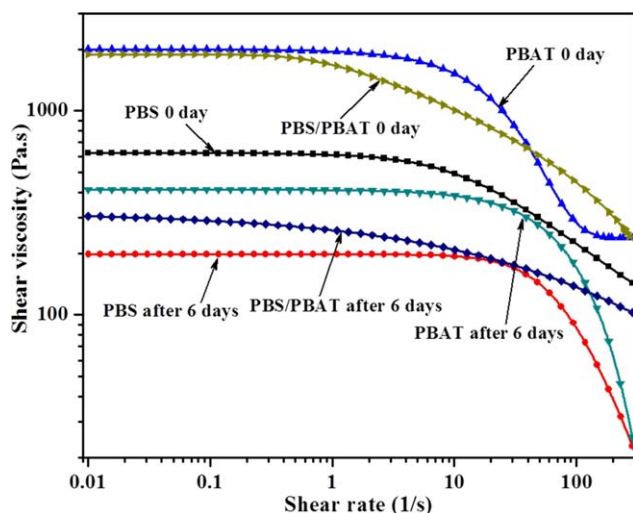


Figure 15. Shear viscosity curves for PBS, PBAT and PBS/PBAT before and after 6 days exposed to 50°C with a RH of 90%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Relative Molecular Weight (M_1/M_2) of the PBS, PBAT, and PBS/PBAT Blend Before and After 6 Days Conditioned at 50°C with 90% RH

Samples	Zero shear viscosity (Pa s)		Viscosity ratio (η_1/η_2)	Relative molecular weight (M_1/M_2)
	Before (η_1)	After (η_2)		
PBS	621.51	198.54	3.13	1.40
PBAT	2004.7	411.9	4.86	1.59
PBS/PBAT	1897.1	318.74	5.95	1.70

The position of each $\tan \delta$ peak is affected slightly after conditioning at 50°C with 90% RH. In general, T_g value of the amorphous phase in semicrystalline polymers depends on the degree of crystallinity.⁴⁶ Initially, the PBS and PBAT had T_g values of -17°C and -20°C , respectively. In PBS/PBAT blend, a single T_g (-19°C) was observed. This is due to the fact that T_g values of both neat PBS and PBAT were very close to each other and thus T_g may be overlapping in the PBS/PBAT blend.¹⁶ After 30 days conditioning, T_g of the PBS increased from -16.72°C to -14.24°C . This slight change can be attributed to the enhanced crystallinity, as corroborated by DSC result. As reported in Table II, the crystallinity of the PBS increased from 58.62% to 73.43% after 30 days exposed to 50 C with 90% RH. Similar observations have been reported by Harris and Lee for PLA.¹⁴ However, after 30 days conditioning, the T_g values of the PBAT and PBS/PBAT reduced marginally with slightly increased in crystallinity. This can be related to the plasticization effect by the diffused moisture, which induces an increase in the amorphous chain mobility.³⁰ A similar type of negative T_g shift was observed in the PLA films²⁰ and PET composites³⁰ after exposure to elevated temperature and humidity.

Rheological Properties

Figure 15 represents the shear viscosity of the samples before and after 6 days of conditioning at the elevated temperature and humidity. It was observed that, all the samples showed Newtonian and non-Newtonian flow behavior at lower and higher frequencies, respectively. The 6 days conditioned samples exhibit a slight decrease in the shear viscosity compared with the before conditioned samples. As expected, this behavior should be due to the molecular weight reduction by random chain scission after being exposed to elevated temperature and humidity. The molecular weight changes can be correlated with shear viscosity of the sample at low shear rate. According to the literature,⁵⁰ the weight average molecular weight (M) is directly proportional to the viscosity of the polymer melt at a zero shear rate. However, molecular weight distribution is independent to zero shear viscosity (η_0). Generally, the η_0 is obtained from extrapolation of the shear viscosity at lower shear rate (Newtonian region), which considered as weight average molecular weight.⁵¹ This relationship can be explained as follows:⁵⁰

$$\eta_0 = KM^{3.4} \quad (4)$$

where K and M are the material constant and molecular weight, respectively. In this study, relative molecular weight (M_1/M_2) of

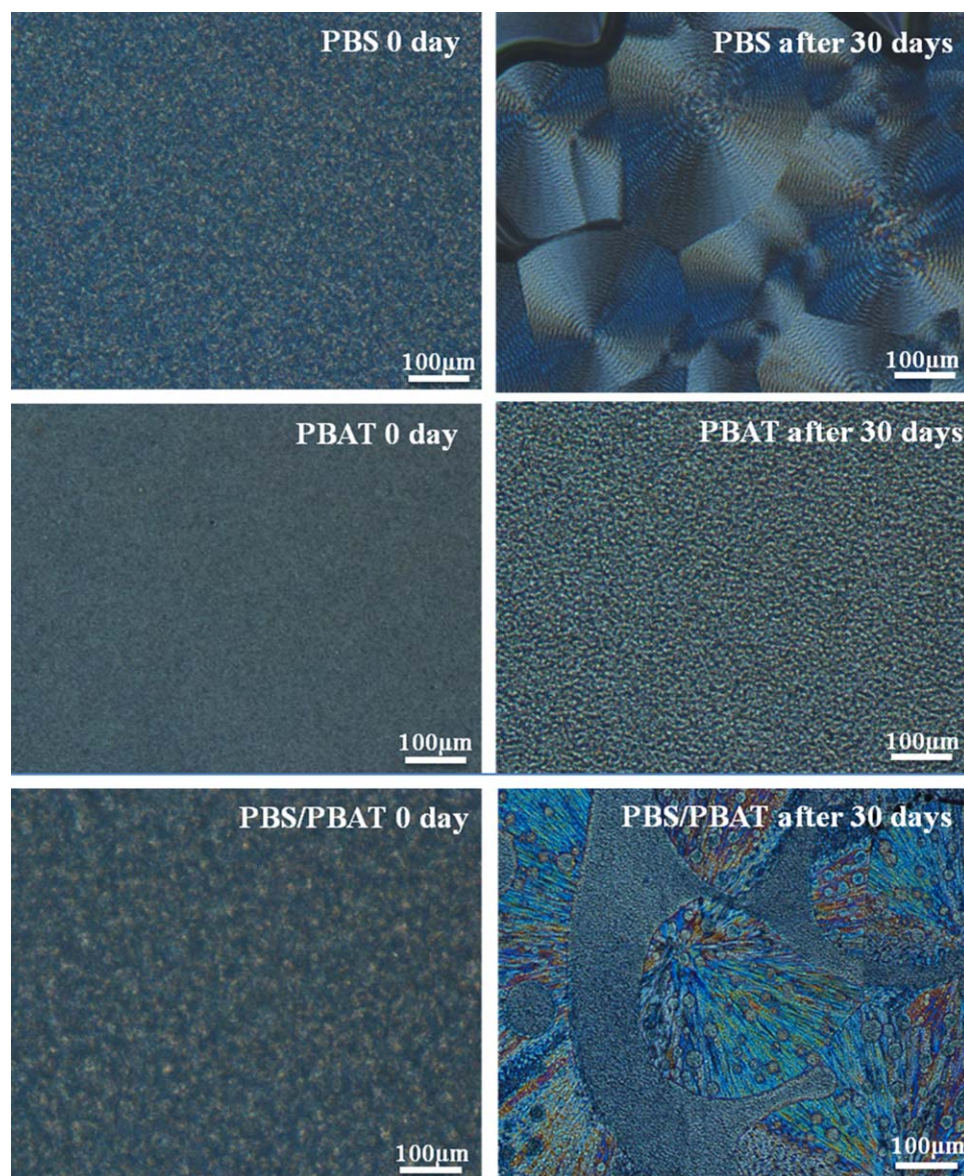


Figure 16. Polarized optical micrographs of PBS, PBAT, and PBS/PBAT before and after 30 days conditioned at 50°C and 90% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the samples before and after conditioning can be calculated by using following equation:

$$\log\left(\frac{\eta_1}{\eta_2}\right) = 3.4\log\left(\frac{M_1}{M_2}\right) \quad (5)$$

where η_1 and η_2 are the Zero shear viscosity of the samples before and after conditioning.

The molecular weight reduction is permanent damage caused by hydrolysis of the ester functionalities on the polyesters backbone. Phua and coworkers⁸ have studied the molecular weight of hydrolytically degraded PBS samples. The authors found that the molecular weight reduction was higher with an increasing conditioning period. Table III reports the zero shear viscosity, viscosity ratio and relative molecular weight [calculated from eq. (5)] of the samples before and after 6 days of conditioning.

After 6 days conditioning, a significant reduction in molecular weight and viscosity were observed for all the samples. As mentioned before, PBS and PBAT are susceptible to the moisture. Therefore, it can be expected that the moisture can easily hydrolyze the PBS and PBAT at 90% RH and it leads to a decrease in the molecular weight as well as viscosity.¹³ The molecular weight of the PBS/PBAT blend was 1.70 times lower after being subjected to hydrolytic degradation. This is relatively high compared with PBS and PBAT. This may be due to the hydrolysis product of PBS or PBAT accelerating the molecular weight reduction of the PBS/PBAT blend. After 6 days of exposure to heat (50°C) and humidity (90%), the molecular weight reduction occurred in the following order PBS/PBAT > PBAT > PBS, as shown in Table III. This result agrees with the observed mechanical properties of the conditioned samples as studied.

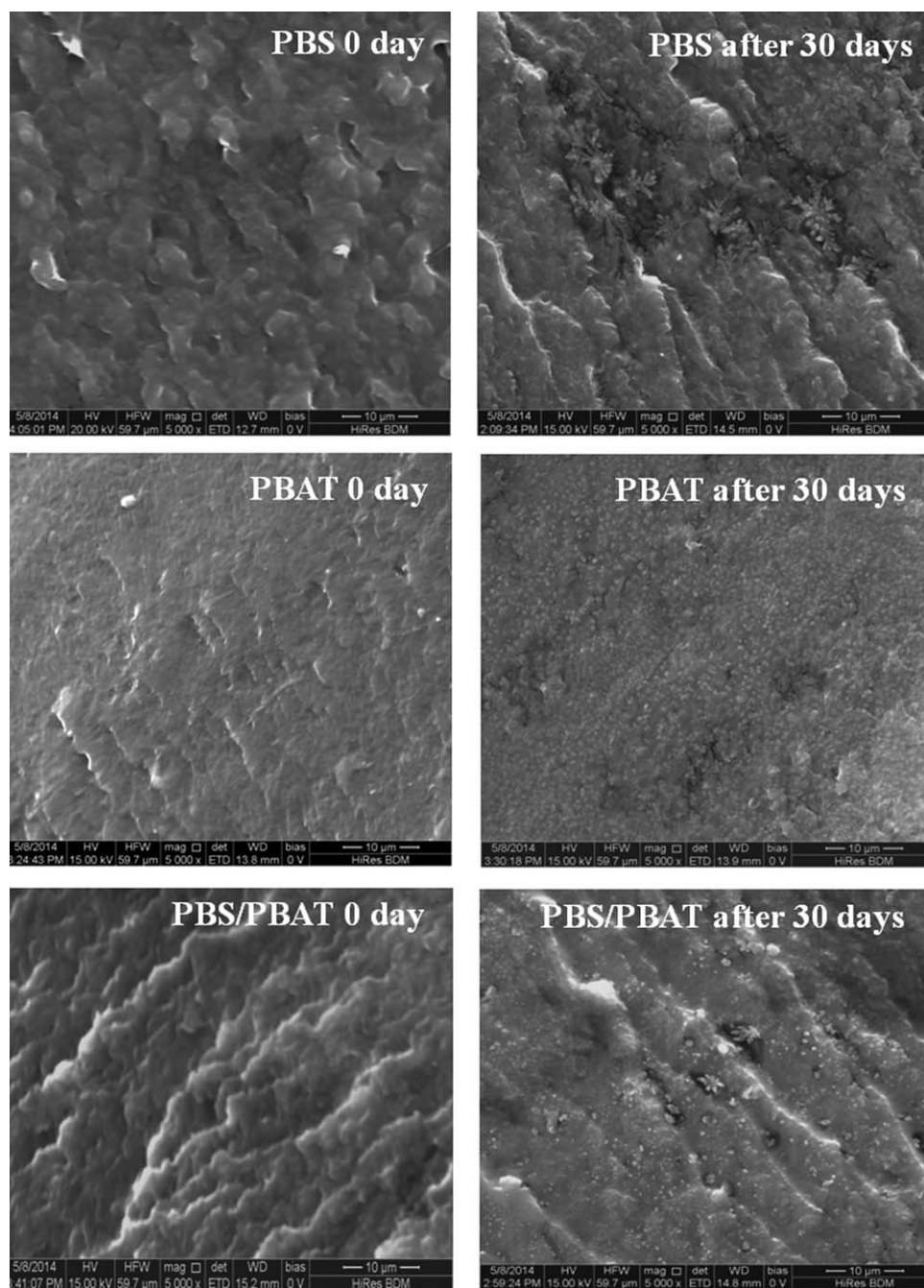


Figure 17. SEM micrographs of PBS, PBAT, and PBS/PBAT before and after 30 days conditioned at 50°C and 90% RH.

Optical Polarizing Microscopy

Figure 16 shows the spherulite morphology of PBS, PBAT, and PBS/PBAT before and after 30 days of exposure to raised humidity and temperature. The spherulite morphology of the samples was analyzed at close to crystallization temperature (90°C). Before being exposed to hydrolysis conditions, it was difficult to notice clear spherulite morphology at 90°C for all the samples. However, after 30 days the conditioned samples exhibited an obvious spherulite structure. It is generally agreed that the amorphous region is more susceptible for hydrolysis

than crystalline regions in semicrystalline polymers. Therefore, these findings have good agreement with the improved percentage of crystallinity which was observed by DSC. This type of phenomenon is commonly found in the polymers when exposed to a degradation environment.^{52,53} Interestingly, the amount of spherulite formation was higher in the samples with a lower percentage of crystallinity. For instance, the PBS and PBS/PBAT blend showed less number of spherulites than PBAT after 30 days exposed to hydrolysis. This is attributed to the nucleation density difference in the samples. A similar trend has

been observed in the degraded polypropylene sample.⁵³ In addition, the PBS had a less amount of nucleation sites than PBAT because of the severe molecular weight reduction by hydrolytic degradation. This phenomenon was consistent with observed crystallization temperature by the DSC analysis. Furthermore, the spherulite morphology of the 30 days exposed PBS and PBS/PBAT exhibits clear ring-banded spherulites, which can be attributed to their reduced molecular weight. This finding has good agreement with a previous study.⁵² According to Kfoury *et al.*⁵⁴ the percentage of crystallinity, size of crystallites, and spherulite morphology have great influence on the impact strength. The stress concentration ability of crystallites has been increased with an enhanced percentage of crystallinity. Consequently, this could lead to a reduction in the impact strength. In this study, observed impact strength had good agreement with the spherulite morphology and crystallinity.

Morphological Analysis

To investigate the hydrolysis caused by moisture and temperature, SEM analysis was carried out before and after 30 days conditioned samples. SEM micrographs of the PBS, PBAT, and their blend are depicted in Figure 17. Before exposure to hydrolysis environment, a smooth surface morphology was observed for all the samples. On the other hand, after 30 days of hydrolysis test, the PBS, PBAT, and PBS/PBAT blend showed deep holes, cavities as well as eroded regions. This observation indicates that the biodegradable polyesters (PBS, PBAT, and PBS/PBAT blend) can readily undergo severe degradation after being exposed to elevated humidity and temperature. A similar type of physical damage in the hydrolytically degraded PBS and PLA samples has been observed by Kanemura *et al.*³³ and Deroine *et al.*⁵⁵ These studies suggest that the formed irregular surface morphology is ascribed to the dissolution of the oligomers during hydrolysis process.⁵⁵ It can be seen that the SEM image (Figure 17) of the PBS showed significant erosion pits and large eroded regions compared with PBAT and PBS/PBAT. This is corresponding to the higher rate of hydrolytic degradation of PBS after conditioning for 30 days under the simulated environment.⁸ In addition, an irregular fractured surface was observed in the 30 days conditioned PBS sample. This is possibly due to the increased crystallinity after being exposed to the hydrolysis environment.

CONCLUSIONS

The hydrolytic degradation of PP, PBS, PBAT, and PBS/PBAT samples was examined after exposure to elevated temperature and humidity. As a result of chain scission through the hydrolysis mechanism, the elongation at break and tensile strength of the PBS, PBAT, and PBS/PBAT were significantly affected after conditioning. However, the flexural and tensile modulus of the PP, PBS, and PBS/PBAT were slightly improved after exposure to heat and humidity. This could be due to the improved crystallinity by molecular weight reduction during the exposure time. The increased crystallinity was consistent with observed spherulite morphology. The zero shear viscosity of the 6 days exposed samples was lower compared to corresponding unexposed samples. This suggests that the molecular weight of the exposed sample is reduced as a result of hydrolytic degradation.

Interestingly, it was found that the impact strength of the PBAT was not affected significantly over the entire exposure time, whereas for PP, PBS, and PBS/PBAT impact strength decreased up to 6 days of conditioning. Over the hydrolysis time, the samples had rough surfaces and corrosive holes in the SEM micrographs. This result agrees with the considerable reduction in the mechanical properties of the samples after being exposed to elevated temperature and humidity. Our findings allow us to conclude that the hydrolytic degradation of biodegradable polyesters need to be reduced under high humidity and temperature for diversifying their applications.

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