Characterization and Biodegradability of Poly(butylene adipate-*co*-succinate)/Poly(butylene terephthalate) Copolyester

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SYNOPSIS: Characterization of poly(butylene adipate-*co*-succinate) (PBAS)/poly(butylene terephthalate) (PBT) copolyesters resulting from the intermolecular ester-exchange reaction between molten PBAS and PBT have been analyzed using ¹H-NMR spectroscopy, differential scanning calorimetry, wide-angle X-ray diffraction, and total organic carbon lab analyzer. Using the assignment of proton resonance due to homogeneous and heterogeneous dyads, the average block lengths were investigated over the entire range of copolymer composition. A decrease in melting temperature was observed with the increase of a terephthalate unit in the composition. The result of X-ray diffraction curve matches well with that of average block length and thermal property. When a rich component is crystallized, the poor component is excluded completely in a crystal formation. The biodegradability in copolyesters also depended on the terephthalate unit in the composition and average block length of the aromatic unit. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 593–608, 1999

Key words: PBAS/PBT copolyesters; sequence distribution; block length; biodegradability

INTRODUCTION

Due to the heavy usage of plastics as packaging materials, much public concern in the management of plastic waste has been created. Development of biodegradable polymers for packaging, agricultural mulching films, disposable goods, and similar short-life items is potentially the most promising approach for the waste management of plastics.

Consequently, a recent trend in polymer research is focused on the development of a wide range of biodegradable polymer products with a predetermined lifetime.¹⁻⁶

To date, it has been found that the most attractive biodegradable synthetic polymers are aliphatic polyesters, which are susceptible to microbial attack because of their ester bond in the main chain. But, unfortunately, aliphatic polyesters have poor physical and mechanical properties.^{7–9}

On the other hand, aromatic polyesters^{10,11} possess excellent physical and mechanical properties, compared with aliphatic polyesters, but are very resistant to bacterial or fungal attack and hence do not degrade under environmental conditions. Therefore, in developing biodegradable polymers, it is important to design the polymers to have the desirable combination of mechanical properties and biodegradability.

To obtain biodegradable polymers with useful mechanical properties and satisfactory biodegradability, some researchers¹²⁻¹⁸ have aimed at

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Scheme 1 Preparation and structural formula of PBAS/PBT copolymers.

the synthesis of copolyesters composed of aliphatic and aromatic units. Tokiwa and colleagues^{12,13} have prepared copolyesters by the transesterification reaction between aromatic and aliphatic polyesters and then studied their susceptibility to *rh. delemar* lipase. Witt and colleagues¹⁴ have also studied copolyesters prepared by the polycondensation of aliphatic and aromatic monomers.

In this article, we report on the preparation and characteristics of new biodegradable copolyesters [poly(butylene adipate-*co*-succinate) (PBAS)/ poly(butylene terephthalate) (PBT) copolymer] that were prepared by the transesterification reaction of PBAS and PBT. PBAS is an aliphatic polyester that possesses hydrolyzable units in the main chain. PBT¹⁹ is a widely used aromatic polyester with excellent mechanical properties.

By the transesterification reaction,^{20,21} hydrolyzable linkages of PBAS were added to PBT chains and randomly distributed along them. The average block length of each unit in the PBAS/ PBT copolyester was controlled.

For various prepared copolyesters, the average block length of aromatic and aliphatic units and the degree of randomness of the copolyesters were calculated from the nuclear magnetic resonance (NMR) spectra. Thermal and crystallization behavior, mechanical property, and biodegradability were also investigated with respect to the mole fraction of the aromatic compound.

EXPERIMENTAL

Materials

Polymerization of PBT was conducted by a twostage process in a 1000-mL reaction vessel, equipped with a stainless-steel agitator and an inlet for nitrogen. A condenser with a provision for applying a vacuum was attached through a sidearm. Dimethyl terephthalate was reacted with 1,4-butanediol in the presence of zinc acetate dihydrate (1.5×10^{-4} mol mol⁻¹ dimethyl terephthalate) as a catalyst. The catalyst used is dissolved in ethylene glycol. The reactor was heated to 210°C, and this temperature was maintained for 120 min. After that, antimony trioxide (1.5 \times 10 $^{-6}$ mol g $^{-1}$ oligomer) as a catalyst and trimethyl phosphate $(1.0 \times 10^{-6} \text{ mol g}^{-1} \text{ oligomer})$ as a stabilizer was introduced into the reactor, and the polycondensation reaction was continued 285°C. Then the pressure was reduced to a spec-

	Mixing Condition		PBT Content in Copolymer				Mechanical Property			
Copolymers	Time (min)	Temperature (°C)	Input (wt %)	Analysis by NMR (mol %)	$\begin{array}{l} Inherent\\ Viscosity\\ (dL\ g^{-1}) \end{array}$	Density (g cm ⁻³)	Tensile Strength (kg cm ⁻²)	Elongation (%)	Tear Strength (kg cm ⁻¹)	
PBAS	_	—	0	0.0	0.56	1.257	151	436	199	
T10-0	0	290	10	2.6	0.51	1.260	_	_	_	
T10-10	10	290	10	6.7	0.47	1.261	_	_	_	
T10-20	20	290	10	8.0	0.45	1.261	—	—	—	
T10-30	30	290	10	8.3	0.49	1.261	103	13	69	
T20-0	0	290	20	12.9	0.44	1.271	—	—		
T20-10	10	290	20	14.8	0.45	1.271	_	_	_	
T20-20A	20	260	20	2.9	0.54	1.272		—		
T20-20B	20	270	20	7.5	0.48	1.271	_	_	_	
T20-20C	20	280	20	13.4	0.45	1.271	_	_	_	
T20-20	20	290	20	15.2	0.41	1.271	—	—	—	
T20-30	30	290	20	17.4	0.40	1.271	100	14	16	
T30-0	0	290	30	6.7	0.38	1.279	_	_	_	
T30-10	10	290	30	20.7	0.46	1.277	_	_	_	
T30-20	20	290	30	25.4	0.43	1.278	—	—	_	
T30-30	30	290	30	25.9	0.44	1.282	134	661	95	
T40-0	0	290	40	9.3	0.34	1.288			_	
T40-10	10	290	40	32.8	0.47	1.289			_	
T40-20	20	290	40	33.7	0.45	1.289	—	—	—	
T40-30	30	290	40	35.2	0.42	1.289	101	557	94	
T60-0	0	290	60	18.7	0.51	1.296	_	_	_	
T60-10	10	290	60	44.8	0.56	1.297			_	
T60-20	20	290	60	49.6	0.56	1.297	—	—	—	
T60-30	30	290	60	50.7	0.56	1.296	286	718	137	
T80-0	0	290	80	24.2	0.55	1.309				
T80-10	10	290	80	76.2	0.65	1.310		_		
T80-20	20	290	80	76.0	0.66	1.309	—	—	—	
T80-30	30	290	80	76.9	0.65	1.310	330	447	251	
PBT	_	_	100	100.0	0.77	1.316	503	10	268	

Table I	Mixing	Condition.	Viscosity.	and Mechanical	Property	of PBAS/PBT	Copolymers

ified level. PBAS was prepared similarly with different reaction temperatures (190°C and 250°C) and a different catalyst (titanium tetrabutoxide; 2 × 10⁻³ mol mol⁻¹ diester) by the reaction of aliphatic diester (mixtures of 80 mol % dimethyl succinate and 20 mol % dimethyl adipate) and 1,4-butanediol. Before mixing, the chips were dried for at least 24 h at room temperature under a reduced pressure of 1.0 mm Hg to minimize possible hydrolysis.

Preparation of Copolyesters

Copolyesters of PBAS/PBT were prepared by melt processing due to transesterification in a 500-mL cylindrical tube equipped with an oil bath, an



Figure 1 500 MHz 1 H-NMR spectra (in CDCl₃ with tetramethysilane) of PBAS, PBT, and T20-20 (290°C, 20 min).

agitator, a thermometer, and a vacuum pump. Without the addition of catalyst, PBAS and PBT polymers were simultaneously preheated for 30 min at 290°C under a nitrogen atmosphere. The time when the pressure was applied was taken as 0 min. The reaction was continued for 10, 20, and 30 min. The usual transesterification temperature was 290°C; temperature effects were measured in the range of 260° to 290°C. Pressure was ordinarily 0.2 mm Hg. Copolymers, as shown in Scheme 1, were prepared covering the entire range of PBT contents. However, due to reasons

Symbol of Proton Atom	Chemical Shift (ppm) from Tetramethylsilane									
	PBA ^a	PBS ^a	PBAS ^a	T20-20ª	T80-20 ^b	PBT				
A ₁	2.32	—	2.32	2.32	2.42	_				
A_2	1.66	_	1.67	1.67	1.66	_				
S		2.62	2.63	2.62	2.73	_				
Т	_	_	_	8.09	8.11	$ m 8.09^{a}$ $ m 8.11^{b}$				
X ₁	4.09	4.12	4.14	4.11-4.43	4.17-4.49	$4.22^{\rm a}$ $4.43^{\rm b}$				
X_2	1.69	1.71	1.71	1.71–1.97	1.72-2.02	$1.95^{ m a}\ 1.97^{ m b}$				

Table II Assignments of Proton Signal and Their Chemical Shift in the ¹H-NMR Spectra

^a CDCl₃ (using solvent).

^b CDCl₃/d-TFĂ (70/30 v/v) (using solvent).

to be discussed later, the main focus of attention in this article is on those copolyesters containing <50 mol % terephthalate. Films were obtained by using a heating press.

Measurements

The inherent viscosity of all the copolyesters were measured in dichloroacetic acid with an Ubbelohde viscometer at 25 \pm 0.1°C. Solutions were prepared by sealing the sample and solvent in test tubes and rotating at elevated temperatures until the solution was homogeneous. Densities were measured in a density gradient column at 25 \pm 0.1°C containing a mixture of *n*-heptane and carbon tetrachloride. Tensile properties of films were measured on a universal test machine (Instron 4301) using ASTM D638. Average values for each exposure level were based on tests of eight specimens. The ¹H-NMR spectra were recorded with a Bruker AMX-500 FT-NMR spectrometer (500 MHz) using tetramethylsilane as an internal standard. The samples were dissolved in chloroform-d (CDCl₃) or a mixture of CDCl₃ and trifluoroacetic acid-d (d-TFA) (70/30, v/v). Differential scanning calorimetry measurement was conducted using a Perkin-Elmer DSC 7 analyzer at a constant heating rate of 10°C min⁻¹ from 30° to 300° C for a specimen of \sim 6 mg under a dry nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) patterns were recorded in the reflec-

tion mode using a Rigaku Denki diffractometer with Ni-filtered CuK_{α} radiation. Enzymatic degradation of samples in aqueous medium was performed similarly to the procedure used by Tokiwa and colleagues,⁸ but using *rh. arrhizus* lipase suspension. The reaction mixture was composed of 100 mg of thin film (20–30 μ m), 2.0 mL of 0.2M phosphate buffer solution (pH 7.0), 0.1 mL of 1.0% plysurf, 1.0 mL of enzyme solution (500 IU mL⁻¹ of lipase), and 16.9 mL of distilled water. Also, the composition of 0.2M phosphate buffer solution was as follows: 8.5 g L^{-1} of KH_2PO_4 , 21.75 g L^{-1} of K_2HPO_4 , 33.4 g L^{-1} of $NaHPO_4 \cdot 7H_2O$, and 1.7 g L^{-1} of NH₄Cl. The enzymatic hydrolysis, including a blank test, was conducted at 37 \pm 0.1°C for 8 weeks. The total organic carbon (TOC) dissolved in the reaction mixture after hydrolysis was measured with a TOC lab analyzer (2001, Astro Resources Corp., League City, TX). TOC values of samples were calculated after subtraction from the blank test.

RESULTS AND DISCUSSION

Viscosity and Mechanical Property

Several characteristic properties of PBAS/PBT copolyesters obtained are listed in Table I. The product of polymerization is a mixture of polymer molecules of different molecular weights. There-

	Possible Diester Environment Centered on Butylene Unit (X)		Chemical Shift (ppm)	
Type of Dyads	Structural Unit	Symbol (No.)	\mathbf{X}_1	\mathbf{X}_2
AlAl	$- \underset{X_1 X_2}{\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{COO}} - $	SXS (3)	$\begin{array}{c} 4.12^{\mathrm{a}} \\ 4.17^{\mathrm{b}} \end{array}$	$1.71^{ m a} \ 1.73^{ m b}$
	$\begin{array}{c} -\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-\\ X_1 X_2 \end{array}$	AXA (4)	NS	NS
	$\begin{array}{c} -\text{OOCCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-\\ X_1 X_2 \end{array}$	SXA (7)	NS	NS
	$\begin{array}{c} -OOCCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_$	AXS (6)	NS	NS
AlAr	$\underbrace{-\text{OOCCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}}_{X_1 X_2} - \underbrace{\text{COO}}_{\text{COO}}$	SXT (5)	$4.17^{ m a} \\ 4.23^{ m b}$	$1.81^{ m a} \ 1.83^{ m b}$
	$- \underbrace{\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}}_{X_1 X_2} - \underbrace{\text{COO}}_{X_2 X_2}$	AXT (8)	NS	NS
ArAl	$- \underbrace{\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{COO}}_{X_1 X_2}$	TXS (2)	4.38^{a} 4.44^{b}	$1.86^{ m a} \ 1.88^{ m b}$
	$- \underbrace{\text{COOCH}_2\text{CH}_2$	TXA (9)	NS	NS
ArAr	$- \underbrace{\operatorname{COOCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{OOC}}_{X_1 X_2} - \underbrace{\operatorname{COOCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{OOC}}_{- \underbrace{\operatorname{COOCH}_2\operatorname{CH}_2\operatorname$	TXT (1)	$4.43^{ m a} \\ 4.49^{ m b}$	$1.97^{ m a}\ 2.01^{ m b}$

Table III	Possible Diester	Environment and	Chemical Shift o	f PBAS/PBT	Copolymers
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NS (no splitting): the chemical shift of this sequence was observed in almost the same range as the peak above.

^a $CDCl_3$ (using solvent).

^b CDCl₃/*d*-TFA (cosolvent; 70/30 v/v) (using solvent).

fore, the majority of polymers have a molecular weight distribution. Hence, it is impossible to add the feed weight of polymer as mole % exactly. But, we can determine the analytic composition of copolymers as mole % from the peak assignment of NMR spectroscopy.

The inherent viscosity had a little variation for the different mixing time and temperature, as well as the PBT content in copolyesters. The viscosities of prepolymers, PBAS, and PBT are somewhat higher than those of PBAS/PBT copolymers. It can be seen that the variations of viscosity depend on the PBT content in copolymers, as well as the degree of transesterification between polymers. The values of density are almost the same, even varying mixing time and temperature, but they increase with increasing terephthalate unit in the compositions. The mechanical properties of T60-30 and T80-30 were somewhat higher than those of T10-30, T20-30, T30-30, and T40-30. The % elongation fell down remarkably for T10-30 and T20-30. T30-30 to T80-30 show the better elongation property. Tear strengths of PBAS/PBT copolymers are much lower than that of pure PBAS, except for T80-30 composition.

Sequence Analysis

¹H-NMR spectra (500 MHz) of PBAS, PBT, and T20-20 produced by the transesterification reac-

tion are shown in Figure 1. and the assignments of proton signals in the spectra are listed in Table II. In the spectrum of copolyester, T20-20, several new proton signals with different chemical shifts of butylene unit, which is not observed in the spectra of corresponding homopolymers, appeared, as shown in Figure 1 and Table III. These new signals represent the existence of heterolinkage with different chemical environment of butylene unit in the copolyester. The transesterification reaction between PBAS and PBT will generate nine kinds of butylene units (-X-) in the copolymer, including five homolinkages and four heterolinkages; four of the homolinkages are SXS. AXS, SXA, and AXS, adjacent to the aliphatic unit (S or A) at both sides, one is TXT, adjacent to the aromatic unit (T) at both sides. Four heterolinkages are TXS, TXA, SXT, and AXT, adjacent to the aromatic unit (T) at both sides. Four heterolinkages are TXS, TXA, SXT, and AXT, adjacent to the aliphatic and aromatic units. Fig-



Figure 2 Change of the butylene proton signals of T20-20 (20 min) with mixing temperature.



Figure 3 Change of the butylene proton signals of T20-20 (290°C) with mixing time.

ures 2 and 3 show how the heterolinkage proton signals of T20 copolymer change as mixing temperature and mixing time. The relative intensities of the heterolinkage signals, SXT, TXS, AXT, and TXA, to those of homolinkage signals, are increased with an increase of mixing temperature and mixing time.

It indicates that the amount of heterolinkages resulting from the transesterification is increased gradually, whereas the amount of homolinkages is decreased, because the intermolecular ester– exchange reaction between PBAS and PBT homopolymers proceeds.

Figure 4 also shows the ¹H-NMR spectra with the change of PBT composition ratio in PBAS/ PBT copolymers. With increasing PBT contents in copolymers, the intensities of the PBT-related peaks named as TXT, TXS, TXA, SXT, and AXT increased more strongly than those of the PBASrelated peaks named as SXS, AXA, AXS, and SXA.



Figure 4 Change of the butylene proton signals of PBAS/PBT (290°C, 20 min) copolymers with various PBT contents.

However, no splitting was observed in the proton signals of the butylene units (SXS, AXA, AXS, and SXA) due to succinate and adipate in PBAS because of the overlap of chemical shifts between those two butylene protons. Considering this point of view, we tried to classify four types of new sequences (AlAl, AlAr, ArAl, and ArAr), as shown in Table III. In Table III, the chemical shift assignments for the butylene protons in the copolymers are quite associated with the environment of the proton atoms [i.e., whether aliphatic diester (e.g., succinate, adipate) or aromatic diester (e.g., terephthalate) residue is neighboring the butylene unit]. Chemical shifts due to the butylene protons are diagnostic of their environment and are sufficient to characterize. From the intensity of each proton signal, therefore, we may quantify the changes in sequence length during the transesterification. In discussing the ¹H-NMR spectra, we will use the terms, homogeneous and heterogeneous dyads to describe the sequences where a butylene unit is flanked by either similar or different diester chain residues.

From these results, the sequence distribution was determined from the relative area of ¹H-NMR spectra on the basis of peaks previously discussed. Each fraction of dyads (f_{AIAI} , f_{AIAr} , f_{ArAI} , and f_{ArAr}) was calculated as the proportion of the integrated intensities of AlAl, AlAr, ArAl, and ArAr signals.

$$f_{\text{AlAl}} = \frac{A_{\text{AlAl}}}{A_{\text{AlAl}} + A_{\text{AlAr}} + A_{\text{ArAl}} + A_{\text{ArAr}}}$$
(1)

$$f_{\rm AlAr} = \frac{A_{\rm AlAr}}{A_{\rm AlAl} + A_{\rm AlAr} + A_{\rm ArAl} + A_{\rm ArAr}}$$
(2)

$$f_{\rm ArAl} = \frac{A_{\rm ArAl}}{A_{\rm AlAl} + A_{\rm AlAr} + A_{\rm ArAl} + A_{\rm ArAr}} \qquad (3)$$

$$f_{\rm ArAr} = \frac{A_{\rm ArAr}}{A_{\rm AlAl} + A_{\rm AlAr} + A_{\rm ArAl} + A_{\rm ArAr}} \qquad (4)$$

where A_{AlAl} , A_{AlAr} , A_{ArAl} , and A_{ArAr} represent the area integrated for butylene proton peaks (i.e., $A_{AlAl} = A_{SXS} + A_{AXA} + A_{SXA} + A_{AXS}$, $A_{AlAr} = A_{SXT} + A_{AXT}$, $A_{ArAl} = A_{TXS} + A_{TXA}$, and $A_{ArAr} = A_{TXT}$. Using these values, the probability of finding unit (P), the average block length ($\overline{L_n}$), and the degree of randomness (B) were calculated by the well-known process suggested by Yamadera and Murano,¹⁵ and collected in Table IV.

Bovey and Tiers²² have also suggested that the sequence distribution can be described by Bernoulli statistics.²⁰ Figure 5 shows the plot of fractions of dyads of hetero-unit, $f_{AlAr} + f_{ArAl}$, vs. PBT mole fractions of the copolymers in a series of mixing time. The solid line in Figure 5 represents a theoretical curve based on Bernoulli statistics. The change from a block copolymer to a random with the lapse of time is shown. The fraction of dyads of the hetero-unit also increases as PBT contents in copolyester increase. Thus, we would define the fraction of dyads of hetero-unit, $f_{AlAr} + f_{ArAl}$, as the extent of transesterification (T_E);

	PBT	Fraction of Dyads Centered on Butylene Unit (X)			Mole Fraction of Diester		Probability of Finding Unit		Average Block Length		Degree of
Copolymers	(mol %)	f_{AlAl}	$f_{\rm AlAr} + f_{\rm ArAl}$	$f_{\rm ArAr}$	$P_{\rm Al}$	$P_{\rm Ar}$	$P_{\rm AlAr}$	$P_{\rm ArAl}$	Ln _{Al}	$\mathrm{Ln}_{\mathrm{Ar}}$	(B)
											_
PBAS	0.0	1.000	0.000	0.000	1.000	0.000	0.000	0.000	_	_	
T10-0	2.6	0.971	0.060	0.024	0.974	0.026	0.003	0.115	324.6	8.7	0.12
T10-10	6.7	0.920	0.027	0.053	0.933	0.067	0.015	0.203	68.8	4.9	0.22
T10-20	8.0	0.892	0.056	0.053	0.920	0.080	0.030	0.345	33.1	2.9	0.38
T10-30	8.3	0.857	0.112	0.031	0.913	0.087	0.061	0.645	16.3	1.6	0.71
T20-0	12.9	0.847	0.043	0.110	0.869	0.131	0.025	0.163	40.5	6.1	0.19
T20-10	14.8	0.822	0.060	0.118	0.852	0.148	0.035	0.203	28.3	4.9	0.24
T20-20A	2.9	0.956	0.010	0.034	0.961	0.039	0.005	0.128	194.0	7.8	0.13
T20-20B	7.5	0.915	0.023	0.063	0.926	0.074	0.012	0.153	82.1	6.5	0.17
T20-20C	13.4	0.786	0.070	0.144	0.821	0.179	0.042	0.195	23.6	5.1	0.24
T20-20	15.2	0.807	0.079	0.113	0.847	0.153	0.047	0.259	21.3	3.9	0.31
T20-30	17.4	0.747	0.151	0.102	0.822	0.178	0.092	0.425	10.9	2.4	0.52
T30-0	6.7	0.923	0.014	0.063	0.930	0.070	0.008	0.100	133.5	10.0	0.11
T30-10	20.7	0.749	0.079	0.173	0.788	0.212	0.050	0.186	20.0	5.4	0.24
T30-20	25.4	0.679	0.132	0.189	0.745	0.255	0.089	0.259	11.3	3.9	0.35
T30-30	25.9	0.633	0.210	0.157	0.738	0.262	0.141	0.400	7.0	2.5	0.54
T40-0	9.3	0.888	0.023	0.089	0.900	0.100	0.013	0.116	77.7	8.7	0.13
T40-10	32.8	0.609	0.126	0.266	0.671	0.329	0.094	0.191	10.7	5.2	0.28
T40-20	33.7	0.574	0.164	0.263	0.565	0.344	0.125	0.238	8.0	4.2	0.36
T40-30	35.2	0.502	0.276	0.222	0.640	0.360	0.216	0.384	4.6	2.6	0.60
T60-0	18.7	0.792	0.049	0.159	0.816	0.184	0.030	0.135	33.0	7.4	0.17
T60-10	44.8	0.475	0.129	0.396	0.540	0.460	0.120	0.140	8.4	7.1	0.26
T60-20	49.6	0.464	0.193	0.343	0.561	0.439	0.172	0.219	5.8	4.6	0.39
T60-30	50.7	0.411	0.232	0.358	0.526	0.474	0.220	0.245	4.5	4.1	0.47
T80-0	24.2	0.715	0.063	0.222	0.747	0.253	0.042	0.124	23.8	8.1	0.17
T80-10	76.2	0.188	0.088	0.724	0.232	0.768	0.189	0.057	5.3	17.5	0.25
T80-20	76.0	0.191	0.125	0.684	0.253	0.747	0.246	0.083	4.1	12.0	0.33
T80-30	76.9	0.164	0.140	0.696	0.234	0.766	0.299	0.091	3.3	10.9	0.39
PBT	100.0	0.000	0.000	1.000	0.000	1.000	0.000	0.000		_	

Table IV Sequence Distribution and Degree of Randomness of PBAS/PBT Copolymers

$$T_{E} = \frac{A_{\text{AlAr}} + A_{\text{ArAl}}}{A_{\text{AlAl}} + A_{\text{AlAr}} + A_{\text{ArAl}} + A_{\text{ArAr}}} = f_{\text{AlAr}} + f_{\text{ArAl}}$$
(5)

Depending on eq. (5), we notice the extent of transesterification increases with blending time in Figure 5.

Denoting an aliphatic diester residue by subscript Al and an aromatic diester residue by subscript Ar, the average block lengths $(\overline{L_{nAl}} \text{ and } \overline{L_{nAr}})$ are given by eq. (6)

$$\overline{L_{nAl}} = \frac{2P_{Al}}{T_E} = \frac{1}{P_{AlAr}} \text{ and } \overline{L_{nAr}} = \frac{2P_{Ar}}{T_E} = \frac{1}{P_{ArAl}} (6)$$

where $P_{\rm Al}$ is mole fraction of the succinate (or adipate) unit, $P_{\rm Ar}$ is mole fraction of the terephthalate unit, $P_{\rm AlAr}$ is probability of finding an



Figure 5 Relationship between fraction of dyads and PBT mole fraction of PBAS/PBT copolymers with mixing time at 290°C.

aliphatic unit next to an aromatic unit, and $P_{\rm ArAl}$ is probability of finding an aromatic unit next to an aliphatic unit.

Values of the average block length should lie between 1 and infinity, where a value of 1 corresponds to a strictly alternating copolymer, and a value of infinity pertains to a simple mixture.²¹ In Figure 6, the values of the aliphatic block length have a tendency to decrease obviously as mixing time increases, regardless of PBT content in the copolymers. The average block length of the rich component is longer than that of the poor component. The aliphatic and aromatic block lengths in copolymers vary with PBT composition ratios (as shown in Figure 6). This implies that the aromatic block length increases remarkably with increasing PBT composition ratios in copolymers.

The degree of randomness (B) can be represented as the degree of transesterification and defined by the summation of two probabilities: $P_{AlAr} + P_{ArAl}$.¹⁵ For random copolymers, *B* is 1. If *B* is <1, each unit in copolymers may exist in blocky form, and the value of *B* is 0 in mixture of homopolymers. If *B* becomes 2, it means an alternating distribution.

Figure 7 shows the degree of randomness *vs.* PBT composition ratio in copolymers varying mixing time. The values of randomness in copolymers were increased with increasing mixing time and became close to unity, which means random distribution. From the results, it is proved that more mixing time allows more transesterification. The degree of randomness also varies with PBT composition ratios in copolymers. However, we could not find any special trends between the degree of randomness and PBT composition ratio.



Figure 6 Relationship between block length and PBT mole fraction of PBAS/PBT copolymers with mixing time at 290°C. (a) Aliphatic unit. (b) Aromatic unit.



Figure 7 Relationship between the randomness and PBT mole fraction, with mixing time at 290°C.

Thermal Property¹¹

Figure 8 shows the DSC curves of PBAS/PBT copolymers with PBT composition ratios in copolymers. In Figure 8(a), the copolymer, T10, molten for 0 min shows three endothermic peaks: a small one, T'_{m1} , in the region of 50°–60°C, which comes from the melting of poly(butylene adipate) crystal; a larger one, T_{m1} , at ~ 100°C from the melting of poly(butylene succinate)²² crystal in the PBAS copolymer; and another small one, T_{m2} , in the region of 220°–230°C from the melting of PBT. In Figure 8(e), the copolymer, T60, molten for 30 min, shows the endothermic peak in the region of 180°–190°C, which seems to be attributed to the melting of the PBT crystal.

After 20 min in T10–T30 copolymers, the PBT endothermic peaks no longer exist. Considering all results of average block length (Figure 6) and thermal analysis (Figure 8), presumably a critical block length is needed for components to crystal-lize.^{17,18} Therefore, we can suggest that the minimum block length for crystal formation may be ~ 4 , regardless of the aliphatic and aromatic units, in PBAS/PBT copolymers.

Figure 8(a) also shows the DSC curves of the PBAS/PBT copolymer, T10, with mixing time. With increasing mixing time, the maximum melting point, T_{m1} , of the PBS-related peak gradually

moves to low temperature and becomes less intense. Similar results are obtained for other compositions of the PBAS/PBT copolymers. With increasing mixing time, the maximum melting point, T_{m2} , of the PBT-related peak in copolymers T60 and T80 moves to a low temperature and becomes weak.

Figure 9 shows the heat of fusion (ΔH_f) with mixing time for PBAS/PBT copolymers. Here, ΔH_{f1} and ΔH_{f2} are obtained from the area of aliphatic $(T'_{m1}$ and $T_{m1})$ and aromatic (T_{m2}) melting peak, respectively. The values for ΔH_{f1} are mostly decreased with increasing mixing time and PBT composition ratio in copolymers. The values for ΔH_{f2} are also decreased with increasing mixing time, but increased with PBT content in copolymers. As a conclusion, the position change of melting peak, the diminution of heat of fusion, and the disappearance of melting peak can be explained as the transesterification process between PBAS and PBT as described earlier.

Crystallization Behavior and Crystal Lattice Spacing

Further information on the crystallization behavior is obtained by means of a WAXD diffractogram. Figure 10 shows the diffraction patterns of PBS, PBAS, and PBT. Samples have been annealed by isothermal crystallization for 24 h after quenching (temperature: 5°C). Unfortunately, the crystal reflections of PBAS and PBS lie quite close to each other.⁹

In the PBAS copolymer, the peak at a diffraction angle of 19.5° is assigned for the (020) plane, and peaks at diffraction angles of 21.6°, 22.5°, and 28.7° are assigned for the (021), (110), and (111) planes, respectively. In the PBT polymer,^{17,19} the peak at a diffraction angle of 16.1° is assigned for the 011 plane. Peaks at diffraction angles of 17.4°, 20.7°, 23.5°, and 25.2° are assigned for the (010), (101), (100), and (111) planes, respectively.

Figure 11 shows WAXD patterns with mixing time for PBAS/PBT copolymers annealed for 24 h. If two copolymers have been heat-pressed for 0 min, crystal patterns of the two components coexist, as shown in Figure 11(a). In Figure 11(b), copolyesters of T10 and T20 confirm only PBSrelated crystals, whereas T60 and T80 make only PBT-related crystals. Also, the crystal intensities of copolymers become weaker with an increase in minor component, and only an amorphous halo is found at T40.



Figure 8 DSC curves of PBAS/PBT copolymers with mixing time at 290°C. (a) T10. (b) T20. (c) T30. (d) T40. (e) T60. (f) T80.

Figure 12 shows the crystalline lattice spacings¹⁰ of the PBAS/PBT copolyester (mixing time: 30 min) with PBT composition ratios. With the increase of PBT composition ratio in copolymers, crystal patterns were obviously divided into two classes. It can be proved that, when a rich component is crystallized, the poor component is excluded completely in a crystal formation. The phenomenon can be explained as a change of average block length in the copolymer. As shown in Figure 6, it can be seen



Figure 9 Relationship between heat of fusion and mixing time in PBAS/PBT copolymers at 290°C. (a) Aliphatic unit. (b) Aromatic unit.



Figure 10 WAXD patterns of PBS, PBAS, and PBT polymer.

that average block length decreases with increasing transesterification and approaches 4. Accordingly, the poor component with a shorter average block length than critical average block length, in which the chain is able to crystallize, might be excluded completely in a crystal formation. The crystal lattice transition also occurred for the copolymers in the range of 35–50 mol % PBT.

Enzymatic Degradation^{7,8,12,13}

Figures 13 and 14 show the biodegradability for PBAS, PBT, and PBAS/PBT copolyesters. The % biodegradability was calculated as follows:

- % Biodegradability
 - $= \frac{\text{Actual TOC during a certain time}}{\frac{\text{period in number of ppm} \times 100}{\text{Calculated TOC that is biodegraded}}}$ (7) totally in the number of ppm

In the case of T20, as shown in Figure 13, the biodegradabilities were primarily increased with the increase of mixing time and temperature, whereas the values for the average block length had a tendency to decrease gradually as the mixing time and temperature increased (as described



Figure 11 WAXD patterns of annealed PBAS/PBT copolymers with mixing time. (a) 0 min. (b) 20 min.

in Table IV). Accordingly, it strongly suggests that the biodegradability of the copolyester depends on the average block length of an aromatic unit related to the degree of transesterification between two polymers.

The biodegradabilities in PBAS/PBT copolymers also decreased with increasing PBT composition ratio (as shown in Figure 14). On the basis of these results, it can be concluded that biodegradability relies on the PBT content in copolyester and the aromatic average block length.

CONCLUSIONS

Transesterification, crystallization behavior, and biodegradability were investigated over the entire



Figure 12 Crystalline lattice spacing $(d_{hkl}$ -spacing) of PBAS/PBT copolymers (290°C, 30 min).

range of PBT composition ratios of PBAS/PBT copolyesters.

The degree of transesterification between PBAS and PBT was increased with increasing mixing time and temperature. The melting point depressions in blend systems occurred with increasing minor components, and the melting and crystalline peaks related to minor components disappear with increasing mixing time. It can be seen that a critical block length is necessary for components to crystallize.



Figure 13 Biodegradability of PBAS/PBT copolymers, T20. (a) Mixing temperature. (b) Mixing time.



Figure 14 Biodegradability with PBT composition ratios in PBAS/PBT copolymers.

PBAS/PBT copolymers also seem to form the crystal composed of only a rich component in the copolymers. Biodegradability of the copolymers was increased gradually as the transesterification reaction proceeded. Also, it was concluded that the biodegradability depends on the aromatic average block length and PBT composition ratios in the copolymers.

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