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Thermoplastic Elastomers Derived from Bio-Based Monomers

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ABSTRACT: Series of copolyesters based on poly(propylene succinate) (PPS) and poly(butylene succinate) (PBS), which can be produced from biological feedstock, and postconsumer poly(ethylene terephthalate) (PET) were synthesized with the aim of developing sustainable materials, which combine the mechanical properties of high performance elastomers with those of flexible plastics. The aliphatic polyesters were synthesized by the catalyzed two-step transesterification reaction of dimethyl succinate, 1,3-propanediol, and 1,4-butanediol followed by melt reaction with PET in bulk. The content of PET segments in the polymer chains was varied from about 10 to 100 wt % per 100 wt % PPS or PBS. The effect of the introduction of the PET segments on the structure, thermal, physical, and mechanical properties was investigated. The composition and structure of these aliphatic/aromatic copolyesters were determined by NMR spectroscopy. The thermal properties were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The level of crystallinity was studied by means of DSC and wide-angle X-ray scattering. A depression of melting temperature and a reduction of crystallinity of copolyesters with increasing content of PET segments were observed. Consequently, the tensile modulus and strength of copolyesters decreased, and the elongation at break increased with PET content in the range of 10−50 wt %. Thus, depending on PET content, the properties of copolyesters can be tuned ranging from semicrystalline polymers possessing good tensile modulus (380 MPa) and strength (24 MPa) to nearly amorphous polymer of high elongation (∼800%), and therefore they may find applications in thermoplastics as well as elastomers or impact modifiers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39815.

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INTRODUCTION

Polyesters are produced in billions of pounds annually worldwide and find use as fibers, films, coatings, and in food and beverage packaging. The vast majority of these engineering polyesters are based on aromatic starting materials, which are produced from petro-chemical sources. There is an increasing demand for novel bio-based materials that can reduce the widespread dependence on fossil-based chemicals. Biodegradable plastics and bio-based polymers from renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable and eco-efficient products that can compete and capture market currently dominated by products exclusively based on petroleum feedstock.[1,2] Two factors that make bio-based polymers attractive are (a) environmental and economic concerns associated with waste disposal and (b) rising cost of petroleum production resulting from the depletion of the most easily accessible reserves. The examples of biopolymers based on renewable resources include aliphatic polyesters, polysaccharides, and proteins. The challenges for the development of biopolymers include that such polymers should be processable on existing equipment, stable during storage and usage, and degrade when disposed off after their intended lifetime. The preferred bio-based polymers are those that degrade into safe low molecular weight compounds in a relatively short time period.[3–5] Because the polymers produced from biological monomers tend to be linear and aliphatic, there is a tendency for such materials to possess relatively low moduli and melting temperatures, traits that could limit their applications. Conversely, the use of such bio-based polymers, with their inherently low processing temperatures, could make them ideal candidates for drug delivery and composites carrying biological cargoes, as these additives tend to be highly sensitive to high temperature exposure.

Aliphatic polyesters, such as poly(propylene succinate) (PPS) and poly(butylene succinate) (PBS), are increasingly become available from monomers, which are commercially produced from renewable sources.[6] These polymers are recognized as environmental friendly, biodegradable, and biocompatible materials, which translate into a wide range of applications including biomedical, adhesives, insulating materials, and consumer products. However, aliphatic polyesters such as PBS, PPS, and polycaprolactone (PCL) typically have a narrow range of physical and mechanical properties that limits their applications.[7] The combination of aromatic and aliphatic units in the same polyester chain has been considered as an attractive approach to obtain novel products encompassing biodegradability and high performance properties.[8,9]

In this article, we report the characterization and properties of copolyesters produced from high molecular weight aliphatic polyesters (PBS and PPS) and postconsumer poly(ethylene terephthalate) (PET). NMR spectral data are used to determine the amount of transesterification and formation of random or block structures. Thermal properties of the polymers were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Mechanical evaluation was carried out to determine their tensile and flexural strength, modulus, elongation at break, and adhesion strength on various substrates. The morphology of the copolyesters is described and the physical and elastic properties of these polymers are interpreted in terms of their unusual two-phase domain structure. The elastomers were synthesized by the equilibrium melt transesterification of PBS with PET, resulting in molecules in which crystallizable PBS segments and amorphous PET segments are randomly distributed along the backbone. The PBS sequences were found to crystallize and exhibit properties similar to the characteristics of the thermoplastic elastomers. The stress–strain behavior of these polymers is discussed in terms of their morphology, and thermal analysis, and X-ray diffraction results are presented.

EXPERIMENTAL

Materials

Dimethyl succinate (DMS), 1,4-butanediol (BD), 1,3-propanediol (PD), and tetrabutyl titanate were purchased from Aldrich and used without further purification. Postconsumer PET was obtained from industry sources.

Polymer Blend

Polyester blends were prepared using a DSM MICRO 5 twin-screw extruder (L/D 8; 50 rpm rotor speed). The extruder temperature was set for each experiment, which varied between 180 and 280°C and a residence time of 3 min.

Polymer Synthesis

PBS and PPS homopolyesters were prepared by polycondensation reactions. A typical reaction is: DMS (292.28 g, 2 mol) and BD (378.5 g, 4.2 mol), and tetrabutyl titanate (100 mg) were charged into a 1000 mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The trans-esterification reaction was carried out at 110–190°C under a nitrogen flow for a period of 1 h with continuous removal of methanol. The polycondensation reaction was continued at 190–215°C under vacuum (500–200 mtorr). The high viscous melt formed was cooled down to 150°C and discharged into water. The solid mass formed was washed with water and dried under a reduced pressure at 50°C for 72 h.

Synthesis of PBS-PET Copolymers

In a similar reaction to the PBS homopolymer (described earlier), except that calculated amounts of postconsumer PET was added to the reactor after high molecular weight PBS or PPS was formed and reaction continued under reduced pressure while temperature increased to 290°C during 1 h. The reaction temperature was kept around 290°C until all the PET pellets disappeared to form a clear homogenous melt. The melt was cooled down to 150°C and discharged.

Measurements

Solution ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 600 MHz NMR spectrometer using deuterated solvents. The thermal properties of the polyesters were evaluated with a METTLER TOLEDO DSC822e at a heating rate of 20°C min^{-1}. All samples analyzed by DSC were as synthesized, unless otherwise mentioned. TGA was conducted with a TA Instruments Q500 at a heating rate of 10°C min^{-1}.

Molecular weights and molecular weight distributions of the polyesters and copolyesters were determined relative to narrow polystyrene standards using an Agilent 1200 series liquid chromatography system equipped with refractive index and variable wavelength detector and two American Polymer Standards (Mentor, OH) linear bed GPC columns. Chloroform was used as the eluent.

Tensile and flexural tests were performed according to ASTM D-638 and ASTM D-790 standards, respectively. All the tests were carried out at ~25°C and an average of at least five test specimens were reported herein. Tensile tests were conducted on rectangular specimens (140 × 12.7 × 3.2 mm^3) made by injection molding using an Instron 5566 Universal testing machine at a crosshead speed of 40 mm min^{-1}. Three point static flexural tests were carried out using 125 × 12.7 × 3.2 mm^3 bar and a 50 mm span length at a crosshead speed of 5 mm min^{-1}.

Melt flow indices (MFIs) of the polymers were determined at 150°C with a melt flow indexer (model D7054, Kayeness, Honey Brook, PA). A 3.7 kg plunger was used in all of the measurements.

RESULT AND DISCUSSION

Structure of Polyesters

High molecular weight PBS and PPS were synthesized from DMS and the corresponding diols in the presence of a typical titanium complex as catalyst (Figure 1). The copolyesters PBS-*co*-PPS produced from various mole ratios of BD and 1,3-propandiol (PD) in the feed were semicrystalline with very low rates of crystallization. The plot of melting temperatures (T_m) of the PBS-*co*-PPS versus composition of glycols in the feed shows a minimum around 38°C for 25 mol % BD and 75 mol % PD (see Figure 2). The compositions of glycols moieties

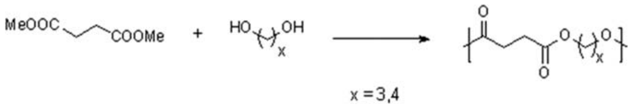


Figure 1. Scheme of the synthesis of PPS ($x = 3$) and PBS ($x = 4$) polyesters.

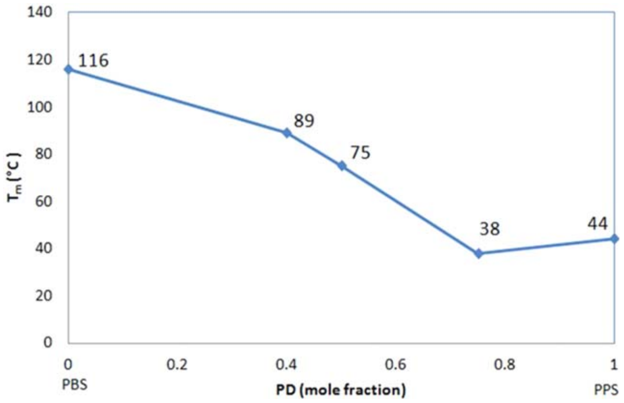


Figure 2. Melting temperature (T_m) vs. mole fraction of glycols for PBS-*co*-PPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the copolymers were determined by ^{1}H-NMR spectroscopy, which showed retained diol ratios slightly different than their compositions in the feed; the higher boiling point BD was retained in the polymer background preferably. Figure 3 shows the ^{1}H-NMR spectrum of a copolyester with a PD : BD ratio of ~70 : 30. The reaction temperature in all the above cases was kept below 215°C to minimize the amount of degradation and discoloration of the products.

Reactive blending is an alternative way to make copolymers and have been used to produce block copolyesters.[10] A mixture of PBS and PPS homopolymers (1 : 1 w/w) were blended in a micro blender/extruder at various temperatures and the resulting materials were studied for formation of copolyesters. DSC analysis was used to determine the influence of thermal treatment on the thermal transition of polymer blends and copolymers. Figure 4 shows the heating thermograms of PBS/PPS blends extruded at different temperatures. Polymer blends extruded at temperatures below 260°C show two distinct T_m at 115 and 45°C corresponding to PBS and PPS homopolymers, respectively, while the blends extruded at 260 and 280°C show only one melting transition from the melt of copolyester PBS-*co*-PPS. The crystalline melting peak of PBS-*co*-PPS becomes weaker and wider and T_m decreases as the extrusion reaction temperature increases. Mixtures of PPS/PET with various PET contents were extruded at 280°C. The extruded products showed glass transition temperature (T_g) around −30°C from the aliphatic portion of the copolymer and no crystalline melting was detected. Although reactive extrusion is a convenient way to make copolyesters, sever discoloration was observed in all cases because of relatively low thermooxidative stability of aliphatic chains and exposure to air at high temperature during extrusion.

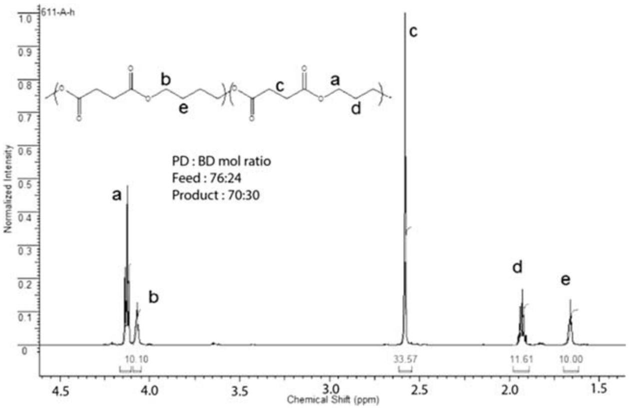


Figure 3. ^{1}H-NMR spectrum of PBS-*co*-PPS.

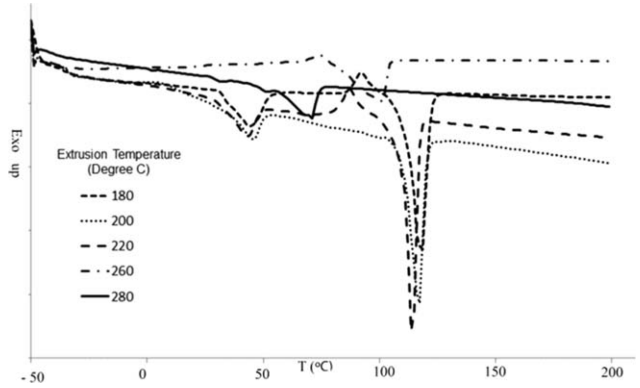
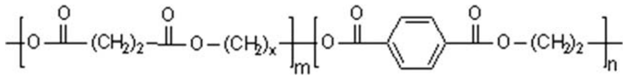


Figure 4. DSC thermograms of reaction blended PBS/PPS at various temperatures (180–280°C).

Melt copolymerization of aliphatic polyesters with PET in a batch reactor under controlled atmosphere; however, produced materials with much lower discoloration and better properties (Figure 5). Two copolyesters made from PPS and PET (weight ratio of PPS : PET 80 : 20 and 70 : 30) were amorphous yellow to brown soft materials at room temperature. The inherent viscosity (η_{inh}) of the PPS and its copolyesters were calculated from the relative viscosity, which were obtained from the flow time of the pure solvent and polyester solution in chloroform at 20°C and at the concentration of 0.5 g dL^{-1} using an Ubbelohde viscometer. The η_{inh} of PPS, PPS-PET-20, and PPS-PET-30 was 0.21, 0.40, and 0.88 dL g^{-1}, respectively (Table I). Among polymers of comparable molecular weight, rigid polymers possessed higher viscosity values than their flexible counterparts. Addition of PET segments to flexible PPS backbone was shown to have a similar effect. Copolyesters produced from PBS and various amounts of PET produced materials with relatively high melt viscosities. PET was added at the final stage of polymerization after high molecular weight PBS was formed and temperature increased to near 300°C for complete transesterification. The PET copolyesters possessed high molecular weights, as indicated by GPC data, and inherent viscosity, which was measured between 0.52–0.89 dL g^{-1}. Molecular weights of the samples using a polystyrene determined calibration curve suggested M_n values in the range of $2.31 \times 10^4 - 3.45 \times 10^4$ Da with corresponding polydispersity values of 2.07–2.63 for PBS-*co*-PET copolyesters. GPC analysis indicated lower molecular



$$\left[O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_x \right]_m \left[O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2 \right]_n$$

Figure 5. Structure of PPS-*co*-PET ($x = 3$) and PBS-*co*-PET ($x = 4$) copolymers.

Table I. Solution Properties of Polyesters

Polyester	η_{inh}[a] (dL g^{-1})	M_n ($\times10^{-4}$)	M_w ($\times10^{-4}$)	M_w/M_n[b]
PBS	0.53	2.32	4.55	1.96
PPS	0.21	0.39	1.42	3.67
PBS/PPS (50 : 50)	0.29	0.40	2.16	5.37
PBS/PET-10	0.84	3.24	6.77	2.09
PBS/PET-20	0.52	3.23	6.68	2.07
PBS/PET-30	0.67	2.47	5.56	2.25
PBS/PET-40	0.89	3.47	7.22	2.09
PBS/PET-50	0.73	2.31	5.50	2.38
PBS/PET-60	0.74	2.39	6.29	2.63
PBS/PET-100	0.73	2.52	5.68	2.26
PPS/PET-20	0.40	1.60	3.46	2.17
PPS/PET-30	0.88	2.31	5.84	2.53

[a] Measured at a concentration of 0.5 g dL^{-1} in $CHCl_3$ at 20°C.
[b] Molecular weights were measured by GPC.

weight values for most PPS and PPS copolymers, which were in agreement with their relatively lower inherent viscosities (Table I).

Proton and carbon NMR spectroscopies were conducted under ambient temperature in $CDCl_3$ solution to study microstructure of PBS-*co*-PET copolyesters. The compositions of the copolyesters were determined from the ^{1}H-NMR spectra using the relative intensities of the proton peaks arising from succinate (PBS) and benzene ring (PET) and the results were in close agreement with the theoretical values (Table II). Addition of PET after formation of high molecular weight PBS and increasing the reaction temperature $>T_m$ of PET (250–260°C) presumably provides condition, which favors transesterification and formation of copolymer with longer PBS and PET block size. The size of the PET block and distribution of the aliphatic moieties in the final copolymer can be deduced from the degree of randomness determined by ^{1}H-NMR (Figure 6). Degree of randomness (b) has been calculated for PBS-*co*-PET copolyesters by comparing the resonance peaks of the aliphatic protons of butylene and ethylene units according to a method reported in Ref. 11. In this method the intensities of the peaks associated with methylene protons (for butylene (B) or ethylene (E) units) adjacent to succinic (S) or terephthalic (T) moieties were used to estimate probability of the presence of different structural units in the backbone of the copolyesters. Highest degree of randomness (1) was obtained for PBS-PET-100 and other copolyesters showed lower values. This value is equal 1 for random copolymers and close to zero for block copolymers. In a similar approach to study composition of the copolyesters, the ^{13}C NMR spectrum of PBS-PET-100, which contains nearly equal amounts of PBS and PET structural units, reveals two peaks at 62–63 ppm for ethylene carbon and two peaks at 64–65 ppm for $—O—CH_2—$ residue of butylene group. These peaks show nearly equal integration leading to the similar conclusion that PBS-*co*-PET-100 was a random copolyester. Carbonyl groups of terephthalate (165 ppm) and succinate (172 ppm) also split as a result of three types of dyads in each case (ETE, ETB and BTE, BTB; BSB, BSE and ESB, ESE). Nonprotonated aromatic carbons (135 ppm) appear to be more sensitive to neighboring groups and show multiple split.[12]

Table II. Molecular Properties of Polyesters

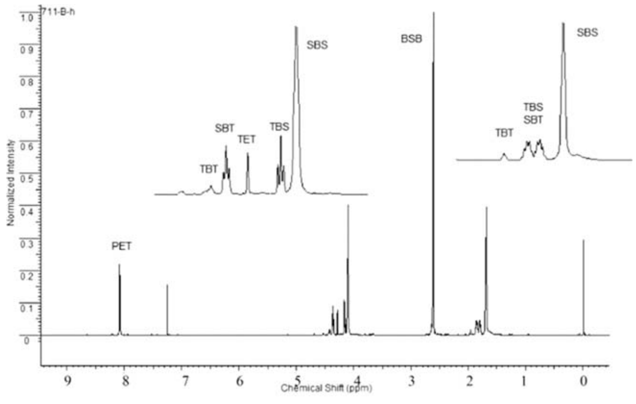
	PET (mol %)		
	Feed	^{1}H-NMR	b
PBS	0	0	–
PBS/PET-10	8.2	7.8	0.64
PBS/PET-20	14.9	12.9	0.88
PBS/PET-30	21.2	19.9	0.72
PBS/PET-40	26.3	23.5	0.81
PBS/PET-50	30.9	28.3	0.85
PBS/PET-60	34.6	30.7	0.90
PBS/PET-100	47.4	46.2	1.00

PPS, PBS, and their copolyesters with PET were readily soluble in halogenated solvents such as, chloroform and chlorobenzene and sparingly in ketones and xylenes.

Physical and Thermal Properties

All the PBS-PET copolyesters of this study were yellow colored as a result of thermal sensitivity of aliphatic polyesters to high temperature. PBS-*co*-PET were injection moldable materials and formed flexible fibers from melt. The times of crystallization for the copolyesters decreased with PET content and vary from few seconds to several hours. PPS homopolyester exhibits a low degree of crystallinity as compared to PBS with a $T_m \sim 38°C$, crystallizing sufficiently slow that crystallization was not detected even at 1°C min^{-1} cooling rate in the DSC experiment. The slow crystallization behavior of PPS as compared to PBS, which crystallize around 75°C during cooling cycle is attributed to the reduced symmetry of the repeating unit of the polymer and especially to the presence of the propylene segment having an odd number of carbon atoms. PBS-*co*-PPS copolyesters are semicrystalline with melting temperatures between those of the neat homopolymers PBS and PPS. Figure 2 presents the relationship between the T_m and composition of PBS-*co*-PPS. Crystallization behavior of these polyesters depends on their molecular weight and the lower molecular weight samples of PPS and PBS-*co*-PPS show higher crystallinity. This is because of the higher chain mobility in the case of low molecular weight polymers, which results in easier and faster crystallization. PPS-*co*-PBS of molecular weight 4000, 8000, and 12,000 g mol^{-1} were prepared that show crystallization temperature around 25°C.

Aromatic polyesters, such as PET, have higher T_m values and superior thermal and mechanical properties as compared with fully aliphatic polyesters. PBS-*co*-PET copolymers with PET content ranging from 10 to 100 wt % PET per 100% PBS were studied for their physical and mechanical properties. Copolymers of PBS and PPS with various PET contents showed lower T_m as compared with their homopolymers. Two copolyesters



T = terephthalate; S = succinate; B = butyl; E = ethyl

Figure 6. ^{1}H NMR spectrum of PBS-*co*-PET.

PPS-PET-20 and PPS-PET-30 (numbers indicates part PET per 100 part PPS) showed T_g's at −25 and −18°C, respectively and no crystalline melting point was detected.

Table III lists the T_g and T_m determined by DSC and Figure 7 shows first heating curve for PBS-*co*-PET copolyesters. As expected, the addition of PET lowered the T_m and crystallinity of PBS copolyesters evidenced by decreasing enthalpies of melting and disappearance of crystallization signals during heating and cooling curves. Figure 8 illustrates a systematic melting point depression with increasing the PET unit content, showing a pseudoeutectic behavior[13]; this can be clearly seen by shifting and broadening of melting transition on DSC curves (Figure 7). Two T_g's have been detected in samples of PBS-*co*-PET on their first heating cycle, which appeared at temperatures between the T_g of either PBS (−31°C) and PET (68°C). T_{g1} located between −25 and −30°C for PBS-*co*-PET-10 increased with PET content and reach 4°C for PBS-*co*-PET-100. Second transition (T_{g2}), however, seems to remain at ~35–40°C and became undetectable and merged with the melting transition of the copolyesters in samples with high PET content. Upon second heating following rapid cooling of samples first glass transition (T_{g1}) remained nearly unchanged while T_{g2} and crystalline melting transition completely disappeared in all copolyesters. In amorphous random copolymers, T_g is usually a monotonic function of composition, which can be predicted by Fox equation,[11] however, in this case presence of two T_g's is assumed to be characteristic of two new phases. These phases arise from transesterification between PBS and PET and formation of new blocks consist of four structural units separated by short blocks of PBS and PET segments. T_{g1} and T_{g2} were assigned to the new phases rich with aliphatic segments and aromatic segments, respectively. Disappearance of T_{g2} in second heating cycle cast some uncertainty about its origin, which requires further investigation. The variation of T_{g1} with the content of PET units along the copolyesters is plotted in Figure 9.

Thermal stability has been well known to play an important role in the practical application of each polymer, for instance, the processing temperature and processing temperature window are controlled by the thermal stabilities of the polyesters and copolyesters. Thermal stabilities of the copolyesters were determined by TGA under two different atmospheres of nitrogen and air. It was found that the thermal decomposition of copolymers occurs in a single stage with the maximum rate of decomposition at 380°C. Polyesters start to decompose above 300°C with 5% of the initial weight being lost around 336–369°C under nitrogen and air and only 5% remaining at 600°C (Table III). Aliphatic polyesters, such as PBS, are known to be less stable as compared with aromatic ones at high temperature. The results, however, show similar TGA traces for all samples regardless of their PET compositions. It has been shown that for copolymer, step-wise thermal degradation of the individual building blocks may merge into one-step style of thermal degradation, and the temperature at maximum thermal degradation rate would be an average between two individual temperatures of maximum degradation rates attributable to corresponding homopolymers.[14]

Table III. Physical Properties of Polyesters

	DSC 1st heating						DSC cooling		TGA (°C)^a	
Polyester	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	T_{c1} (°C)	ΔH_m (Jg^{-1})	ΔH_c (Jg^{-1})	Tc_2 (°C)	ΔH_c (Jg^{-1})	N_2	Air
PBS	−31	-	116	89	85.3	7.2	74	70.7	365	355
PPS	−30	-	40	-	28.9	-	-	-	340	336
PBS/PPS (50 : 50)	−36	-	75	58	31.4	1.1	-	-	341	338
PBS/PET-10	−26	30	98	84	47.9	3.1	43	57.2	360	358
PBS/PET-20	−30	38	85	72	29.3	0.6	-	-	359	355
PBS/PET-30	−20	35	65	-	40.7	-	-	-	366	369
PBS/PET-40	−21	-	46	-	21.1	-	-	-	363	365
PBS/PET-50	−16	-	50	-	5.3	-	-	-	365	361
PBS/PET-60	−18	-	49	-	3.4	-	-		364	366
PBS/PET-100	4	-	49	-	2.3	-	-		368	362
PPS/PET-20	−25		-	-	-	-	-		344	339
PPS/PET-30	−18		-	-	-	-	-		351	349

^{a} Reported for 5% weight loss.

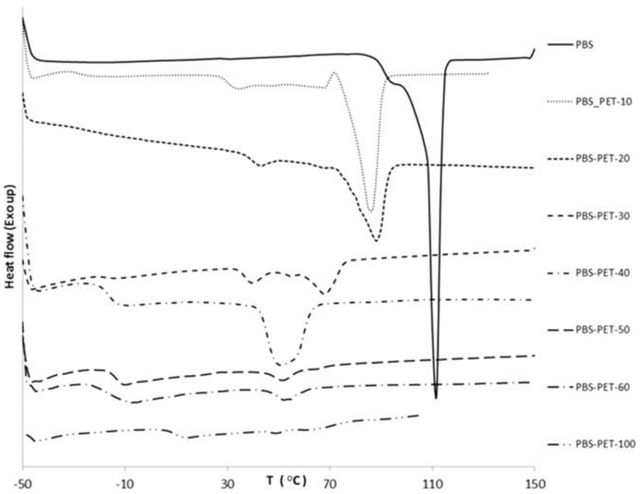


Figure 7. DSC thermograms for PBS and PBS-*co*-PET samples.

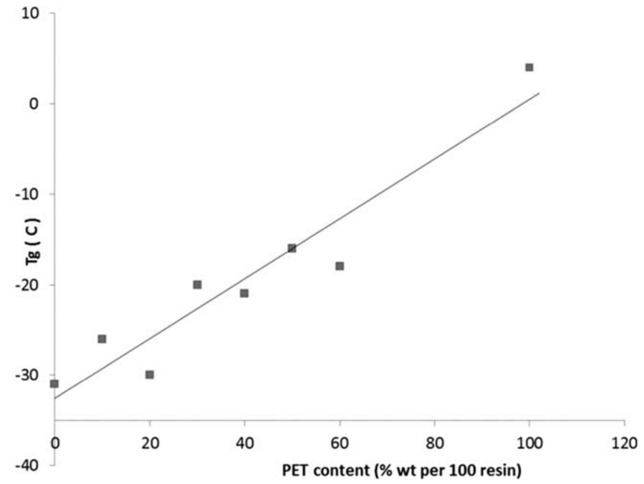


Figure 9. Glass transition (T_{g1}) vs. PET content for PBS-*co*-PET samples.

The MFIs of neat PPS, PBS and their copolymers with PET were determined, and the results are shown in Table IV. The neat PPS had higher MFI than PBS and PBS-*co*-PET under the measurement conditions. This can be partially because of the low T_m value of PPS. PBS-*co*-PET samples exhibited high viscosities and low MFI values ranging from 19 to 51 g × 10 min^{-1} under the processing conditions.

Mechanical Properties

Table IV presents mechanical properties and Figure 10 shows the tensile stress–strain curves for PBS and PBS-*co*-PET copolymers. The results indicate that presence of PET improves ductility and elastic properties while lowers tensile strength. Values of tensile modulus and tensile strength decreased with the incorporation of PET component, exhibiting a tendency similar to that of heat of melting, T_m and crystallinity. This trend apparently reaches a minimum value for PBS-*co*-PET-60 and increases in the case of PBS-*co*-PET-100. The homopolymer PBS, which has the highest degree of crystallinity, exhibits the maximum tensile strength, 24 MPa, modulus of 635 MPa and lowest elongation at break (12%). Elongation at break increases with PET content to 800% for PBS-*co*-PET-60 and starts to decrease afterward, which agrees with their tensile and modulus behavior. Similar trend in mechanical properties of copolyesters of PET with PBS has been reported by Muñoz-Guerra and coworkers[15]; they synthesized copolyesters of PET/PBS with molar composition of PET : PBS from 90 : 10 up to 50 : 50, and showed that the elastic modulus and tensile strength of the copolymers decreased with the content of PBS, whereas, on the contrary, the elongation at break increased.

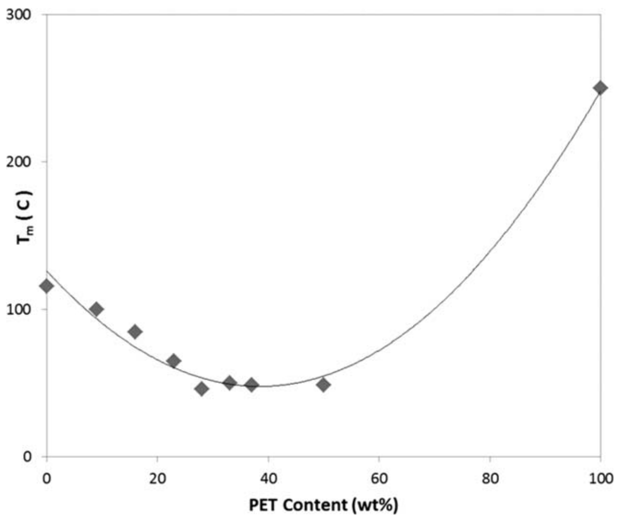


Figure 8. Melting temperature (T_m) vs. PET content for PBS-*co*-PET samples.

X-Ray Diffraction Study

The morphology of PET, PBS, their composites and blends have been widely studied by X-ray diffraction techniques.[16–22] In this work the microstructure of neat PBS, postconsumer PET and their copolymers was investigated with SAXS and WAXS. Figures 11 and 12 show the SAXS and WAXS patterns of homo- and copolyesters crystallized at 100°C. Both PBS and PET show broad peaks, indicating fairly well lamellar stacks in these homopolymers. The PET pattern is characterized by five prominent reflections at 5.5, 5.1, 4.2, 3.9, and 3.4 Å.[12] The WAXS pattern for PBS is characterized by two reflections at 4.6 and 4.0 Å, which are essentially the same pattern regarding both spacing and relative intensities shared by copolyesters with low content in PET, revealing that the similar crystal structure of PBS must be retained in polyesters.[9,13,15] High concentration of PET in copolyesters elastomers makes long range ordered structures nearly diminish and peaks become almost undetectable. PBS-*co*-PET-10 and −40 samples exhibit almost the same diffraction patterns and positions as PBS. However, the intensity of the peaks decreases with PET content indicating that the concentration of crystalline phase is reduced with formation of amorphous random copolyester phase.

The elastomers were synthesized by the equilibrium melt transesterification of PBS and PET, resulting in molecular structures in which crystallizable PBS and PET segments along with amorphous PBS-*co*-PET segments are randomly distributed along the backbone. In agreement with DSC results, copolyesters

Table IV. Mechanical and Melt Flow Properties of Polyesters[a]

Polyester	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	MFI[b] g 10 min^{-1}
PBS	635 (±70)	24 (±5)	12 (±6)	30 (±6)
PBS/PET-10	302 (±30)	22 (±4)	22 (±8)	19 (±10)
PBS/PET-20	267 (±51)	11.6 (±0.8)	39 (±17)	58 (±8)
PBS/PET-30	144 (±25)	8.1 (±2.4)	187 (±23)	51 (±19)
PBS/PET-40	39 (±12)	4.7 (±1.2)	430 (±40)	17 (±4)
PBS/PET-50	7 (±3)	1.4 (±0.5)	283 (±74)	34 (±7)
PBS/PET-60	6 (±1.5)	2.3 (±0.2)	800 (±120)	34 (±2)
PBS/PET-100	12 (±0.5)	3.8 (±2.1)	325 (±135)	33 (±6)

[a] Minimum of 5 samples were tested.
[b] 150°C, 3.7 kg.

containing up to 50% of PET produced clear diffraction scattering distinctive of semicrystalline material, whereas samples with higher PET content show profiles characteristic of amorphous material. Unlike some block copolymers such as polystyrene-polybutadiene-polystyrene (SBS) or elastomeric polyurethanes (TPUs) the crystalline regions of the copolyesters are not well defined, but rather form continuous and highly interconnected.[23] Similar to the glassy regions in the SBS or some TPUs; however, the crystalline or pseudo crystalline domains act as physical crosslinks, which lead to the formation of a three-dimensional network structure. As a result of physical crosslinking they undergo plastic deformation when heated above the T_m of the crystalline region and show characteristic of elastomers when cooled down again and new crosslinks are established. This means that they show elastic properties that are similar to those of elastomers, while allowing for repeat deformation and recovery as known from thermoplastics.[24] The copolyesters did not show any discrete reflection characteristic of crystalline PET homopolymer suggesting that the size of PET blocks in copolyesters is too short to form a distinct crystalline phase.

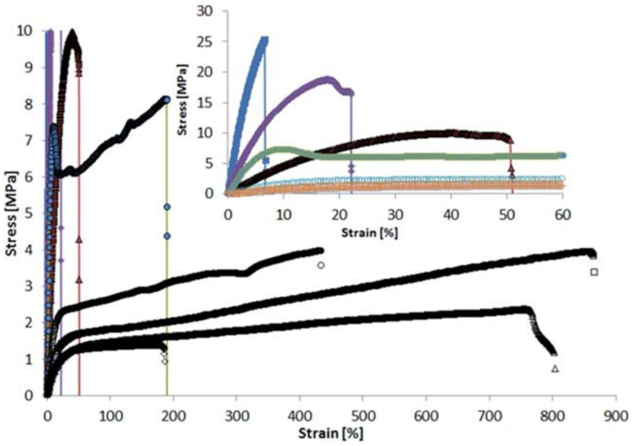


Figure 10. Stress–strain curves for PBS (■), PBS-*co*-PET-10 (◆), PBS-*co*-PET-20 (▲), PBS-*co*-PET-30 (●), PBS-*co*-PET-40 (○), PBS-*co*-PET-50 (◇), PBS-*co*-PET-60 (Δ), and PBS-*co*-PET-100 (□) copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

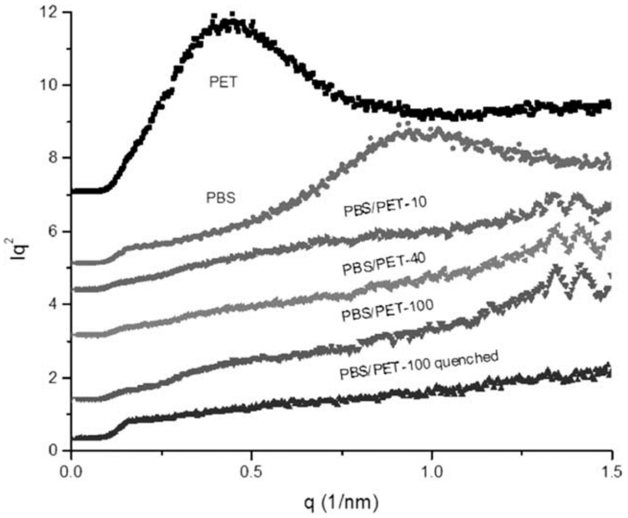


Figure 11. SAXS difractograms of PBS, PET, and PBS-*co*-PET copolymers.

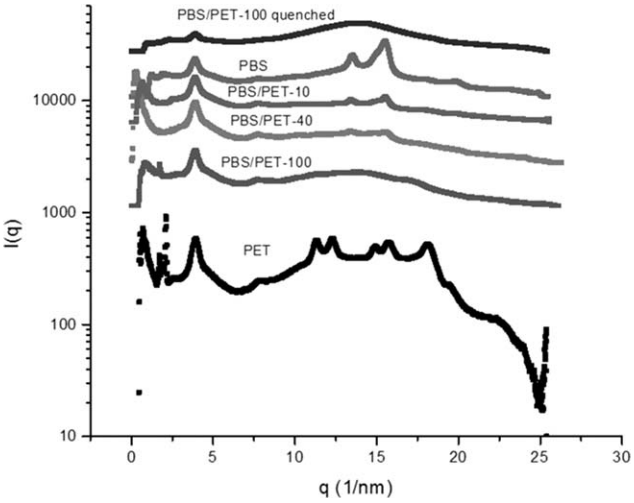


Figure 12. WAXS difractograms of PBS, PET, and PBS-*co*-PET copolymers.

CONCLUSIONS

Two sets of polyesters derived from dimethyl esters of succinic acid, PD, and BD were melt-reacted with postconsumer PET to obtain copolyesters in two step polycondensation reaction. The resulting copolyesters have compositions close to those used in the feed and all have a mixture of random and segmented structures with degree of randomness estimated around 0.7. All the synthesized polyesters are melt processable and displayed enhanced solubility as compared to PBS and PET in halogenated solvents such as chloroform. The incorporation of PET units up to 50 : 50 (PBS : PET) increased the glass-transition temperature of PBS-*co*-PET while decreased their melting point. Mechanical moduli and tensile strength of copolyesters showed a sharp decrease with PET content and reached a minimum at the composition of 100 : 60 (PBS : PET). Elongation at break, on the other hand, showed an opposite trend and increased up to 800% showing a behavior similar to thermoplastic elastomers. The crystallinity and crystallization rate of the copolyesters decreased with increasing PET content indicated by DSC and X-ray diffraction study. X-ray diffraction patterns revealed that the crystalline structure of PBS is preserved for most of the semicrystalline copolyesters whereas no sign of the crystalline phase entirely made of the aromatic PET was observed.

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