Multiblock copolymers consisting of polyolefin and polyester blocks: 1. Thermal and mechanical behaviour

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Three -(AB)$_n$- type multiblock copolymers, consisting of soft segments of polyolefin and hard segments of poly(ethylene terephthalate) (PET), were synthesized through melt polycondensation by reacting a hydrogenated hydroxy-terminated polybutadiene and dimethyl terephthalate with a stoichiometric excess of ethylene glycol. The synthesized copolymers are not soluble in toluene, *m*-xylene, *m*-cresol or phenol/tetrachloroethane because of the very different solubility behaviour of the two incompatible blocks. These copolymers exhibit two clear melting temperatures as determined by differential scanning calorimetry and two glass transition temperatures as observed by dynamic mechanical analysis. The melting temperatures of the polyolefin and PET blocks increase with increasing weight fraction of the corresponding block. The glass transition temperatures of the polyolefin and PET blocks are around −17°C and 79°C, respectively. As the PET weight fraction is decreased to 15%, its glass transition temperature (tan δ peak) becomes broader because of interference by the melting transition of the polyolefin block.

(Keywords: multiblock copolymer; polyolefin; polyester)

INTRODUCTION

Segmented block or multiblock copolymers consisting of alternating soft and hard segments offer many possibilities for tailor-made copolymers by varying block length and composition. Examples of these engineering thermoplastic elastomers include Hytrel and Arnitel, commercial products of du Pont and Akzo Plastics, respectively. Such copolymers containing poly(butylene terephthalate) (PBT) and poly(tetramethylene glycol) blocks exhibit an extraordinary combination of elasticity, toughness, low-temperature flexibility and strength[1]. Details of synthesis and characterization of several poly(ether ester)s have been reported in the literature[1–4]. The crystallization rate of such copolymers is extremely important, particularly in high-speed processes such as injection moulding. PBT-based thermoplastic elastomers crystallize rapidly, whereas those based on PET crystallize slowly[5]. The properties of PET-based copolymers can be improved by adding a nucleating agent[6]. More recently, segmented polyurethanes have also been investigated by Cuve *et al.*[7,8]. These polyurethanes were synthesized by reacting the diisocyanates with varying amounts of 1,4-butanediol (chain extender) and hydrogenated hydroxy-terminated polybutadiene (HHTPB, soft segment).

Blending of incompatible polymers has been the subject of intense research activity in both academic and industrial laboratories. The performance properties of incompatible blends depend on the morphology and interactions between the components. Addition of a block copolymer as a compatibilizer for incompatible polymers has been widely used to modify the morphology and improve the mechanical properties of the resulting blends. The aim of this work was to prepare segmented block copolymers of polyolefin and PET with controlled composition and block lengths. The thermal and mechanical behaviour of HHTPB–PET segmented polyesters is described in this paper. Polymeric emulsions consisting of high-density polyethylene (HDPE) and PET resins have been prepared using these copolymers as compatibilizers. The morphological, thermal and mechanical behaviour of these solid emulsions will be reported separately[9].

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and ethylene glycol were used to synthesize the hard segments (PET block) of the multiblock copolymers. Hydrogenated hydroxy-terminated polybutadiene (HHTPB, trade name Polytail H, M_W 2000, average functionality $\bar{f}_{n,\mathrm{HHTPB}}$ 1.8) was obtained from Kennedy & Klim Inc. to produce the soft segments. Calcium acetate hydrates and antimony trioxide were used as catalysts for the multiblock copolymer synthesis. 1,1,2,2-Tetrachloroethane, phenol, *m*-xylene and *m*-cresol were used as solvents in the solubility tests. All chemicals used, except HHTPB were obtained from Aldrich Chemical Co.

Synthesis of multiblock copolymers

Three multiblock copolymers with different weight ratios of soft to hard blocks were prepared in a 250 ml

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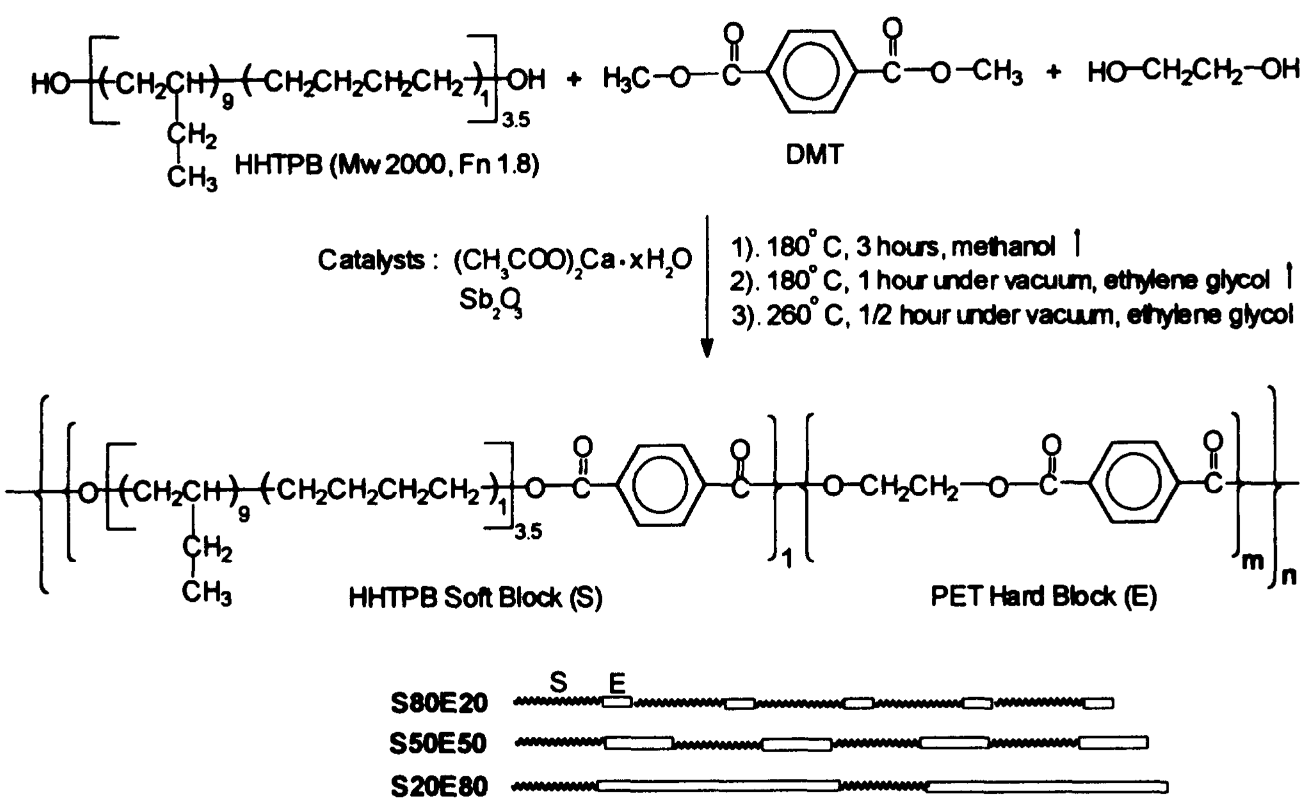

Scheme 1

Table 1 Recipes for melt polycondensation

Ingredient (g)	S80E20	S50E50	S20E80	PET
HHTPB	80	50	20	–
DMT	20	50	80	100
Ethylene glycol	20	40	70	100
$Ca(CH_3COO)_2 \cdot xH_2O$	0.5	0.5	0.5	0.5
Sb_2O_3	1.0	1.0	1.0	1.0

round-bottomed flask equipped with a three-necked 24/40 glass joint, a condenser and a receiver. A motor-driven stainless steel blade inserted vertically through the three-necked joint served as the stirrer. A no. 5 rubber stopper, with a punched hole at the centre, was used as an adaptor between the 24/40 glass joint and the stirring shaft. A heating mantle filled with sea sand was employed as the heat source. A thermometer was inserted into the sea sand near the bottom of the flask for monitoring temperature.

An outline of the synthesis is given in *Scheme 1*. In a typical batch, HHTPB and DMT at a weight ratio of 80/20, 50/50 or 20/80, a stoichiometric excess of ethylene glycol (more than twice the required molar amount of DMT) and catalysts [$Ca(CH_3COO)_2 \cdot xH_2O$ and Sb_2O_3] were heated at 180°C. Initially, the condenser was inserted vertically on top of the three-necked joint for effective refluxing. During reflux, the mixture was mechanically stirred and nitrogen gently purged through the joint with its side-arm tilted upward. The recipes for the different polymerizations are listed in *Table 1*. The copolymers are coded S80E20, S50E50 and S20E80 to represent the weight ratio of HHTPB to DMT in the reaction mixture. The methanol from the ester-exchange reaction was condensed and collected in a receiver. When no further methanol could be condensed (typically after 3 h), the side-arm of the joint was placed downward and the vertical condenser switched to a horizontal position. Ethylene glycol was then distilled off under vacuum using an aspirator pump. The vacuum port was located in a joint between the condenser and the receiver. In about an hour, no further ethylene glycol was collected. The aspirator pump was then replaced by a mechanical pump to generate higher vacuum. The temperature was slowly raised to 260°C under vacuum with stirring reduced to a lower rate to prevent excessive heating of the rubber stopper due to friction. The receiver was cooled with a mixture of dry ice and ethanol to drive the reaction to equilibrium. While the amount of ethylene glycol collected decreased with time, the melt viscosity (hence, molecular weight of the polymer) increased gradually, as indicated by a decrease in the rotational speed of the mechanical stirrer. When the viscosity of the polymer melt became too high, the motor was turned off to prevent overheating. The shaft was then rotated momentarily by hand and a heat gun used to drive the residual condensate into the receiver. The melt polycondensation reaction was continued for 30 min after the motor was turned off. After removing the heating mantle, the flask was allowed to cool slowly to room temperature under vacuum. The polymer foam appeared homogeneous with no macroscopic phase separation and adhered strongly both to the glass wall and to the stainless steel shaft. The flask had to be broken to collect the polymer.

Characterization

Square sheets (120 mm × 120 mm × 1.4 mm) of the multiblock copolymers were prepared by compression moulding (Carver Laboratory Press, Model 30 TON, Fred S. Carver Inc.) of the polymers at 260°C and 20 000 psi (137.8 MPa) for 10 min. The samples were then cooled to room temperature in about 30 min. The square sheets were cut into dog-bone shaped specimens according to ASTM-638 IV. The gauge length of the specimens was 30 mm. Tensile properties of the copolymers were measured using an Instron at a crosshead speed of 2 mm min^{-1}.

Dynamic mechanical properties were measured using a dynamic mechanical analyser (d.m.a., Perkin–Elmer DMA 7) in parallel plate mode with the upper plate (and probe) moving up and down at a frequency of 1 Hz. Tablet samples (diameter 10 mm, thickness 1.4 mm) were deformed under constant stress (static stress 900 Pa, dynamic stress 80% of static stress). Mercury (onset melting point −38.9°C) and indium (onset melting point 156.6°C) were used as two standards for d.m.a. temperature calibration. The temperature was calibrated at the onset of melting by observing the sharp drop in storage modulus or probe displacement during controlled heating at 5°C min^{-1} with helium purging. The samples were programme heated from room temperature to about 5°C above the melting point, which is indicated by a dramatic decrease in storage modulus or increase in tan δ. The samples were cooled to −50°C and then reheated to a maximum of 300°C. The heating and cooling rates were 5°C min^{-1}. The glass transition temperature (T_g) is reported in this paper as the tan δ peak observed in the second heating curve in order to erase any effects of thermal history during sample preparation.

A differential scanning calorimeter (d.s.c., Perkin–Elmer DSC 7) was used to determine the melting temperature (T_m) and the heat of fusion (ΔH) of HHTPB, PET and the copolymers. Temperature calibration was performed with nitrogen purging using mercury and indium (ΔH 28.4 J g^{-1}) as standards. In all cases, samples were heated from −50 to 300°C at 10°C min^{-1}, cooled to −50°C at 10°C min^{-1} and reheated at the same rate for the second or third scan. The peak position and the area under the peak of the endotherms for the second or third heating scan were recorded as T_m and ΔH, respectively.

RESULTS AND DISCUSSION

Synthesis of multiblock copolymers

The characterization data of the synthesized multiblock copolymers as well as HHTPB and PET are summarized in *Table 2*. Calibrated weight ratios of HHTPB to PET blocks in the copolymers are based on the assumption that there was no loss of HHTPB or DMT during polymerization due to low volatility. Stoichiometric balance of reacting groups is obtained in the condensation reaction after the excess of ethylene glycol is distilled off under reduced pressure. The number of repeat units of PET block per HHTPB block is denoted as *m* (see *Scheme 1*). The values of *m* are calculated from the charged HHTPB/DMT weight ratios. For the S80E20 multiblock copolymer, for example, the charged HHTPB/DMT weight ratio is 80/20 = 4 (see *Table 1*). Thus the charged HHTPB/DMT molar ratio is $(80/\bar{M}_{\mathrm{n,HHTPB}})/(20/\bar{M}_{\mathrm{n,DMT}}) = 0.388$, where $\bar{M}_{\mathrm{n,HHTPB}}$ and $\bar{M}_{\mathrm{n,DMT}}$ are number-verage molecular weights of HHTPB (2000 g mol^{-1}) and DMT(194 g mol^{-1}), respectively. Because some DMT molcules are incorporated into the soft (S) block and others into the hard (E) block (see *Scheme 1*) the weight fractions of the soft and hard blocks are different from those of the HHTPB and DMT charged. The value of *m* is calculated by:

$$m = \frac{\dfrac{W_{\mathrm{DMT}}}{\bar{M}_{\mathrm{n,DMT}}}\bar{f}_{\mathrm{n,DMT}} - \dfrac{W_{\mathrm{HHTPB}}}{\bar{M}_{\mathrm{n,HHTPB}}}\bar{f}_{\mathrm{n,HHTPB}}}{\dfrac{W_{\mathrm{HHTPB}}}{\bar{M}_{\mathrm{n,HHTPB}}}\bar{f}_{\mathrm{n,HHTPB}}} \qquad (1)$$

where $\bar{f}_{\mathrm{n,HHTPB}}$ and $\bar{f}_{\mathrm{n,DMT}}$ are number-average functionalities of HHTPB (1.8) and DMT (2.0). After calculating the value of *m*, the weight fraction of soft (W_{Sblock}) and hard (W_{Eblock}) blocks can be calculated as

$$W_{\mathrm{Sblock}} = \frac{M_{\mathrm{Sblock}}}{M_{\mathrm{Sblock}} + M_{\mathrm{Eblock}} \times m} \qquad (2a)$$

and

$$W_{\mathrm{Eblock}} = \frac{M_{\mathrm{Eblock}} \times m}{M_{\mathrm{Sblock}} + M_{\mathrm{Eblock}} \times m} \qquad (2b)$$

where M_{Sblock} and M_{Eblock} are formula weights per repeat unit for S (2124 g per repeat unit) and E (192 g per repeat unit) blocks, respectively. *Table 2* shows that for both S50E50 and S20E80 the respective weight ratio of HHTPB/DMT is close to that of HHTPB/PET (48.9/51.1 and 19.8/80.2, respectively). For S80E20, however, the weight ratio of HHTPB/DMT (80/20) is slightly different from that of HHTPB/PET (85.0/15.0). The density of the copolymers increases with increasing PET weight fraction, as expected.

The molecular weights of the synthesized copolymers could not be determined due to lack of a suitable solvent.

Table 2 Characterization data for HHTPB, PET and synthesized multiblock copolymers

Property	HHTPB	S80E20	S50E50	S20E80	PET
m in $\text{-[-(HHTPB)}_l\text{-(PET)}_m\text{-]}_n\text{-}$[a]	–	2.1	11.4	48.4	–
HHTPB/PET (wt/wt%)	100.0/–	85.0/15.0	48.9/51.1	19.8/80.2	–/100.0
Density (g cm^{-3})[b]	0.89	0.91	1.06	1.19	1.34
$T_{\mathrm{g,HHTPB}}/T_{\mathrm{g,PET}}$ (°C)[c]	–24/–	–18/–[d]	–17/79	–18/79	–/100
$T_{\mathrm{m,HHTPB}}/T_{\mathrm{m,PET}}$ (°C)	75/–	68/245	68/250	64/257	–/258[f]
$\Delta H_{\mathrm{HHTPB}}/\Delta H_{\mathrm{PET}}$ (J g^{-1})	38/–	24/7	13/27	5/53	–/74[g]

[a] The value of *m* is the number of repeat units of PET relative to HHTPB block. The value of *n*, which is related to the overall molecular weight of the multiblock copolymer, was not determined

[b] The densities were measured at room temperature in a calibrated test tube using 100% ethanol as the medium

[c] Glass transition temperatures were determined from the tan δ peaks of d.m.a. curves

[d] T_g of the PET block could not be determined due to overlap with T_m of the HHTPB block

[e] T_m values determined from the melting peaks of d.s.c. curves

[f] T_m of 252°C was observed for commercial PET (polyester 7352, Eastman Kodak Inc.)

[g] ΔH of 47 J g^{-1} was obtained for commercial PET (polyester 7352)

The average functionality of the HHTPB used is 1.8 according to the manufacturer. The presence of monofunctional HHTPB molecules will prevent copolymer chains from further propagation. The formation of a crosslinked network due to a small fraction of tri- or tetrafunctional HHTPB molecules cannot be excluded. The functionality distribution of HHTPB significantly affects the properties of the synthesized multiblock copolymers. Quirk and Kim[10] have reviewed the synthesis of linear and star block copolymers by living polymerization. Numerous examples of the preparation of functionalized polymers have been recently reported[11–15]. However, a detailed analysis of functionality distribution was only reported by Estrin *et al.*[16] for hydroxyoligobutadiene, which is a precursor of HHTPB. Mono-, di- and trifunctional molecules were found in the oligomer ($\bar{M}_w/\bar{M}_n \sim 1.10$) with number-average functionality of about 2.0. The content of the difunctional fraction did not exceed 60%. With a functionality of 1.8, the fractions of non-, mono-, di-, and trifunctional oligomers ($\bar{M}_n$ 2150–2170) were reported to be 0.6, 33.3, 51.3 and 14.5%, respectively. Transmetallation and free-radical centres were suggested as possible mechanisms of functionality distribution during living polymerization. Formation of crosslinked multiblock copolymers cannot be avoided if there is a significant number of trifunctional molecules in the HHTPB.

The synthesized copolymers are not soluble in common solvents because of the very incompatible nature of HHTPB and PET blocks. Solvents tested include *m*-cresol, refluxing toluene and *m*-xylene, and mixtures of phenol/tetrachloroethane (50/50 and 40/60 wt% at 80°C). Toluene and *m*-xylene are good solvents for HHTPB but not for PET, while *m*-cresol and phenol/tetrachloroethane are good solvents for PET but not for HHTPB. Intrinsic viscosities of the copolymers could not be determined because of the unavailability of a suitable solvent. The extracted amount of unincorporated HHTPB (nonfunctional polyolefin) in refluxing *m*-xylene was too low for measurement. S80E20 and S50E50 are good for film formation, as inferred from the thin scraps and the uniform square sheets of the compression moulded samples. However, S20E80 has poor film properties. The sample was slightly yellowish and brittle after compression moulding.

Both crosslinking structure and the different solubility behaviour of HHTPB and PET blocks can potentially cause insolubility in common solvents. The insolubility is primarily due to the nature of the two blocks rather than the crosslinking. First, if highly crosslinked, the copolymers would not be able to flow at elevated temperatures. However, S80E20 and S50E50 did flow under a compression moulder at 260°C and uniform square sheets were obtained. Second, if the copolymers do crosslink significantly, the chain mobility of both blocks will be restricted resulting in no surface-active (emulsification) properties. However, these copolymers are surface-active at the PET/HDPE interface. Without compatibilizer (i.e. emulsifier), large aggregates of PET particles ($\bar{D}_w \sim 10\,\mu m$) in the incompatible HDPE matrix were obtained. With 5.0 wt% S80E20, the PET particle size was dramatically reduced to about 2.2 μm. The effect of emulsifier type and concentration on dispersed particle sizes has been studied in detail and will be reported separately[9]. The emulsification capability of S80E20 exists because the copolymer chain can orient at the PET/HDPE interface with the HHTPB (S) block towards the HDPE phase and the PET (E) block towards the PET phase. If the S80E20 was significantly crosslinked, a plasticizing effect would be observed, rather than an emulsifying effect. Thus, the insolubility of the copolymers is mainly due to the very different solubility of the HHTPB and PET blocks, because the copolymers melt, exhibit flow at elevated temperatures, and have the desired surface-active/emulsification property.

Tensile properties of the copolymers

The stress–strain curves of S80E20 and S50E50 samples are given in *Figure 1*. Tensile properties of S20E80 as well as pure PET were not measured due to partial degradation of the samples in the compression moulder. Both samples were non-uniform in thickness and very brittle. The elongation at break and modulus of compression-moulded PET have been reported to be only 1.1% and 1.27 GPa, respectively[17]. The elongation at break of S20E80 is also expected to be very low. The elongation at break of S80E20 (145%) is higher than that of S50E50 (80%), while the modulus of S80E20 (7.4 MPa) is lower than that of S50E50 (10.6 MPa). This behaviour is expected since S50E50 has a higher weight fraction of PET block than S80E20. The modulus increases and the elongation at break decreases with increasing PET content.

D.m.a. behaviour

Figures 2 to *4* illustrate the dynamic mechanical behaviour of the control samples (*Figures 2a*, *3a* and *4a*: HHTPB and PET) and the synthesized copolymers (*Figures 2b*, *3b* and *4b*: S80E20, S50E50 and S20E80). *Figure 2a* shows the relative displacement (probe position/initial probe position, or equivalently, sample thickness/initial sample thickness) as a function of temperature for HHTPB and PET. When heated to the respective melting temperature under constant stress (static and dynamic), HHTPB and PET begin to melt and are gradually squeezed out of the plate as indicated by the sharp drop of relative displacement. *Figure 2a* shows that the displacement for HHTPB initially increases with increasing temperature up to 18°C. HHTPB exhibits a maximum thermal expansion of about 2% near 18°C. Above 18°C, the relative displacement decreases sharply as a result of melting. The displacement for PET decreases

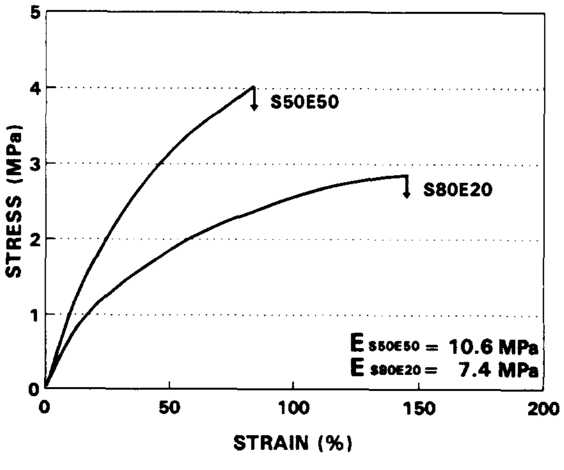

Figure 1 Stress–stain curves of S80E20 and S50E50 copolymers

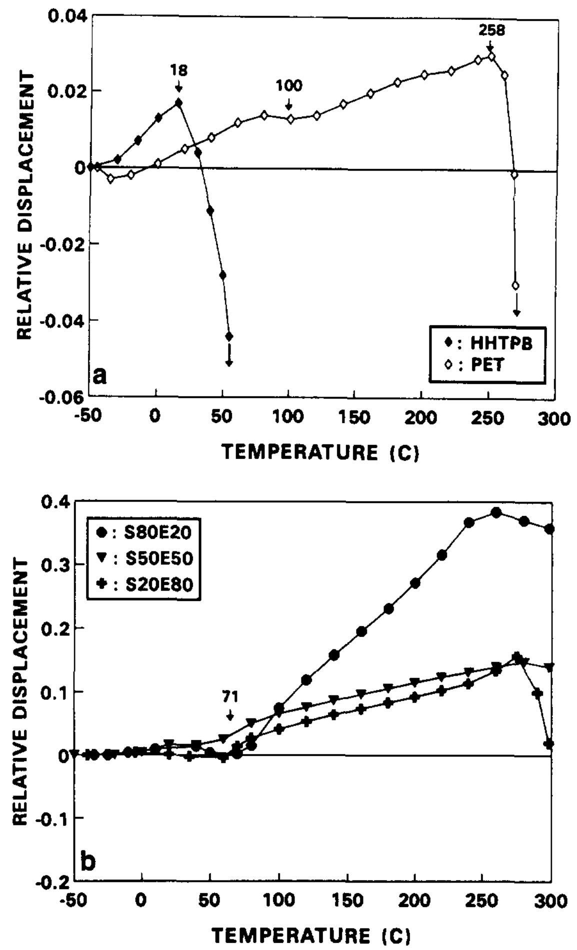

Figure 2 Relative displacement *versus* temperature during d.m.a. scan for (a) control samples (HHTPB and PET) and (b) synthesized copolymers (S80E20, S50E50 and S20E80)

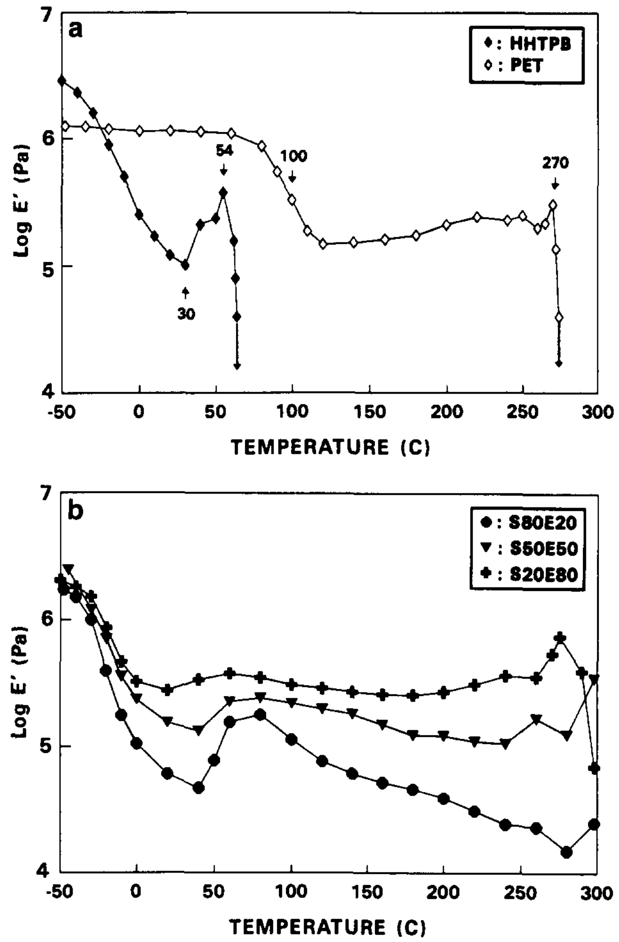

Figure 3 Compressive modulus *versus* temperature for (a) control samples and (b) synthesized copolymers

slightly between −50 and −30°C. It then increases gradually with temperature up to about 80°C due to thermal expansion. The displacement decreases slightly between 80 and 120°C (glass transition), increases significantly between 120 and 258°C (thermal expansion), and finally drops sharply (melting). *Figure 2b* (different scale from *Figure 2a*) shows that the displacements are larger for the block copolymers. There is no sharp drop in probe displacement around the melting temperature of the HHTPB block because HHTPB is chemically bonded to the PET block, which melts above 260°C. These copolymers are dimensionally stable up to 71°C as indicated by the slight increase in relative displacement. Above 71°C, the relative displacement continues to increase because HHTPB segments of the copolymers become more mobile and continue to expand thermally. Furthermore, the sample becomes deformed and is no longer disc-shaped. As the temperature approaches the melting point of PET, the apparent displacement of the copolymer undergoes a maximum. For S80E20 the maximum displacement is observed at about 250°C. Around 120°C, the shape of the S80E20 sample is distorted considerably even without applied stress. S50E50 and S20E80 have better dimensional stability than S80E20 (as indicated by a smaller change in relative displacement) because of lower HHTPB content.

Figure 3a shows the compressive moduli of HHTPB and PET as a function of temperature. As expected, the modulus of HHTPB decreases gradually with temperature from −50° to about 30°C. Above 30°C, the modulus increases to a maximum and then decreases sharply due to complete melting. Since there is no postcure or crystallite reorientation for pure HHTPB, the modulus peak (54°C) around the melting range may be due to thermal expansion and considerable phase transition. A similar observation in the viscosity–temperature behaviour has been reported for a polyaromatic resin using a thermal mechanical analyser[18]. The peak viscosity of the resin was explained in terms of volume increase on melting. The modulus of PET decreases slightly between −50° and about 80°C, which is still below the T_g. As the temperature is further increased from 80 to 120°C, the modulus decreases by almost an order of magnitude as a result of glass transition. Beyond the T_g, the modulus increases slightly with increasing temperature, probably due to slow crystallization of PET. A modulus peak is observed at 270°C immediately before PET melts completely. *Figure 3b* illustrates that the compressive modulus of the copolymers is enhanced with increasing PET content, as expected. Irrespective of the PET content, the moduli are close to each other below the T_g because the copolymer chains are highly restricted and compressed. The change in the modulus around the melting temperature of the HHTPB block is largest for S80E20 and smallest for S20E80. There is a minimum in the modulus between 0 and 80°C, depending on the HHTPB content. The intensity of the subsequent broad peak also reflects the effect of phase transition (and thus

HHTPB content in the copolymer) on the compressive modulus.

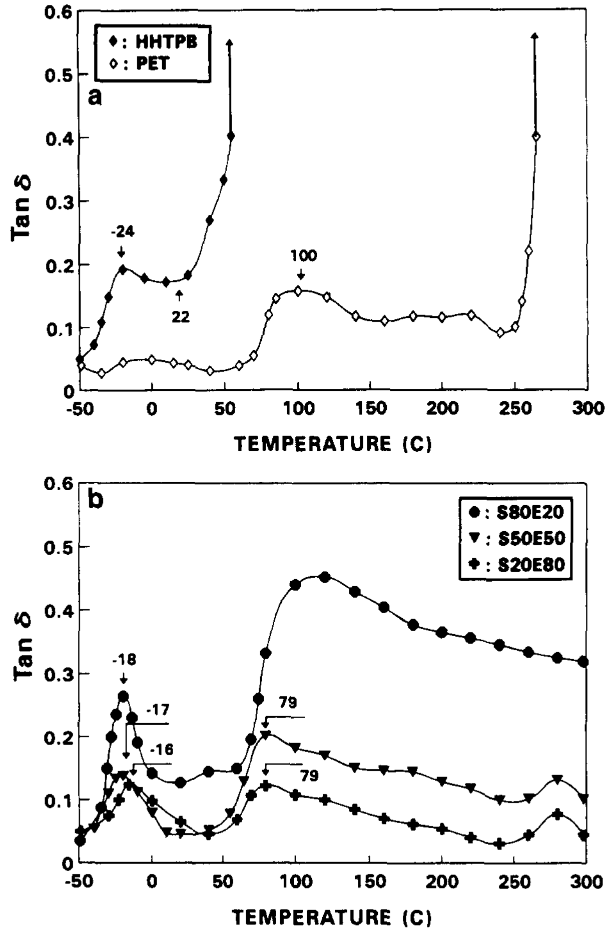

Figure 4 Tan δ *versus* temperature plot for (a) control samples and (b) synthesized copolymers

Figure 4a shows the tan δ of HHTPB and PET as a function of temperature. The T_g is taken as the tan δ peak (*Table 2*). *Figure 4b* indicates that S80E20 has a higher tan δ value at the two glass transitions than S50E50 or S20E80. The highest HHTPB content in S80E20 causes the most damping effect. The T_g of the HHTPB block in the three copolymers can be clearly defined (−16, −17 and −18°C). The values are higher than that of pure HHTPB oligomer (−24°C), indicating less chain mobility of HHTPB in the copolymers than the oligomer. T_g values of −45 and −32°C were reported for pure HHTPB[7] and the HHTPB block of synthesized polyurethanes[8], respectively. The T_g was taken as the onset of the thermal transition observed using d.s.c. at 7.5°C min^{-1} heating rate. The T_g of the PET block of S50E50 (79°C) or S20E80 (79°C) is lower than that of pure PET homopolymer (100°C). The T_g of the PET block of S80E20 could not be determined correctly due to sample distortion and melting of HHTPB blocks.

D.s.c. thermal behaviour

D.s.c. curves of HHTPB, PET and the copolymers are given in *Figure 5*. The copolymers all exhibit two clear melting peaks, one from the HHTPB and the other from the PET block. However, it is difficult to detect the T_gs of HHTPB and PET blocks from the d.s.c. curves. The effect of the weight fraction of the block component on the T_m is plotted in *Figure 6*. The apparent T_ms of the HHTPB and PET blocks in the copolymers are slightly lower than the corresponding homopolymer values. For both S80E20 and S50E50, the T_m of the HHTPB block is about 7°C lower than that of pure HHTPB oligomer (75°C) even though the HHTPB content is high (85.0 and 48.9%, respectively). The T_m of the HHTPB block (64°C) in the S20E80 copolymer is 11°C lower than that of the HHTPB oligomer. The lowering of the T_m of the HHTPB block is greatest for S20E80 because of the highest crystallization interference imposed by the high weight fraction of PET component (80.2%). The decrease in the T_m is probably due to much higher molecular weights (higher viscosities) of the copolymers compared with HHTPB oligomer, and the restriction of HHTPB blocks due the presence of neighbouring PET blocks. Both effects will cause the HHTPB block in the copolymers

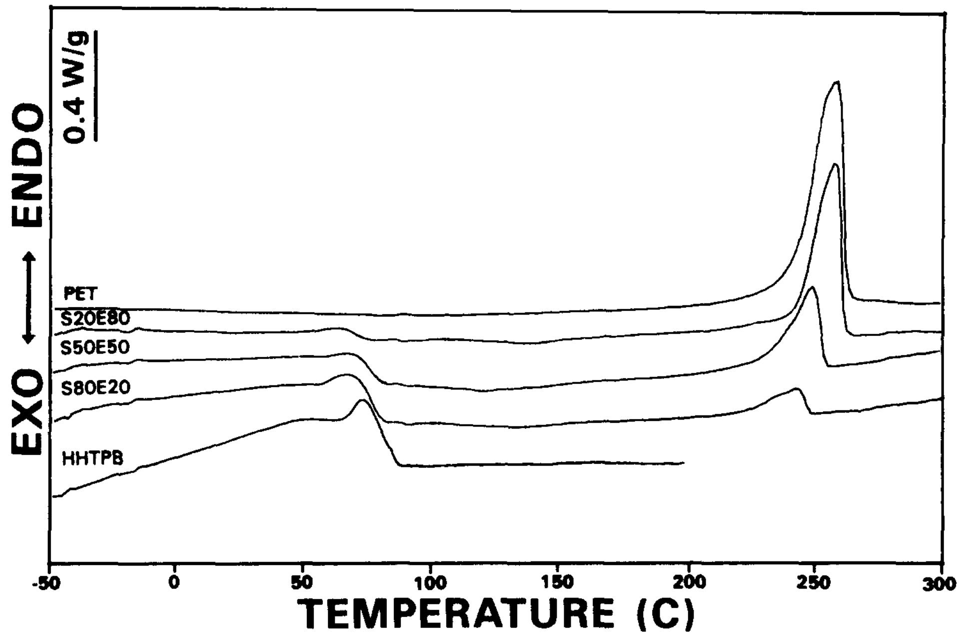

Figure 5 D.s.c. curves of HHTPB, PET and synthesized multiblock copolymers (S80E20, S50E50 and S20E80)

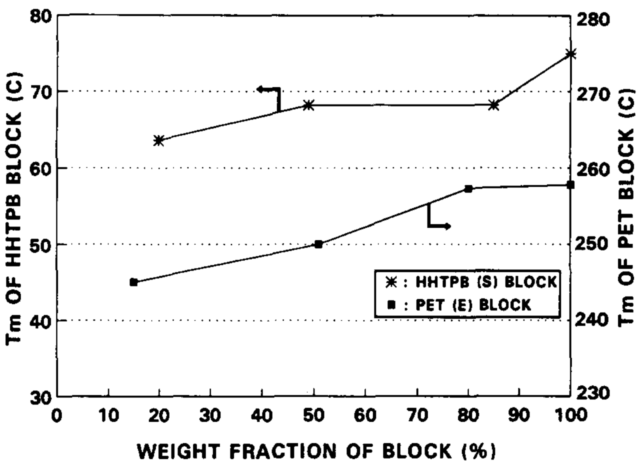

Figure 6 Melting temperature *versus* weight fraction of HHTPB and PET blocks in the block copolymers

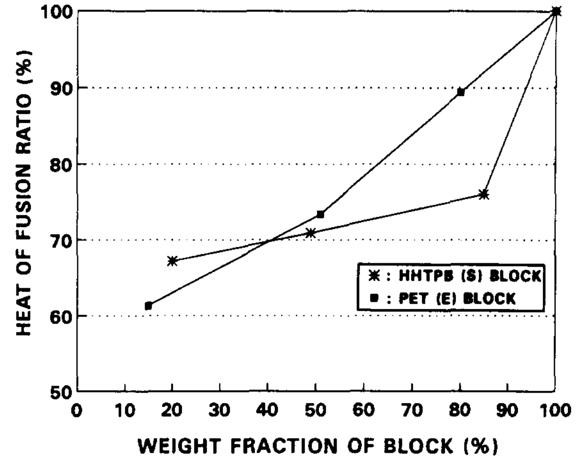

Figure 7 Heat of fusion ratio *versus* weight fraction of HHTPB and PET blocks

to crystallize less easily than the HHTPB oligomer ($M_w \sim 2000$) and lower the apparent T_m. The T_m (257°C) of the PET block in S20E80 is very close to that of the synthesized PET homopolymer (258°C). This behaviour is expected because S20E80 contains a high weight fraction (80.2%) of PET and has long enough repeat units (48.4) which can crystallize in a similar manner to PET homopolymer. The T_m of the PET block is lowest for S80E20 since the average repeat unit of 2.1 is too short and the crystallization of the PET blocks is very much depressed by the presence of neighbouring HHTPB blocks.

Figure 7 illustrates the effect of weight fraction of HHTPB and PET blocks on the heat of fusion ratio (normalized heat of fusion divided by that of pure component, HHTPB or PET). The heat of fusion was calculated as the total area under the endothermic peak between temperatures T_1 where melting begins and T_2 where it ends. While T_2 values can be defined clearly from the d.s.c. curves in *Figure 5*, the choice of T_1 is less obvious. Hence, the T_1 value was based on the d.m.a. data. For example, T_1 of the HHTPB oligomer is taken as the onset (22°C) of the increase in $\tan\delta$ above the T_g, *Figure 4a*. This value of T_1 was used to calculate the heat of fusion for the copolymers. *Figure 7* shows that as the HHTPB content decreases, the heat of fusion ratio also decreases linearly over the range 20 to 85%. The abrupt drop in heat of fusion ratio for HHTPB block from 100% (pure HHTPB oligomer) to 76.2% may be due to the difference in the crystallization behaviour of the oligomer and the copolymer. As the weight fraction of PET decreases, the heat of fusion ratio for the PET block also decreases in an almost linear fashion. The sharper decrease indicates a considerable effect of the weight fraction of the PET block on its crystallization. As the number of repeat units decreases from 48.4 to 11.4 to 2.1, the crystallization of the PET block becomes more and more difficult.

CONCLUSIONS

Multiblock copolymers consisting of two incompatible components (soft and hard blocks) have been prepared through melt polycondensation of hydroxy-terminated polyolefin, dimethyl terephthalate and an excess of ethylene glycol. The synthesized copolymers behave like thermoplastic elastomers because of the presence of both soft and hard blocks. The copolymers are not soluble in common solvents due to the very different solubility of the two incompatible blocks. Their unique balance of softness, chemical resistance and processing flexibility may have great appeal in engineering applications. The T_g of the polyolefin and PET blocks were observed to be -17 and 79°C, respectively. The T_m and the heat of fusion ratio of the block components decrease with decreasing weight fraction in the copolymer. The thermal behaviour for the HHTPB block is less sensitive than the PET block due to unchanged length of HHTPB before and after polymerization.

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