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Research article

Bio-based aliphatic polyesters of 1,4-butanediol with different diacids: Effect of carbon chain lengths on mechanical properties and enzymatic hydrolysis

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Abstract. Polybutylene succinate, polybutylene adipate, polybutylene suberate and their copolyesters were synthesized. The physical properties and biodegradability of these polyesters were controlled by adjusting the composition of carboxyl monomers. Compared with the homopolyesters, the addition of comonomer during polymerization resulted in the formation of copolyesters with lower melting temperatures and crystallinity. Among them, poly(butylene succinate-*co*-adipate) (PBSA) had the lowest crystallinity, and poly(butylene adipate-*co*-suberate) (PBASub) had the lowest melting point. The elongation at break and tensile strength of PBSA was 766.2% and 21.5 MPa, respectively. Enzymatic degradation by *Fusarium solani* cutinase (FsC) showed that both the crystalline and amorphous regions of the polyester were simultaneously degraded by FsC, and the crystal structure of the polyester was not disrupted. FsC preferentially got attached to the surface of polyesters, subsequently attacked the center of the films, and the water penetrated the amorphous region, leading to enhanced enzymatic hydrolysis. The biodegradability of copolyester was higher than that of homopolyesters. PBSA and poly(butylene succinate-*co*-suberate) (PBSSub) were completely degraded in about 10 h, and can be used in agricultural, automotive, electronics, biomedical materials, packaging, *etc*.

Keywords: *aliphatic polyesters, fusarium solani cutinase (FsC), enzymatic hydrolysis*

1. Introduction

The extent of plastic utilization can be considered as a criterion for evaluating the degree of industrialization and standard of living in a country or region [1, 2]. The plastic waste generated due to daily consumption is increasing owing to its aging properties. Most of the waste plastics are resistant to environmental degradation, leading to the death of hundreds of thousands of marine animals every year and permeate the food chain in the form of microplastics and plastic fragments. These pollutants make their way into the drinking water and, eventually, onto dinner tables, posing a threat to human health [3]. Therefore, from the perspective of protecting the environment and sustainable development of mankind, it is imperative to find environmentally friendly biodegradable plastics to replace traditional petroleum-based plastics.

Polybutylene succinate (PBS) can be considered a representative of fully biodegradable polymers and has gradually met the criteria for industrial applications. In addition, polybutylene adipate (PBA) and polybutylene suberate (PBSub) also have similar chemical structures and properties as those of PBS [4, 5]. These polyesters also hold good prospects for development in the field of polymer applications such as food packaging, slow-release materials for fertilizers, agricultural products, apparel, automotive part, and biomedical applications, *etc*. [6–11].

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To develop new degradable PBS-based polyesters, various renewable diacids or diols were used to substitute part of 1,4-butanedioic acid or 1,4-butanediol. This substitution was aimed at reducing the crystallinity of PBS-based polyesters and increasing their hydrophilicity. Huang *et al*. [12] and Cui and Qiu [13] synthesized PBA and PBSub, by melt polymerization, and investigated their crystallization kinetics and thermal stability. Tserki *et al*. [14] synthesized a high molecular weight poly(butylene succinate-*co*-adipate) PBSA by using hexamethylene diisocyanate as a chain extender. Among the above methods for synthesizing PBS-based polyesters, the melt polycondensation method requires a high esterification temperature, and the temperature control during the experiment is challenging. The use of toxic chain expanders in the chain expansion method (*e.g.*, dicarboxylic anhydride, dichloride, bis-epoxy compounds, *etc*.) raises concern about the potential harm. Besides, the raw materials required are costly and the by-product methanol produced in the transesterification process is toxic. Bai *et al*. [15] synthesized PBS, PBA, and PBSub by solution-polymerization at 140 °C using decahydronaphthalene as the solvent. However, the performance of homopolymers may limit their applications, and the synthesis of fully degradable copolyesters with useful properties holds great promise [16].

Lipases and cutinases are the most common enzymes capable of catalyzing the hydrolysis of PBS-based polyesters. In general, cutinase is more efficient in facilitating the degradation of PBS-based polyesters than lipase, with high degradation rates and shorter degradation times. Lipases, on the other hand, generally require several days or even weeks for degradation and have relatively low degradation rates [17–22]. Shinozaki *et al*. [23] studied the enzymatic degradation of PBSA, polylactic acid (PLA), and polycaprolactone (PCL) using cutinase, and the weight loss was found to be up to 50%. Bai and coworkers [15, 24] used Fusarium solani cutinase (FsC) to degrade six polyesters (PBS, PBA, PBSub, polyethylene succinate (PES), PBS, and polyhexylene succinate (PHS). PES, PBS, and PHS were degraded up to 95% after 12 h, while more than 90% degradation occurred in the case of PBA, and PBSub after 24 h. It was also found that polyesters with more methylene groups, low melting points, crystallinity, and glass transition temperatures exhibited better enzymatic degradation performance.

PBS, PBA and PBSub are suitable for applications where environmental impact is a concern [25–28]. In this work, not only homopolymers PBS, PBA, PBSub, but also their copolymers PBSA, poly(butylene succinate-*co*-suberate) (PBSSub), and poly(butylene adipate-*co*-suberate) (PBASub) were synthesised from 1,4-butanediol with different dibasic acid monomers in the ratio of 1:1. The synthesized polyesters were subjected to degradation by FsC. The characterization of the polyesters before and after degradation was carried out by scanning electron microscope (SEM), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetry (TG), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The changes in the structures of the polyesters were investigated. The relationship between the different carbon chain lengths of the carboxyl monomers, the crystalline, thermal properties, and degradation properties of the polymers was explored, providing further theoretical support for their potential applications and production.

2. Materials and methods

2.1. Materials

1,4-butanediol (BDO, 98%), 1,4-succinic acid (SA, 99.5%), 1,6-adipic acid (AA, 99.5%) and 1,8-suberic acid (Sub, 99.5%), titanium isopropoxide (TTIP, 95%), decahydronaphthalene (99%) and stannous chloride were obtained from Shanghai Aladdin Biochemical Company (Shanghai, China). Anhydrous methanol was obtained from the Tianjin Damao Chemical Reagent Factory (Tianjin, China). Chloroform (99.5%) was obtained from Shenyang Xinxing Reagent Factory (Shenyang, China). FsC was prepared following the procedure reported in our previous work [29].

2.2. Synthesis of polyesters and preparation of polyester films

The solution polymerization of the polyesters involves both esterification and polycondensation reactions. A mixture comprising BDO and either one or two of the diacids SA, AA, Sub (the molar ratio of total diacids to BDO was 1:1.1), titanium isopropoxide (1/600 of the total molar mass of the reactants), and 60 mL of decahydronaphthalene was added to a 500 mL three-necked flask and was mechanically stirred. The flask was heated at 140 °C under a nitrogen atmosphere for 4 h during the esterification.

Subsequently, polycondensation was performed at 230 °C for 4 h under a pressure below 3 mmHg. The products were dissolved in chloroform and washed several times with methanol [15].

The polyester films were prepared using the melt-hot-press method. The film was preheated for 5 min initially, then hot pressed for 3 min, and finally, cold pressed for 3 min at 20 MPa, respectively. Two types of films with thicknesses of 0.3 and 1 mm were prepared. The 0.3 mm polyester film was cut into 30×10×0.3 mm strips, while the 1 mm film was cut into dumbbell-shaped strips. Both of them were placed at room temperature for 3 days before use.

2.3. Enzymatic hydrolysis of the polyesters

The polyester films (30×10×0.3 mm) were incubated in potassium phosphate buffer (pH 7.4, 360 U/mL, 10 mL) at 37 °C. The films were taken out every 24 h and soaked in 2% aqueous sodium dodecyl sulfate solution for 2 h, then thoroughly washed with deionized water, and dried under reduced pressure to a constant weight. The dry weights of films before and after hydrolysis were determined to calculate the weight loss of films [30].

2.4. Structural characterization of polyesters

The micromorphology of the surfaces before and after enzymatic degradation was observed using SEM(SU8010, Hitachi, Tokyo, Japan). The analysis was performed by quenching the samples with liquid nitrogen. The samples were gold-spluttered before testing, and an accelerating voltage of 20 kV was applied during the analysis.

The structural compositions of the polyesters were analyzed using Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (AVANCE III™ HD400, Bruker, Billerica, MA, USA). Deuterated chloroform ($CDCl_3$) was used as the solvent, and tetramethylsilane (TMS) was used as the internal standard. Composite films were analyzed in a scanning range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} using ATR-FTIR (Cary 660, Agilent Technologies, Santa Clara, CA, USA).

An XRD (D8 Advance, Bruker, Billerica, MA, USA) with a Cu target was used to study the crystalline structures of the samples. The analysis was conducted at a wavelength of 0.1541 nm, a tube current of 40 mA, a tube pressure of 40 kV, a step size of 5°/min, and a scanning range of 10° to 50°.

The melting behavior was investigated using DSC (Q20, TA Instruments, New Castle, DE, USA). Approximately 8 mg of the sample was heated from room temperature to a rate of 10 °C/min under a nitrogen flow rate of 30 mL/min. The sample temperature was maintained at 200 °C for 5 min, then reduced to room temperature at the rate of 10 °C/min, maintained for 5 min, and then reheated to 200 °C at the same rate.

The thermal decomposition behavior was determined by a Thermal Gravimetric Analyzer (TGA, Q600, TA Instruments New Castle, DE, USA). About 8 mg of thin film was placed in a crucible and heated in a temperature range of 30~500 °C with a rate of 10 °C/min under a nitrogen flow rate of 30 mL/min.

The mechanical properties were tested by a Digital Display Electronic Tensile Tester (LDS-02, Jinan Chuanbai Instrument Co., Jinan, China). The sample was cut into a dumbbell shape, with a size of 30×10×1 mm, and the tensile properties were evaluated at a test speed of 10 mm/min. For the evaluation of bending properties, a long rectangular bending sample strip with dimensions of 30×10 mm was used, and the bending speed was set at 2 mm/min. The tests were repeated multiple times for each sample to ensure accuracy, and the average values of these multiple measurements were considered for the final results.

Gel Permeation Chromatography (GPC, 1515, Waters, Milford, MA, USA) was used to calculate the molecular weights of polyesters. Chloroform was used as the eluent solution, and the elution was carried out at a flow rate of 0.80 mL/min at 35 bar. Waters Styragel HT3 (7.8×300 mm) and HT4 column (7.8×300 mm) were used for the analysis, and the polystyrene standard within the range of 2000–100 000 g/mol was used for the calibration.

3. Results and discussion

3.1. Structural composition of the polyesters

The structural compositions of the synthesized polyesters were determined by ^{1}H NMR and are displayed in Figure 1 and Table 1. For illustration purposes, PBASub is considered as an example. The proton peaks at 4.10 and 1.70 ppm are attributed to α-methylene and β-methylene protons in butanediol, respectively. Peaks at 2.32 and 2.29 ppm originate from the α-methylene protons of the adipic and octanedioic acid units, respectively. Peaks at 1.70, 1.66,

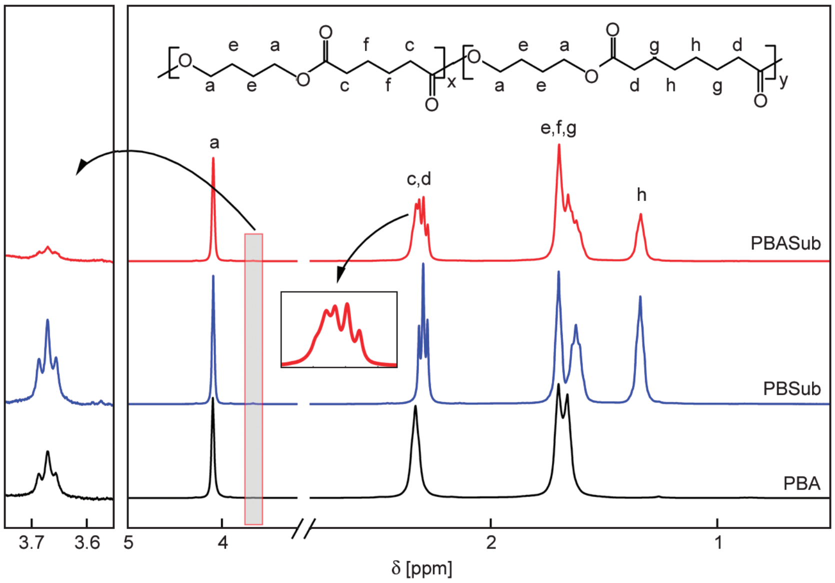

Figure 1. ^{1}H NMR spectra of PBA, PBSub, and PBASub.

Table 1. The peak positions and attributes of ^{1}H NMR spectra of the synthesized polyesters.

Sample	**Position [ppm]**					**Actual ratio [mol%]**
	Peak a	**Peak b**	**Peak c, d**	**Peak e, f, g**	**Peak h**	
PBS	4.12	2.63	–	1.71, –, –	–	–
PBA	4.10	–	2.33, –	1.70, 1.66, –	–	–
PBSub	4.10	–	2.31, –	1.70, –, 1.62	1.34	–
PBSA	4.10	2.63	2.33, –	1.70, 1.66, –	–	50.8:49.2
PBSSub	4.10	2.63	–, 2.30	1.70, –, 1.62	1.34	50.5:49.5
PBASub	4.10	–	2.32, 2.29	1.70, 1.66, 1.62	1.34	50.7:49.3

and 1.62 ppm are attributed to β-methylene proton of butanediol, adipic acid, and octanedioic acid. A proton peak at 1.34 ppm corresponds to the γ-methylene structure in octanedioic acid. The proton peak due to the CH_2 group linked to the terminal hydroxyl group appears at around 3.68 ppm, observable only upon magnification, and the indistinguishable clustered peaks can indicate the high viscosity of copolyester [31, 32]. In contrast to PBASub, the presence of a butanedioic acid segment in both PBSA and PBSSub resulted in an additional proton peak at 2.63 ppm. The actual molar ratio of adipic acid to octanedioic acid can be calculated from the area ratio of the α-methylene proton peaks (H_c:H_d) [33, 34]. It can be observed from the data in Table 1 that the actual ratio deviates slightly from the feed ratio, probably due to the higher volatilization of the alcohol monomer during the reaction.

Figure 2 shows the ATR-FTIR spectra of the synthesized polyesters. The gray and blue regions are partially magnified regions. The antisymmetric and symmetric stre*tc*hing vibration absorption peaks of $–CH_2–$ in the polyester correspond to 2930 and 2860 cm^{-1}, respectively. The absorption peaks at 1720 and 1160 cm^{-1} correspond to $\upsilon_{C=O}$ and $\upsilon_{C–O}$ of the ester bond, respectively [9, 35]. The absorption peak due to the terminal hydroxyl group around 3500 cm^{-1} was not observed, indicating that the molecular weight of the resulting polyester was high [36]. Notably, the differences in the infrared spectra of different synthesized polyesters were mainly concentrated in the 1400–1100 cm^{-1} band. For crystalline straight-chain aliphatic compounds, the CH_2 segments are arranged in a Z pattern in the crystals. This gives rise to a series of nearly equally spaced absorption peaks appearing in this range, and these bands are considered to be the out-of-plane rocking vibrations of CH_2 [37]. Considering PBASub as an illustrative example (Figure 2c), it could be seen that the copolymer exhibited several major absorption peaks, specifically at 2937 cm^{-1} (υ_{asCH}), 2868 cm^{-1} (υ_{sCH}), 1725 cm^{-1} ($\upsilon_{C=O}$), and 1165 cm^{-1} ($\upsilon_{C–O}$). Each of these absorption peaks corresponded to the peaks observed for copolyesters PBA and PBSub [38].

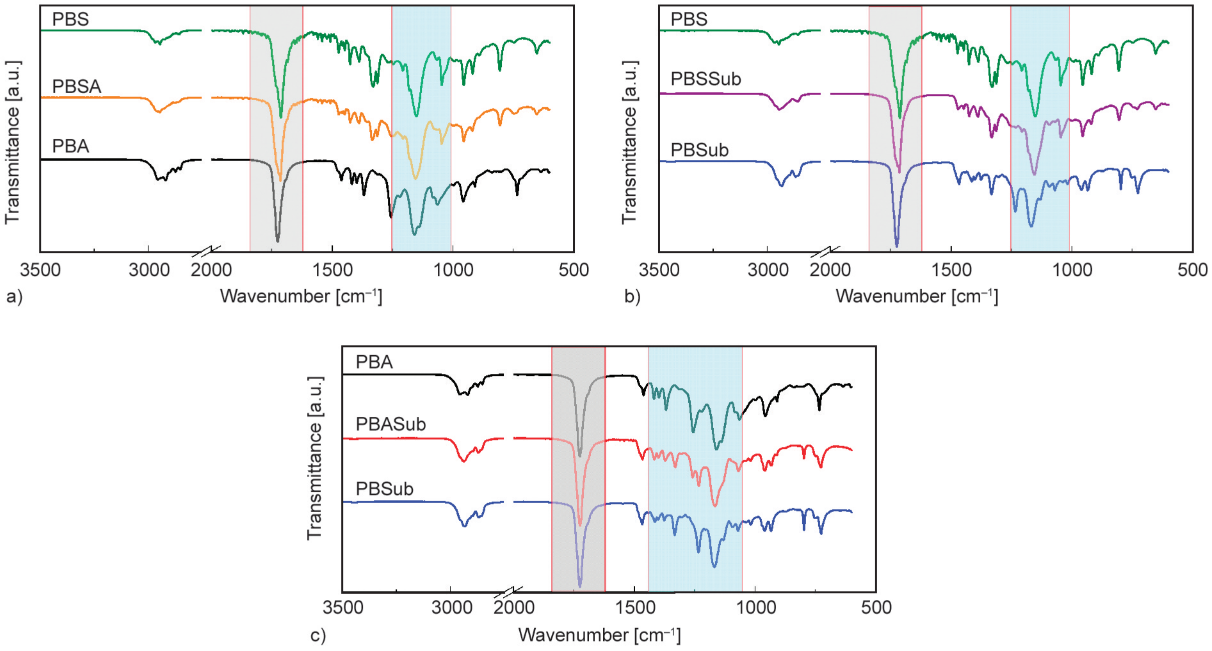

Figure 2. ATR-FTIR spectra of PBA, PBS, PBSub, and their copolyesters. a) PBS, PBSA, and PBA, b) PBS, PBSSub, and PBSub, c) PBA, PBASub, and PBSub.

3.2. Crystalline properties of the polyesters

PBS exhibited a monoclinic crystal structure with the main diffraction peaks located at 19.5°, 21.9°, and 22.6°, corresponding to (020), (021), and (110) crystal planes (Figure 3) [14]. PBA, also belonging to the monoclinic crystal system, displays main diffraction peaks located at 21.7°, 22.4°, and 24.1°, corresponding to the (110), (020), and (021) crystal planes. The main diffraction peaks of PBSub were located at 21.3° and 24.6°, corresponding to the (120) and (040) crystal planes, which belong to the rhombohedral crystal system [39]. All the synthesized polyesters showed clear crystallization peaks, and the diffractograms of the copolyesters PBSA, PBSSub, and PBASub were similar to their corresponding parent homopolyesters, with no new crystallization peaks appearing. This result indicates that the introduction of comonomer unit does not change the crystal structure of corresponding homopolyesters. Based on the analysis of XRD patterns, isodimorphic character is evident for PBSA, PBSSub, and PBASub copolyesters [40, 41].

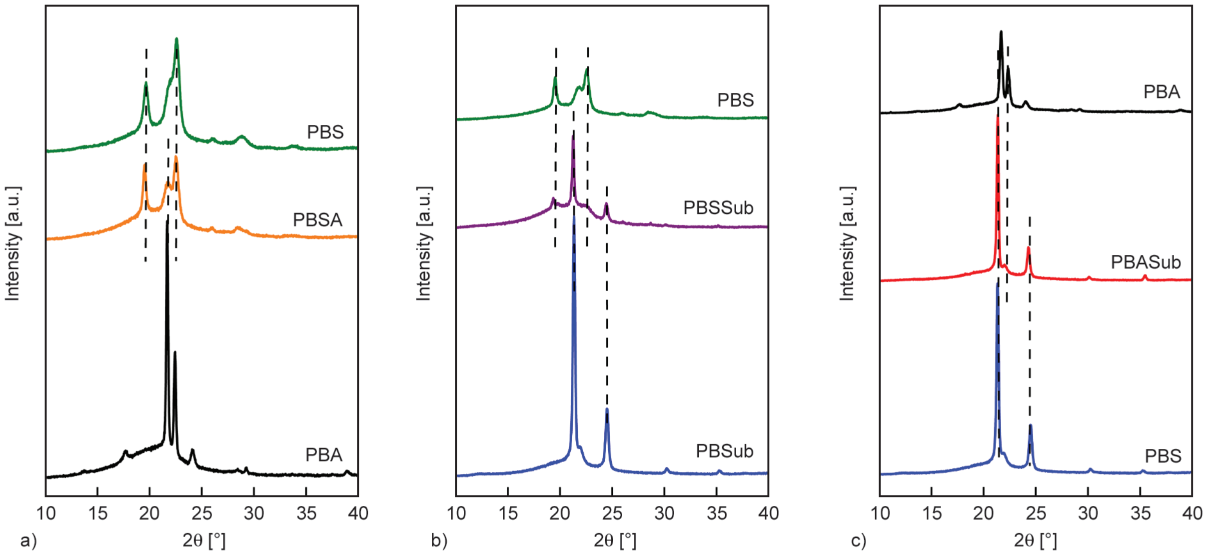

Figure 3. XRD patterns of PBA, PBS, PBSub, and their copolyesters.a) PBS, PBSA, and PBA, b) PBS, PBSSub, and PBSub, c) PBA, PBASub, and PBS.

Table 2. Thermal properties of homopolyesters and copolyesters degraded for different time.

Polymer	Degradation time [h]	T_m [°C]	ΔH_m [J/g]	T_i [°C]	T_p [°C]	$X_{c\text{-XRD}}$ [%]
PBS	0	114.8	54.1	328.1	359.3	52.6
	2	114.9	45.1	327.5	358.7	52.1
	4	114.2	46.3	328.6	358.1	51.1
	8	114.3	45.0	327.4	359.0	50.1
	12	114.3	38.7	328.2	358.7	49.7
	20	114.2	42.2	328.0	358.9	48.3
PBA	0	62.1	50.8	339.1	369.4	41.3
	2	58.8	47.0	338.8	368.2	46.7
	4	62.0	48.8	335.4	366.8	42.1
	6	60.8	42.2	332.4	363.4	40.5
	8	61.7	34.1	330.7	361.2	40.8
PBSub	0	57.5	46.5	373.4	411.6	55.3
	2	57.3	32.7	373.4	411.8	49.8
	4	58.1	47.8	373.2	410.9	48.5
	6	56.8	47.1	373.1	411.1	49.7
	8	56.8	47.0	372.9	411.2	48.9
	20	56.9	40.0	372.5	410.2	50.7
PBSA	0	48.0	28.8	323.0	399.3	36.7
	2	47.6	26.6	320.5	396.3	34.7
	4	46.8	27.4	321.2	392.8	35.9
	8	47.2	29.7	310.3	385.2	36.1
	12	46.5	26.8	308.4	384.2	34.9
PBSSub	0	53.0	28.9	342.8	409.1	44.0
	2	52.8	20.6	340.3	407.2	44.2
	4	52.9	21.5	340.1	405.1	43.6
	6	53.1	23.4	308.4	372.5	40.6
	8	52.4	24.6	290.6	355.4	40.8
PBASub	0	26.7	29.5	340.7	392.2	50.7
	2	27.3	27.2	335.8	387.8	45.5
	4	26.9	28.4	330.7	382.9	46.6
	6	26.4	29.8	320.2	370.5	46.8
	8	25.8	26.3	309.6	361.2	46.0

T_i: the initial temperature;
T_p: the temperature corresponding to the maximum degradation rate.

Additionally, the crystallinity (X_c) of the six polyesters can be calculated from the XRD diffractograms, as shown in Table 2. Gigli *et al*. [38] confirmed that the X_c of polyesters is generally considered to be the main factor affecting their enzymatic degradation properties. Enzymatic degradation generally occurs initially in the amorphous region where segments are irregularly arranged. Bikiaris *et al*. [39] proposed that the initial crystallinity of the polymer is the main factor influencing the biodegradability of polyesters. Under the same conditions, the lower the X_c of the polyester, the better the enzymatic degradation. The X_c of the synthesized polyesters was in the order PBSub > PBS > PBASub > PBSSub > PBA > PBSA. The crystallinity of the copolyesters was lower as compared to the homopolyesters, with PBSA demonstrating the lowest crystallinity. As a result, it exhibited the greatest weight loss and the fastest degradation rate during enzymatic degradation. Therefore, the degradation rates of PBSSub, PBASub, and PBA are anticipated to be faster under the same conditions.

3.3. Thermodynamic properties of the polyesters

DSC analysis results of the six polyesters are displayed in Table 2. All homopolyesters and copolyesters exhibit single crystallization as well as melting peaks. It indicates that the copolymers are capable of crystallization in the entire composition range, and the resultant crystals formed in the non-isothermal crystallization process do not show segregation. The frequent interruption of the crystallizable sequences of one comonomer by the other does not perturb the crystallization process. Thus, thermal analysis suggests the occurrence of isodimorphic behavior for the obtained PBSA, PBSSub, and PBASub copolyesters [28, 29].

It has been shown that the melting points (T_m) of polyesters are usually considered to be an important factor affecting the enzymatic degradation properties of polymers. The lower the T_m of polyester, the easier the enzymatic degradation [42]. The T_m of the polymers were in the order PBS > PBA > PBSub > PBSSub > PBSA > PBASub. The copolyesters possessed lower T_m than the homopolyesters. With the increase in the methylene chain length, the flexibility of the molecular chains increased. Thus, it became less likely for the molecular chain segments to form an aligned lattice structure [43], decreasing the T_m of the polyesters.

The initial temperature (T_i) and the temperature corresponding to the maximum degradation rate (T_p) of the six polyesters are listed in Table 2. The thermal decomposition of the polyesters occurs mainly due to the volatilization of the small molecules in the temperature range between 260 and 310 °C [44]. In the temperature range between 320–450 °C, the ester bond of the polyester molecule undergoes random cleavage accelerating the rate of decomposition [42, 45]. In general, the thermal stability of the copolyesters was slightly lower than that of the homopolyesters. However, the T_p of the copolyesters was higher than that of the homopolyesters, especially a T_p of 409.1 °C was observed for PBSSub. This implies that the progress of decomposition of the homopolyester is slowed down. The straight-chain aliphatic polyesters are comparable to polyolefins having some ester bonds added to chain segments. With the increase in the length of the dibasic acid, the concentration of the ester bonds gradually decreases. Simultaneously, their structural and thermal stability gradually align with those of polyolefins. Therefore, the number of methylene groups in the diacid significantly affects the thermal stability of homopolyester. An enhancement in the thermal stability of the polyester could be observed with the increase in the chain length of the diacid used [44, 46]. The thermal decomposition temperature of the synthesized polyesters exceeded 320 °C. This indicated that the polyesters did not undergo thermal degradation during the synthesis process as well as during the actual processing and molding.

3.4. Enzymatic hydrolysis of the polyesters

Figure 4 shows the degradation curves of the six polyesters in the presence of FsC. Rapid degradation occurred in the case of copolyesters PBSA, PBSSub, and PBASub over the entire period of degradation. The homopolyesters, however, showed a faster degradation rate initially, which subsequently dwindled and got eventually stabilized. In the initial phase of degradation, the enzyme adheres to the surface of the film and cleaves the polyester macromolecules under the suitable temperature and pH conditions provided by the buffer solution [47]. The buffer solution created a conducive environment for the degradation of polyester, causing FsC to continuously erode inward from the surface of the film. As a result, the degradation occurred at a faster rate at this stage. However, after a certain period of degradation, the composition and concentration of the buffer solution changes due to the accumulation of a large number of oligomers and small molecules. The optimal conditions for enzyme-catalyzed degradation of polyester were disrupted, hindering the rapid degradation of polyester film by FsC. Consequently, the rate of enzymatic degradation of the material slowed down [39]. After 8 h of degradation, PBS, PBSub, and PBA exhibited weight loss of 30.5, 57.8, and 46.5%, respectively, while it was 78.2, 65.8, and 73.4% for copolyesters PBSA, PBSSub, and PBASub, respectively. The time required for complete

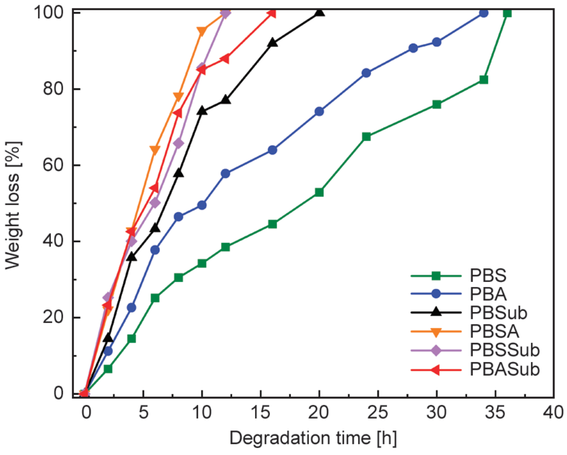

Figure 4. The weight loss of PBA, PBS, PBSub, and their copolyesters.

degradation of PBS, PBA, PBSub, PBSA, PBSSub, and PBSAub was 36.0, 20.2, 36.2, 10.1, 9.9, and 16 h, respectively.

In summary, both crystallinity and melting temperature are important factors affecting the degradation rate. In a comparison between the degradation rates of the three homopolyesters, the faster weight loss in the case of PBA was due to its lower crystallinity and melting temperature [38, 39, 48]. The poor symmetry of the polyester molecular chain resulted in low crystallinity of the molecule, leading to the increased weight loss of the polyester. For the copolymers, adipic or suberic acid introduced in the polymer chain resulted in loosening and disordering of the molecular structure, creating favorable conditions for the enzyme attachment to the ester bond of the polyester, thus accelerating the degradation. In contrast, the melting temperature of PBSA and PBSSub was the closest to the optimum temperature for enzymatic degradation. Owing to this property coupled with the low crystallinity, the highest rates of enzymatic degradation were observed for PBSA and PBSSub. The degradation rate of the above six polyesters was in the order PBSA ≈ PBSSub > PBASub > PBA > PBSub > PBS. Nikolic and Djonlagic [46] studied enzymatic degradation of PBS, PBA, and the copolyester PBSA by *Candida cylindracea* lipase. After 100 h of degradation, the weight loss in the case of PBS and PBA was insignificant, whereas it was significant in the case of PBSA. They proposed that the enhanced flexibility in the case of copolyester as compared to the homopolymer served as an accelerator of enzymatic hydrolysis. Rizzarelli *et al.* [47] found that the length of the polyester carbon chain was the primary factor affecting the degradation properties of polyesters. They used PBSA and poly(butylene succinate-*co*-butylene sebacate) as the substrates for enzymatic hydrolysis. It was found that the breaking of ester bonds in polyesters during enzymatic hydrolysis was not random but selective. Enzymatic hydrolysis tended to occur preferentially on the ester bonds containing more carbon atoms between the ester groups. Similarly, Bikiaris *et al.* [48] investigated the enzymatic degradation of aliphatic polyesters derived from 1,3-propanediol and dibasic acid monomers of different carbon chain lengths (C4-C9). The experimental results showed that aliphatic polyesters with more carbon atoms in the carboxylic acid monomers had a faster degradation rate. Consistent with the results obtained by the previous authors, the degradation rate of the homopolyesters followed the order PBSub > PBA > PBS. In addition, copolymerization or polymer blends are both conducive to accelerating enzymatic degradation [49].

The extent of degradation of the polyesters at different time intervals was analyzed by SEM, DSC, XRD, ATR-FTIR, and TG. The effect of factors such as surface morphology, T_m, X_c, and crystal structure on the enzymatic degradation rate of the polyesters is discussed in the following section.

3.5. Mechanical properties and molecular weight of the polyesters

The mechanical properties of the six polyesters are shown in Table 3: the tensile strength of PBS, PBA, and PBSub showed a gradual decrease with the increase in the number of methylene groups between the ester groups. The introduction of methylene groups rendered a structural complexity to the polyesters that resulted in the reduced symmetry and regularity of the chain, increased the intermolecular distance, and decreased the interaction forces, ultimately leading to a decrease in the tensile strength of polyesters [15, 24]. The lower melting points of PBA and PBSub may also contribute to the lower tensile strength of polyester. Crystallinity is considered the most important factor affecting the elongation at the break of polymers, and an increase in crystallinity typically leads to a decrease in the elongation [30]. The elongation at break of the homopolyesters PBS, PBA, and PBSub were 284.5, 582.3, and 679.4%, respectively. This trend is opposite to the one observed for crystallinity. However, PBSub, which had a slightly higher crystallinity than PBA, exhibited a relatively higher elongation at break, which may be attributed to the higher molecular weight of PBSub. Moreover, the lower melting temperatures of the terpolyesters than that of the

Table 3. Mechanical properties, viscosities, and M_n of the polyesters.

Polymer	Tensile strength [MPa]	Elongation at break [%]	M_n [g/mol]	M_w/M_n
PBS	29.9±1.54	284.5±4.56	34799	1.58
PBA	20.2±1.28	582.3±6.89	30665	1.54
PBSub	14.2±1.42	679.4±8.24	38269	1.53
PBSA	21.5±1.02	766.2±7.42	32564	1.58
PBSSub	15.6±1.48	519.8±5.82	30453	1.55
PBASub	12.5±1.37	486.5±6.79	29567	1.59

homopolyesters may result in lower tensile strength of copolyester than the homopolyesters. The reduced crystallinity of the copolyester PBSA led to an increase in its elongation at break. The elongation at break values of the copolyesters PBSA, PBSSub, and PBASub were 766.2, 519.8, and 486.5%, respectively.

When the molecular weight of the polyester exceeded 4000 g/mol, the degradation rate was independent of the molecular weight [15]. The molecular weights of the three butanediol-polyesters synthesized in this experiment were all about 30 000 g/mol.

3.6. Macro and micromorphology of the polyesters degraded for different time

The left column of Figure 5 shows the macromorphology of the polyesters before enzymatic degradation. Before degradation, the surfaces of the above polyester films were smooth, free of wrinkles, and dark colored. However, with the gradual increase in degradation time, the ester bonds in the polyester molecules were degraded by FsC. This resulted in the discoloration of the polyester films, reduction in the thickness, and then cracking. PBSA and PBSSub with lower initial crystallinity showed notable degradability. The intact samples were degraded into small fragments or even particles that could not be collected. The degradation behavior of PBS was investigated by Jiang *et al*. [50] and Shi *et al*. [30], and the results showed that enzymatic degradation occurred preferentially on the surface of the polyester.

As can be seen from Figure 5, the micromorphologies of the surfaces of the above polyesters were flat and smooth before degradation. The degradation process of PBSA did not result in the appearance of voids or gaps but in the formation of warped lamellae. Some of the lamellae detached and fell off when degradation continued for 8 h. This is also in line with the results of the degradation curve in Figure 4, where PBSA had the shortest degradation time. After 4 h of degradation of PBSSub, petal-shaped lamellae were formed, which disappeared subsequently forming numerous cavities of different sizes. After PBASub had been degraded for 4 h, the gaps on its surface were deepened and lengthened, completely eroding the originally smooth surface of the polyester. This appeared like a mass of pine needles. When the polyester was subjected to 8 h of degradation, deeper grooves appeared on the surface under the pine needle morphology. After 8 h, the degradation rate of PBSSub was larger than that of PBSA, which is in accordance with the slope of curve in Figure 4.

In summary, during the initial stage of enzymatic hydrolysis, FsC preferentially got adsorbed on the surface of the polyesters. This led to the reduction of the thickness of the film while maintaining the same area. In the last stage, enzyme molecules attacked the center of the films, resulting in the formation of cracks and holes as water penetrates the amorphous region, which in turn leads to enhanced enzymatic hydrolysis [39].

3.7. Crystallinity properties of the polyesters degraded over different time intervals

A reduction in the peak intensity and area of the polyester samples was observed by XRD with the increase in degradation time (Figure 6). The diffraction peaks of PBSub exhibited a consistent shape and position with the increase in degradation time. However, the intensity gradually weakened, suggesting a degradation-induced reduction in crystallinity (X_c). The presence of low molecular weight chain segments, oligomers, and water absorption can lead to reduced crystallinity [51, 52]. For the copolyesters of suberic acid, PBSSub and PBASub, the crystallinity decreased to a greater extent. The shape, position, and intensity of the diffraction peaks of PBS, PBA, and PBSA remained unchanged after degradation. This further confirmed that the crystal structure of the samples did not change during the degradation of these polyesters by cutinase [53]. This is consistent with the findings of Bai *et al*. [24]. From the conclusions obtained from ATR-FTIR and XRD, it can be inferred that the degradation of the polyesters by FsC occurs in both the crystalline and amorphous regions.

3.8. Thermodynamic properties of the polyesters degraded over different time intervals

The T_m for PBS was 114.8 °C, and the T_m for both PBA and PBSA was below 100 °C (Table 2). This difference can be due to two main factors. Firstly, as the length of the $–CH_2–$ chain between the ester groups increases, the density of the ester groups in the polyester molecule decreases, the mobility of the polymer molecular chain is enhanced, and the T_m of the polyester decreases. Secondly, the melting point of PBA was 52.7 °C lower than that of PBS. This

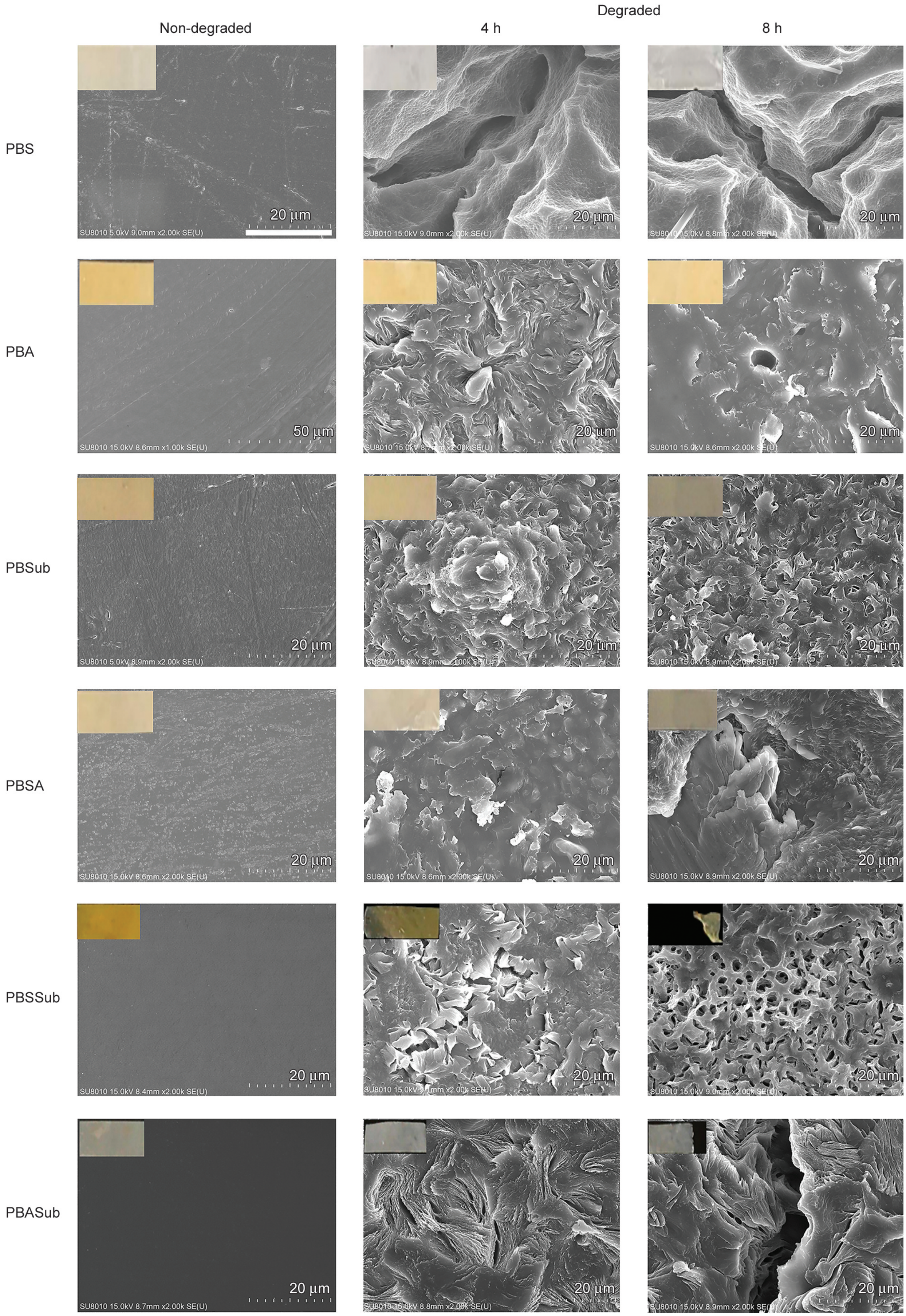

Figure 5. Macro (upper left) and micromorphology of the films degraded over different time intervals.

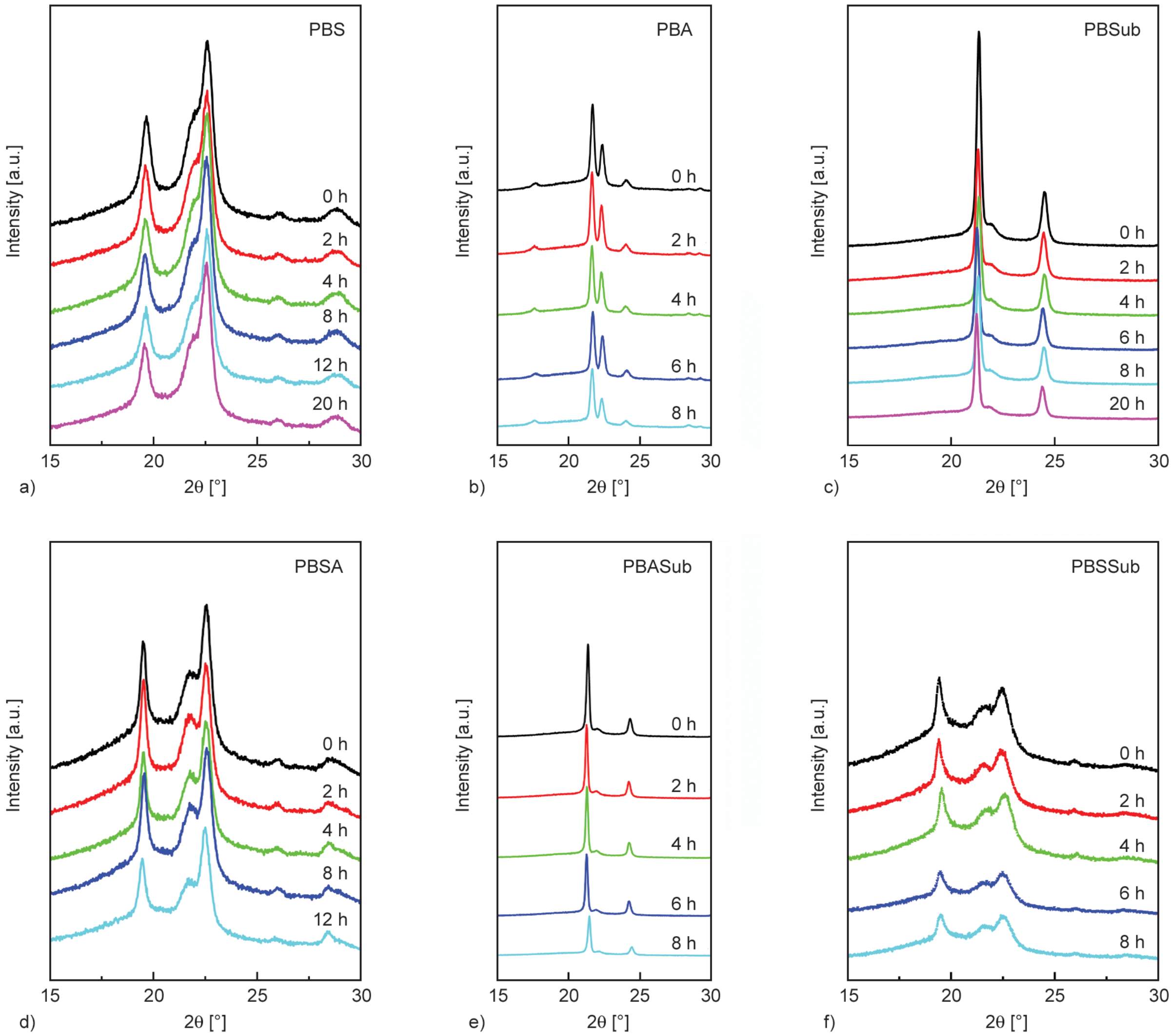

Figure 6. XRD patterns of the polyesters degraded over different time intervals. a) PBS, b) PBA, c) PBSub, d) PBSA, e) PBASub, f) PBSSub.

could be because the acid and alcohol units in PBS have the same number of carbon atoms, resulting in a more regular and ordered molecular chain structure [54]. The earlier research [24, 29, 30] has pointed out that Tm is one of the factors that influence enzymatic degradation. When the Tm of polyester is closer to the temperature of enzymatic degradation, there is an increase in weight loss. The T_m of the three copolyesters was closest to the degradation temperature (37 °C), leading to faster weight loss than that of homopolyester. Thus, PBS with higher T_m and higher difference between the degradation temperature and T_m, experienced slower weight loss.

With the increase in degradation time, there was an insignificant change in the melting points of the six polyesters, while the crystallinity decreased slightly. The recombinant FsC used in this experiment exhibited excellent polyester degradation capacity, degrading both the crystalline and the amorphous regions of the samples, leading to a slightly decreased X_c. Among the six polyesters, PBSA and PBSSub exhibited not only lower melting temperatures but also lower crystallinity. Consequently, the enzymatic degradation rates of these two polyesters were remarkable.

The changes in the thermal decomposition temperatures of the homopolyesters were minimal, while a more significant decrease was observed in the case of three copolyesters with a prolonged degradation time. Notably, the thermal decomposition temperature of PBSSub decreased by about 50 °C after enzyme degradation for 8 h. This can be attributed to the fact that with the progress of enzymatic degradation, the polyester is broken down into oligomers or small molecular fragments. These fragments require less energy for thermal decomposition, consequently lowering the thermal decomposition temperature [55]. Earlier studies have demonstrated that the functional groups present at the chain ends could accelerate the thermal decomposition of polyesters [55, 56]. The cleavage of the ester bonds during enzymatic degradation also leads to the lowering of the thermal decomposition temperature of the polyester. In addition, the changes in the molecular weight and molecular weight distribution of polyester during enzymatic degradation are also responsible for the decrease in the thermal decomposition temperature of polyester [44, 57].

4. Conclusions

The solution polymerization method, using isopropyl titanate as a catalyst and decahydronaphthalene as a solvent, was employed to synthesize the homopolyesters PBS, PBA, and PBSub, and copolyesters PBSA, PBSSub, and PBASub with improved performance. The polymerization was carried out by adjusting the composition of the comonomers 1,4-butanediol and different dibasic acids. It was found that the thermal decomposition temperatures of all the polyesters were higher than 320 °C, meeting the temperature requirements for industrial production. The similar results had been obtained by Bai and coworkers [15, 24]. The crystalline properties of the copolyesters and homopolyesters were similar. The main factors affecting the mechanical properties of polyesters were the number of methylene groups between the ester groups and the crystallinity of the polyester. The introduction of methylene groups led to a decrease in the tensile strength of polyesters. The increase in crystallinity typically led to a decrease in the elongation. PBSA copolyester has the higher tensile strength and the biggest elongation at break. The main factors affecting the biodegradability of the polyesters were the composition of carboxyl monomers, melting temperature, and crystallinity. Polyesters with lower melting temperatures and crystallinity demonstrated faster biodegradation rates. The enzymatic hydrolysis occurred in both crystalline and amorphous regions of the polyesters, revealing the capability of FsC to act in both regions [30]. The enzymatic hydrolysis process occurred on the surface of the entire polyester film, disrupting the polymer structure without changing the crystal structure of the polyesters before and after degradation. PBSA and PBSSub exhibited superior mechanical properties and degradation performance. The complete degradation time of them can be as low as about 10 h compared to commercial grade PBS (24 h) [58]. Control of degradation rates and mechanical properties of copolyester and homopolymer by controlling their chain lengths, making it a promising candidate for applications in many fields such as food packaging, agriculture, apparel, textile field, biomedical, automotive parts and other industries.

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