Polymer Degradation and Stability 146 (2017) 223–228

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Hydrolytic and compost degradation of biobased PBSF and PBAF copolyesters with 40–60 mol% BF unit

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ARTICLE INFO

Article history:
Received 28 June 2017
Accepted 15 July 2017
Available online 17 July 2017

Keywords:
Biobased polymers
Biodegradable polymers
Aliphatic-aromatic copolyesters
Furandicarboxylic acid
Biodegradation

ABSTRACT

To further assess the biodegradability of biobased copolyesters poly(butylene adipate-co-butylene furandicarboxylate)s (PBAFs) and poly(butylene succinate-co-butylene furandicarboxylate)s (PBSFs), compost as well as hydrolytic degradation of PBAFs and PBSFs with 40–60 mol% butylene furandicarboxylate (BF) unit and high intrinsic viscosity (1.1–1.8 dL/g) were investigated. The hydrolytic degradation was accelerated under acidic and alkaline in comparison to neutral condition. Faster weight loss was observed under alkaline condition but lower intrinsic viscosity was observed under acidic condition due to the distinct water solubility and diffusibility of the degradation products at various pH values. All the copolyesters reached 90% or higher biodegradation in less than 110 days at standard composting conditions. Copolyesters with higher BF content showed slower biodegradation, and PBAFs degraded faster in compost than PBSFs with the same composition. Very interestingly, these copolyesters showed easier biodegradation in compost even at higher aromatic content when compared with their terephthalic acid (TPA)-counterparts.

1. Introduction

Using disposable plastics made of biobased and biodegradable polymers instead of non-degradable polymers are regarded as an effective means to realize the carbon-neutral industrial ecological cycle and to solve the problem of white pollution faced [1–6]. As the most representative biobased and biodegradable polymers, poly(lactic acid) (PLA) is deemed as real green and sustainable materials from cradle to grave. PLA has been successfully commercialized in large scale and it has been used in a variety of fields from disposable to durable items [7]. To expand the property spectra of biobased and biodegradable polymers and to avoid some inherent performance deficiency of PLA [8], researchers have been taking efforts to develop new biobased and biodegradable polymers with more desirable performance.

Aliphatic-aromatic copolyesters like poly(butylene adipate-co-terephthalate) (PBAT) [9,10] and poly(butylene-co-succinate terephthalate) (PBST) [11–13] have superior comprehensive performance over PLA and have been proven to be biodegradable within given composition (aromatic content < 50 mol%) [14–16]. As a petroleum-based copolyester, PBAT has been commercialized and applied in many fields for about two decades. Poly(butylene adipate-co-furandicarboxylate) (PBAF) and poly(butylene succinate-co-furandicarboxylate) (PBSF) are newly emerged biobased and potentially biodegradable aliphatic-aromatic copolyesters [17–20]. They are synthesized from 1,4-butanediol, 2,5-furandicarboxylic acid (FDCA) and adipic or succinic acid via melt polycondensation. FDCA is a biobased monomer derived from massive and renewable cellulose resources [21]. It also is one of the twelve top value-added platform chemicals derived from biomass [22]. The molecular structure of FDCA is similar to terephthalic acid (TPA) to certain extent [23], even if FDCA is less aromatic but more rigid than TPA [24]. Therefore, FDCA-based polyesters usually have thermo-mechanical properties comparable to their TPA-based counterparts [17–20,25], but also display some uniqueness like superior gas barrier properties in poly(ethylene furandicarboxylate) *vs.* poly(ethylene terephthalate) [26]. For PBAF and PBSF, they

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https://doi.org/10.1016/j.polymdegradstab.2017.07.016
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have lower melting temperature but higher glass transition temperature than their respective TPA-counterparts [17–20], namely, PBAT and PBST. Provided that their molecular weight is high enough, we found in a very recent study that PBSF and PBAF showed mechanical properties even better than their TPA-based counterparts at the same aromatic content [27].

Although synthesis [17–20,28,29], thermo-mechanical properties [17–20,29], hydrolytic [27,30–32], enzymatic [19,29] and compost degradations [20] of some FDCA-based aliphatic-aromatic copolyesters have been reported in recent years, the knowledge and understanding of their biodegradability are still limited. Compost degradation is an important way to assess the biodegradability of polyesters. During composting, polyesters are first hydrolytically degraded by extracellular enzymes excreted by microorganisms and then the produced monomer and short enough oligomers are metabolized by intracellular enzymes. Chemo-catalyzed hydrolysis also takes place during compost degradation. Recent researches proved that PBAFs with aromatic content below 50 mol% are enzymatically degradable in the presence of lipase from porcine pancreas [19] and PBSFs with aromatic content less than 20 mol% are compost biodegradable [20]. Poly(ethylene succinate-co-furandicarboxylate) (PESF) with up to 80 mol% aromatic unit show measurable weight loss during enzymatic hydrolysis using Rhizopus delemar and *Pseudomonas cepacia* lipases [29]. But whether or not PBSFs and PBAFs with aromatic content equal to (or even higher than) that in commercial PBAT (ca. 45 mol%) can be degraded in compost is still unknown. This is an important question to answer in view of larger scale industrialization of PBAFs and PBSFs because the copolyesters in such a composition range are regarded to possess desirable thermo-mechanical properties [17–20].

In previous studies, we reported the synthesis and thermo-mechanical properties of PBSF and PBAF copolyesters in whole composition range [17,18]. For PBAFs and PBSFs with 40–60% butylene furandicarboxylate (BF) unit, we also reported the hydrolytic degradation behaviors at room temperature and under neutral condition [27]. Under these conditions, it was found that these copolyesters displayed exponential decrease of intrinsic viscosity but very slight weight loss and they still retained sufficient mechanical properties for a period as long as 22 weeks. In this study, we further investigated the hydrolytic degradation of these copolyesters under acidic and alkaline conditions and compared it with that under neutral condition. Furthermore, compost degradation of these copolyesters was also assessed under standard composting conditions. Excellent biodegradability was demonstrated for PBAFs and PBSFs with aromatic unit even up to 60 mol%.

2. Experimental

2.1. Materials

The PBSF and PBAF copolyesters used in this study had been synthesized as reported recently [27]. Their composition (BF unit 40–60 mol%), intrinsic viscosity (1.1–1.8 dL/g) and melting temperature are gathered in Table 1. Film specimens with thickness of 100 ± 10 μm were prepared by solvent casting following the method reported by some of us [27]. Thin-layer chromatography-level cellulose (Alatin) was used as control for composting experiments. Two kinds of compost named NG and GL were purchased from Beijing Nangong Compost Co., China and Hangzhou Guanlv Compost Co., China, respectively. A 45/55 w/w mixture of them was used in the composting experiments so as to fulfill the requirement for composting activity: 50–150 mg CO2 per gram “volatile solid” should be generated in the first 10 days from the compost itself. The water content, volatile solid percentage, C/N element ratio, pH and composting activity of the composts are listed in Table 2.

Table 1
Properties of the copolyesters used in this study.

Sample	ϕ_{BF}[a] (mol%)	M_w[b] (g/mol)	$Đ$[c]	[η][d] (dL/g)	T_m[e] (°C)	ΔH_m[f] (J/g)
PBAF40	38.4	99 000	1.91	1.46	53.6	13.0
PBAF45	44.9	128 500	1.87	1.80	73.8	14.9
PBAF50	48.0	109 300	2.17	1.37	86.9	19.8
PBAF55	53.6	/	/	1.15	98.6	24.8
PBAF60	58.3	110 300	2.18	1.45	108.1	30.4
PBSF40	39.8	162 100	2.07	1.43	55.5	28.3
PBSF45	43.2	165 400	2.00	1.53	73.1	18.4
PBSF50	49.1	167 200	1.95	1.34	85.6	22.4
PBSF55	53.8	162 800	2.05	1.36	96.8	26.3
PBSF60	58.8	/	/	1.12	112.0	34.2

[a] Molar percentage of the butylene furandicarboxylate (BF) repeat unit.
[b] Weight-average molecular weight.
[c] Molecular weight dispersity.
[d] Intrinsic viscosity.
[e] Melting temperature.
[f] Melting enthalpy in the first DSC heating at 10 °C/min.

2.2. Hydrolytic degradation at acidic and basic conditions

Hydrolytic degradation was conducted at acidic (pH 4.0) and basic (pH 12.0) buffer solutions prepared from NaH_2PO_4 (0.2 M)/acetic acid and sodium acetate/NaOH (0.2 M/0.2 M), respectively. The buffer solutions were sterilized at 100 °C for 3 h and then used for hydrolytic experiments. For each sample, 15 × 6 film specimens were placed in 15 Schott bottles (50 mL) containing 40 mL buffer solution. All the bottles were placed in a shaking table at 25 °C. The hydrolytic experiments lasted for 22 weeks. The buffer solutions were monitored by pH meter and replaced with fresh solutions every week to keep constant pH. Every 1–2 week(s), 6 specimens in one bottle of each sample were taken out. The specimens were washed by deionized water, dried at 40 °C in a vacuum oven for 48 h and used for weighing and intrinsic viscosity measurement. The intrinsic viscosity was measured at 25 °C by an automatic viscosity tester (ZONWON IVS300, China) equipped with a Ubbelohde viscometer with a diameter of 0.88 mm. Mixture of phenol and tetrachloroethane (3/2 w/w) was used as solvent. The solution concentration was 5 mg/mL. The intrinsic viscosity was calculated via Billmeyer empirical formula $[\eta]=(\eta_{sp}+3\ln\eta_r)/4C$ [33].

2.3. Compost degradation

Compost degradation of PBSF and PBAF copolyesters were assessed according to the standard ISO 14855-1:2005 and GB/T 19277.2–2013 in a self-made composting device composed of four parts: (1) air pretreatment, (2) bioreactors (3 L*21), (3) gas drying and (4) CO_2 adsorption. For each sample, the film specimens (20 × 20 mm^2, ca. 15 g*3) were mixed with 1.5 kg compost in 3 bioreactors. Compressed air (~30 mL/min) was pretreated by removing CO_2 (to < 30 ppm) and humidifying (to relative humidity 50%) and then entered into the bioreactors. During composting, the temperature and relative humidity were kept at 58 ± 1 °C and 50%, respectively. The gas mixture emitted from the reactors was dried to remove moisture generated in the bioreactor, and the CO_2 in it was then adsorbed by soda lime. From the weight change of the adsorbent, the weight of CO_2 generated was obtained and used to calculate the biodegradation percentage of the polyester samples. Average was obtained from three trials for each blank, control and test samples.

Table 2
Properties of the composts.

Compost	NG/GL (w/w)	H_2O[c] %	Volatile solid[d] %	C/N[e]	pH	Ac[f] (mg/g)
Requirement	–	45–50	>30	10–40	7.0–9.0	50–150
NG[a]	100/0	50	31.9	15.6	8.3	>150
GL[b]	0/100	50	54.1	9.7	8.1	51
NG/GL	45/55	50	44.0	12.4	8.2	132

[a] The NG compost was made from municipal solid wastes.
[b] The GL compost was made from animal wastes.
[c] Water content of the compost.
[d] Dry base volatile solid content represents the content of organics in a dry compost.
[e] The C to N element weight ratio.
[f] Composting activity means the amount of CO_2 generated from the compost itself at standard composting condition in the first 10 days, the unit is mg CO_2/g volatile solid.

3. Results and discussion

3.1. Hydrolytic degradation

In our previous report [27], it was found that PBSF and PBAF copolyesters with 40–60% BF unit degraded slowly with only a little mass loss observed at neutral condition and room temperature. As hydrolysis of polyesters is catalyzed by acid or base, the hydrolytic degradation of these copolyesters at acidic (pH 4.0) and alkaline (pH 12.0) conditions were also investigated and compared with that carried out at neutral condition (pH 7.0). The degradation lasted for 22 weeks.

The time evolutions of relative weight and intrinsic viscosity of two typical copolyesters, PBAF45 and PBSF45, during hydrolytic degradation at various pH values, are shown in Fig. 1 and Fig. 2. The weight loss of both copolyesters was very slow at neutral condition. Only slight weight loss (1.4–1.8%) was observed after hydrolysis for 22 weeks at neutral condition. The weight loss at acidic condition was even slightly slower as it reached only ca. 1% after 22 weeks. However, the weight loss proved much faster at alkaline condition. It reached 14% for PBSF45 and 52% for PBAF45 after 22 weeks. However, the decrease in intrinsic viscosity showed opposite pH dependence. The intrinsic viscosity decreased much more rapidly at acidic condition than at neutral and alkaline conditions.

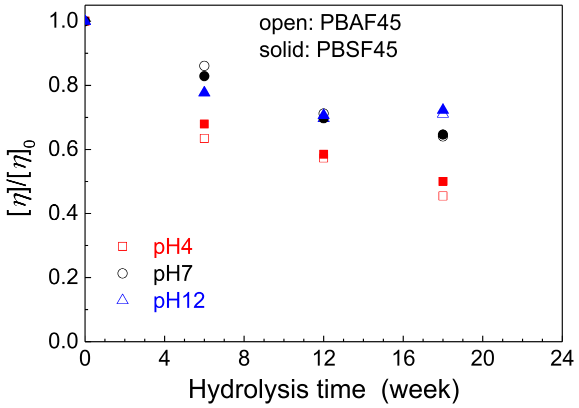

Fig. 2. Time evolution of relative intrinsic viscosity of PBAF45 and PBSF45 during hydrolytic degradation at various pH values (4.0, 7.0 and 12.0).

The different effects of pH on the changes of weight loss and molecular weight can be explained from hydrolysis mechanism and solubility/diffusion of the degradation products. In hydrolysis of polyesters, water diffused into the bulk of the specimen and the ester bonds were hydrolyzed to form oligomers or shortened polyester chains with hydroxyl and carboxyl end groups. At neutral condition, the carboxyl end group of polyesters or oligomers could auto-catalyze the reaction. At acidic or alkaline conditions, hydrolysis could be accelerated by external acidic and alkaline catalysis. During hydrolysis, oligomers with various chain lengths were continuously formed and some of them diffused into aqueous phase, and therefore decrease of molecular weight and weight loss were observed. The observed weight loss and decrease of molecular weight were determined not only by the scission rate of ester bond but also by the water solubility and diffusion of the oligomers. The water solubility is determined by the chain length and end groups. Oligomers had low enough molecular weight could be dissolved in water and diffused into aqueous phase. When the carboxyl end group was neutralized/salified at alkaline condition, the water solubility and diffusibility of the oligomers were enhanced, therefore they were easily dissolved and diffused from the bulk of the water-absorbed specimen into the free aqueous phase. At acidic or neutral condition, the formed oligomers were clearly less water-

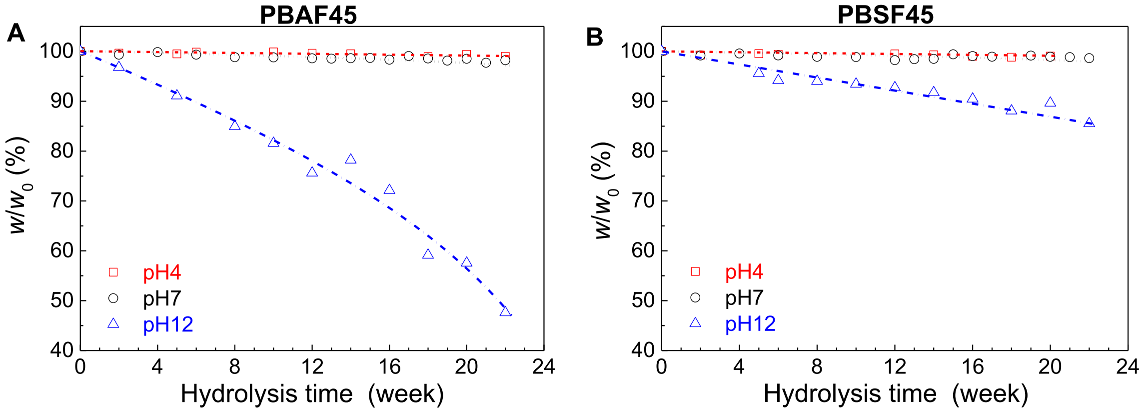

Fig. 1. Time evolution of relative weight (w/w_0) of PBAF45 (A) and PBSF45 (B) during hydrolytic degradation at various pH values (4.0, 7.0 and 12.0).

soluble and therefore difficult to diffuse into the aqueous phase. Most of them remained in the bulk of the specimen. In other words, the specimen degraded at alkaline condition was mainly composed of polymer chain with relatively high MW because most of the formed oligomers had been neutralized/salified and entered into the aqueous phase, so bigger weight loss but less decrease in molecular weight were observed. At acidic or neutral conditions, most degradation products with low molecular weight remained in the specimen, therefore only slight weight loss but more significant decrease in (average) molecular weight were observed. For poly(1,3-propylene adipate-co-furandicarboxylate) (PPAF) and poly(1,3-propylene succinate-co-furandicarboxylate) (PPSF), Hbaieb *et al* [32] also reported that there was only less than 1% weight loss observed after hydrolysis in an acidic PBS buffer solution for 4 weeks.

It can be seen from Fig. 1 that PBAF45 degraded faster than PBSF45. Other PBAF copolyesters also exhibited faster weight loss than the PBSF counterparts at the same composition, see Fig. 3. The rapider degradation of PBAFs was attributed to their lower crystallinity as reported previously [27]. On the other hand, because the scattering of some of the weight loss data, no clear conclusion could be drawn on the composition dependence of the weight loss rate.

3.2. Compost degradation

The compost degradation was conducted under standard conditions regulated in ISO 14855-1:2005 and GB/T 19277.2–2013. As the compost activity of single compost did not fall into the range required (50–150 mg CO_2/g), the NG and GL composts were mixed in various ratios to assess their compost activities. A NG/GL 45/55 mixture with compost activity of 132 mg CO_2/g was used for the composting experiments, which were conducted at 58 °C and 50% humidity.

The time evolutions of biodegradation percentage of several copolyesters and cellulose used as reference are shown in Fig. 4. The biodegradation percentage of the cellulose reached 88.8% at 45 day. It was higher than the required value of 70%, suggesting the composting conditions were reliable. It can be seen that all the five samples tested passed the requirement of the standard EN 13432, which requires 90% biodegradation in less than 180 days. In fact, they all reached 90% biodegradation in 110 days. Therefore, these copolyesters proved to exhibit excellent biodegradability.

For both kinds of copolyesters, the biodegradation speed decreased when the BF unit content increased, and therefore the time needed to reach 90% biodegradation elongated from 71 to 106 days and the biodegradation percentage at 100 day decreased, as shown in Fig. 5. The composition dependence of the biodegradation speed can also be seen from the slope of the linear part of the biodegradation-time curves. The slope represents the percentage of CO_2 released per day. The plot is shown in Fig. 6. The results indicate

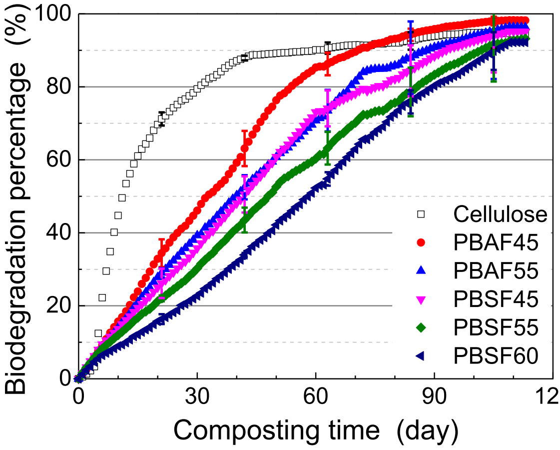

Fig. 4. Time evolution of biodegradation percentage of various FDCA-based copolyesters and cellulose used as control. For clarity, error bars were given only for several representative data points though all data were obtained from three parallel measurements.

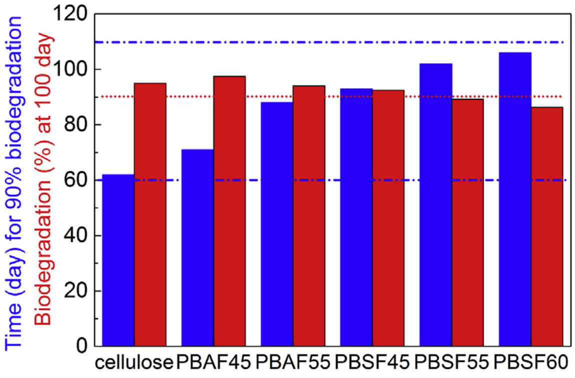

Fig. 5. The time reaching 90% biodegradation (blue) and the biodegradation percentage at 100 day (red) during compost degradation of various FDCA-based copolyesters and cellulose used as control. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

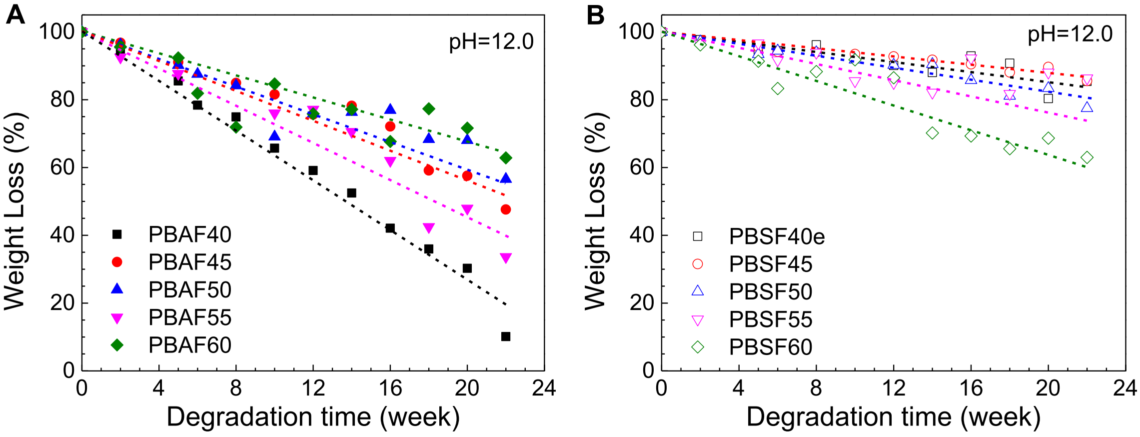

Fig. 3. Time evolution of relative weight (w/w_0) of PBAF (A) and PBSF (B) with various compositions (40–60 mol% BF unit) during hydrolytic degradation at pH of 12.0.

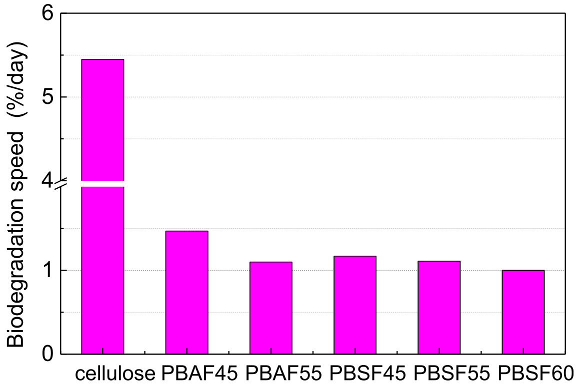

Fig. 6. Biodegradation speed or percentage of CO_2 released per day calculated as the slope of the linear part of the biodegradation-time curves in Fig. 4.

that the aromatic BF unit was less sensitive to compost degradation than the aliphatic BA or BS units. In a previous work, Zhou *et al* [19] also reported that the enzymatic biodegradation of PBAF slowed down with increasing BF fraction. Similar composition dependence in enzymatic or compost degradation was extensively observed in TPA-based copolyesters like PBAT [10,14] and PBST [34–36]. Unlike aliphatic polyesters, aliphatic-aromatic copolyesters like PBAT and PBST are less biodegradable and the biodegradation speed strongly depends on the copolymer composition: the more the aromatic unit, the slower the biodegradation. It has been confirmed that the aromatic sequences of butylene terephthalate (BT) in PBAT with degree of polymerization (DP) more than two are difficult to be biodegraded [14,16]. As the content of aromatic unit increases, the fraction of BT sequences with DP higher than 2 also increases, therefore the biodegradation speed slows down. In addition, the higher crystallinity at higher aromatic composition also accounted for the slower biodegradation.

On the other hand, it can be clearly seen that these FDCA-based copolyesters degraded faster in compost than their TPA-counterparts. Commercial PBAT with about 45 mol% BT unit can pass the requirement of 90% biodegradation in 180 days. But for PBAT and PBAT copolyesters with higher aromatic content, the biodegradation percentage is often less than 90%, according to open literature [37] as well as some undisclosed documents. Thus, the aromatic content of TPA-based biodegradable copolyesters is usually limited to 50 mol%. Differently, the PBAF and PBSF copolyesters in this study passed the biodegradation requirement at BF unit fraction up to 60 mol%. Similarly, good compostability was reported for poly(butylene sebacate-co-furandicarboxylate) (PBSeF) containing 60–70% BF unit in a recent patent from Novamont [38]. Therefore, in comparison with TPA-based aliphatic-aromatic copolyesters, FDCA-based ones can be biodegraded at higher aromatic unit content. The excellent biodegradability provides wider composition window to tune the thermo-mechanical properties. The rapid biodegradation up to 60 mol% BF unit suggests that BF sequence with DP higher than 3 could be metabolized by microorganisms. The better biodegradation possibly resulted from their unique chemical structure. The less aromatic, oxygen-containing and therefore more hydrophilic furan ring may be more favorable than benzene ring to the attack by the extracellular enzymes excreted by microorganisms as well as to the metabolism by the intracellular enzymes. Further study is needed for detailed biodegradation mechanism.

Besides, it can be seen that PBAF degraded faster in compost than PBSF at the same composition, especially when PBAF45 was compared with PBSF45. The faster degradation of PBAF copolyesters was attributed to their less crystallinity, which had been discussed in a previous report [27]. Less crystallinity was beneficial to the adhesion and erosion of microorganisms, as a result, enzyme- and auto-catalyzed hydrolytic degradations were more likely to happen. Therefore, the PBAFs exhibited faster biodegradation than PBSFs.

4. Conclusions

Hydrolytic degradation under acidic and alkaline conditions and biodegradation in compost of PBAF and PBSF copolyesters with 40–60% BF unit and high molecular weight were assessed in this study. The hydrolytic degradation was accelerated under both acidic and alkaline conditions as compared with under neutral condition. However, due to the distinct water solubility and diffusibility of the degradation products under various pH values, the weight loss was much more pronounced under alkaline condition than that at neutral and acidic conditions. The compost degradation showed clear composition and crystallinity dependences. Copolyesters with higher BF content showed slower biodegradation, and PBAF degraded faster than PBSF at the same composition. All the copolyesters fulfilled the requirement of 90% biodegradation in 180 days and therefore can be regarded as biodegradable polymers. More importantly, these copolyesters showed easier biodegradation even at higher aromatic content as compared with their TPA-counterparts. Such excellent biodegradability up to high aromatic content provides wider composition window to tune the thermo-mechanical properties.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51373152), the National Key Research and Development Program of China (2016YFB0302402) and 151 Talents Project of Zhejiang Province.

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