Influence of Interchange Reactions on the Miscibility of Polyesterurethanes/Polycarbonate Binary Blends

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ABSTRACT: A series of thermoplastic polyurethane elastomers (TPUs) with various hard-segment contents was prepared using 4,4'-diphenylmethane diisocyanate and 1,4-butanediol as the hard segment and poly(ethylene adipate)diol or poly(butylene adipate)diol, whose number-average molecular weight is 2000, as the soft segment. The miscibility of TPU/polycarbonate (PC) blends observed by differential scanning calorimetry was enhanced by the interchange reaction at high temperature. Both hard and soft segments were suggested to be involved in the interchange reaction with PC. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2363–2369, 1997

Key words: polyesterurethane; polycarbonate; blends; miscibility; interchange reaction

INTRODUCTION

Polymer modification through blending can be used to obtain materials with a balanced combination of specific properties. Thermoplastic polyurethane elastomers (TPUs) can have a wide range of chemical structures, because various monomeric materials are now commercially available.[1–3] Because tailor-made structures appropriate for blending can be obtained by combining various monomeric materials, TPUs are expected to show practical promise in polymer blends.[4–7]

The aliphatic polyester, such as poly(ethylene adipate) or poly(butylene adipate), are miscible with polycarbonate (PC) or poly(styrene-*co*-acrylonitrile) with an appropriate acrylonitrile content.[8,9] This explains the good compatibility of some TPU/PC or TPU/poly(acrylonitrile–butadiene–styrene)(ABS) blend systems and their commercial availability.[10,11]

Polymers containing ester or carbonate groups may undergo an interchange reaction during melt blending.[12–14] The understanding and the controlling of this reaction are important to obtain blends with good properties.

In the present study, we prepared various kinds of TPUs with an aliphatic polyester soft segment. The change of miscibility behaviors in the blends of these TPUs with PC under various thermal histories was followed by differential scanning calorimetry (DSC) and thermogravimetric analysis.

EXPERIMENTAL

Materials

TPU was synthesized from 4,4'-diphenylmethane diisocyanate (MDI, Tokyo Chemical Co., EP grade), 1,4-butanediol (BD, Junsei Chemical Co., first grade), and poly(ethylene adipate)diol

(PEA) or poly(butylene adipate)diol (PBA) (M_n = 2000, respectively, Songwon Industry Co.). The dimers of MDI were removed by precipitation at 50°C. BD was used after immersing 4 Å molecular sieves (Yakuri Pure Chemicals Co.) for more than 3 days to remove dissolved moisture. PEA and PBA were used after drying in a vacuum (15 mmHg) for more than 10 h at 70°C prior to use. The solvent for synthesis was *N,N*-dimethylformamide (DMF, Junsei Chemical Co., EP grade).

PC (Idemitsu Toughlon FN-2500, commercial grade) was used as received. Pyridine (Junsei Chemicals Co., EP grade) was used as a solvent for blending after immersing 4 Å molecular sieves for more than 3 days.

Synthesis of TPU

A series of TPUs with various hard-segment contents was synthesized in two steps using the prepolymer method. First PEA or PBA was reacted with an excess amount of MDI at 68°C in DMF for 1 h. Subsequently, BD was added for the chain extension reaction. The total weight of the reactants was about 50 g. DMF was added until a concentration of 30 w/v % was reached. It took 3–5 more h to obtain a highly viscous solution, after which 1–2 mL of methanol was added to terminate the reaction. The final polymer sample was obtained by precipitation in a 10-fold volume of methanol and subsequent drying in an 80°C vacuum oven.

The mol ratios of the reactants (MDI/BD/PEA or PBA) were 2/1/1, 5/4/1, 9/8/1, 24/23/1, and 1/1/0, which correspond to a hard-segment content of 24, 40, 60, 80, and 100 wt %, respectively. An excess amount of MDI in the range of 1–5 mol % was used to compensate for the losses by the reaction of isocyanate functional group with ambient moisture. The structure and the hard-segment content of synthesized TPU were verified by ^{1}H-NMR. The samples were named according to the polyester structure and hard-segment content. For example, PEA–PUH40 denotes the sample synthesized using PEA with a hard-segment content of 40 wt %. Poly(MDI–BD) is the sample composed only of a hard-segment structure.

Blending

The blended films of TPU and PC were obtained by casting the pyridine solution (2–5 w/v %) of the polymers on aluminum plates, followed by drying first in a convection oven and then in a

vacuum drying oven, respectively, at 80°C for more than 3 days.

Differential Scanning Calorimetry (DSC)

Since thermal transitions of a TPU soft segment are observed in subambient temperatures, a Mettler TA-3000 DSC with a liquid nitrogen cooling attachment was used for DSC analysis. Samples of 10–14 mg each in an Al pan were used with a heating rate of 20°C/min under a N_2 atmosphere.

Thermogravimetric Analysis (TGA)

To investigate the thermal stability of the blends, a Perkin-Elmer TGS-2 was used. The samples of 10 mg each in an alumina crucible were used with a heating rate of 20°C/min under N_2.

RESULTS AND DISCUSSION

Characterization of TPU

The structure of synthesized PU was verified using ^{1}H-NMR. The content of the hard segment was calculated algebraically from the integrated peak intensity of the peaks and was found to be consistent with the feed ratio of the reactants. The microphase separation behavior of the soft and hard segments of TPU is strongly influenced by the thermal history and the mechanical deformation that the sample has gone through. It is therefore required to anneal the samples above certain temperatures (usually 10–20°C above T_m) and to quench down to sub-T_g temperatures (around −120°C) to remove the effect of the previous thermal history. We used two different temperatures for annealing the samples prior to scanning in DSC, i.e., 230 and 270°C, for 3 min each. In Figures 1 and 2, we can observe the difference in the thermal behavior of PEA–TPUs according to the different annealing temperatures. PBA–TPUs, not shown, also showed similar behavior.

In Table I are shown the T_g's of the TPUs. For both PEA– and PBA–TPUs, the T_g's were detected at higher temperatures as the hard-segment content increased. The T_g's were 2–9°C higher when annealed at 270°C than when annealed at 230°C. Also, the cold crystallization temperature (T_{cc}) was detected only when annealed at 270°C.

The thermal behaviors of TPU according to the annealing temperatures can be interpreted as fol-
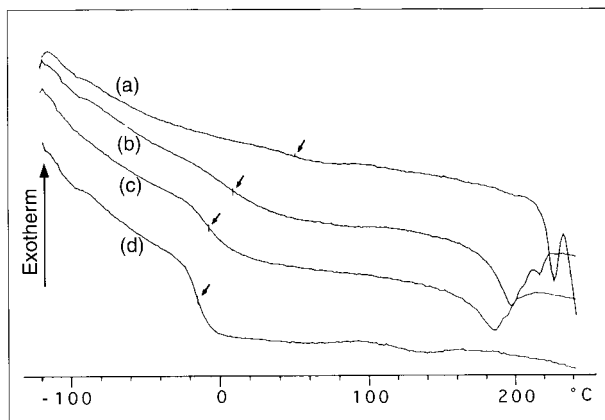
Figure 1 DSC thermograms of PEA-based TPU samples annealed at 230°C for 3 min: (a) PEA–PUH80/PC; (b) PEA–PUH60/PC; (c) PEA–PUH40/PC; (d) PEA–PUH24/PC.

lows: The soft and hard segments of the TPU multiblock copolymer exist in a microphase-separated state in ambient temperature. When heated above the melting temperature of the hard segment, however, a single phase is formed by the mixing of the two domains.[15–17] Upon heating at 270°C, the mixing between the soft and hard segments seems to be facilitated more than when heated at 230°C, which results in a higher degree of mixing between the two domains. Also, upon subsequent reheating after quenching, the hard segment dissolved in the soft segment domain shifts the T_g of the soft segment to higher temperatures. The absence of T_{cc} in TPUs preheated at 230°C can be explained by the fact that either the melting of the hard-segment paracrystalline domains were insufficient on heating at 230°C or crystallization could have taken place quickly upon quenching because the extent of the phase mixing was not thorough enough.

Thermal Properties of Poly(MDI–BD)/PC Blend

To investigate the miscibility between PC and the hard-segment portion of TPU, poly(MDI–BD) was synthesized and blended with PC. The structure of poly(MDI–BD) was verified by ^{13}C-NMR, and its intrinsic viscosity was 0.82 dL/g.

The effect of annealing conditions on the poly-(MDI–BD)/PC (5/5 by weight) blend is represented by the DSC thermograms shown in Figure 3. The samples of the blend film were annealed at temperatures between 230 and 270°C for 10 min. When annealed at 230°C, two distinct T_g's,

115°C for poly(MDI–BD) and 155°C for PC, were observed, which implies the immiscibility of the two polymers. As annealing temperature increased, the two T_g's shifted nearer to each other, with the T_g of PC shifting more than that of poly(MDI–BD), to the apparent single T_g at 119°C when preheated at 270°C. The melting peak of poly(MDI–BD) gradually disappeared as annealing temperature increased.

In Figure 4, the effect of repeated DSC scans to the thermal behavior of the poly(MDI–BD)/PC (5/5 by weight) binary blend is shown. Each blend sample was heated in the DSC in the temperature range of 30–270°C with a heating rate of 20°C/min, followed by subsequent quenching and rescanning. As with the case of increasing annealing temperatures, the repeated exposure to high temperatures resulted in the gradual shift of the T_g's of the two polymers closer to each other, as well as in the diminishing of the melting peaks of poly(MDI–BD).

We attributed the behavior of the poly(MDI–BD)/PC blend described above to the reaction between the two polymers since it had a close similarity to the behavior of the polyester/PC and polyester/polyester blends in which transesterification could be observed.[18–21] PC is a relatively thermally stable polymer by itself. When blended with condensation polymers such as polyesters or polyamides, however, it was reported that interchange reactions could be observed at high temperatures, by which thermal stability of PC was jeopardized. In such blends, the shift of T_g's and the disappearance of T_m due to the interchange
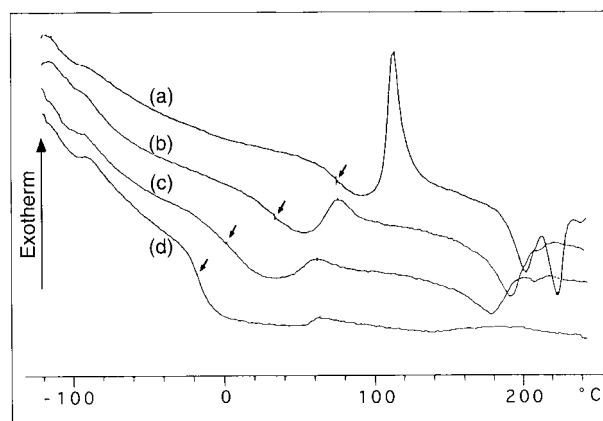

Figure 2 DSC thermograms of PEA-based TPU samples annealed at 270°C for 3 min: (a) PEA–PUH80/PC; (b) PEA–PUH60/PC; (c) PEA–PUH40/PC; (d) PEA–PUH24/PC.

Table I T_g **of TPUs Annealed at Different Temperatures for 3 Min**

Hard Segment Content (Wt %)	T_g of TPU (°C)			
	PEA-based TPU		PBA-based TPU	
	Annealed at 230°C	Annealed at 270°C	Annealed at 230°C	Annealed at 270°C
24	−16	−17	−27	−26
40	−9	7	−18	3
60	7	29	−8	21
80	53	72	35	76

reaction were also observed, as in the current poly(MDI–BD)/PC blend.

TGA results shown in Figure 5 also support the possibility of an interchange reaction between poly(MDI–BD) and PC. Up to about 290°C, the weight loss of the poly(MDI–BD)/PC (5/5 by weight) blend maintained the value which is about the average of the weight loss of the two individual polymers. Above the temperature, however, the weight loss for the blended sample was greater than the average value, clearly showing a negative effect on thermal stability. It can be assumed from this analysis that the reaction between poly(MDI–BD) and PC takes place when exposed to high temperatures, which presumably accelerates weight loss by the evolution of low molecular weight byproducts.

Thermal Properties of TPU/PC Blends

PEA and PBA used as the soft segment of TPU are aliphatic polyesters known to be miscible with PC. The hard-segment portion, however, is found to be immiscible with PC in the absence of an interchange reaction. Thus, TPU possesses both PC miscible and immiscible segments within its chain structure.

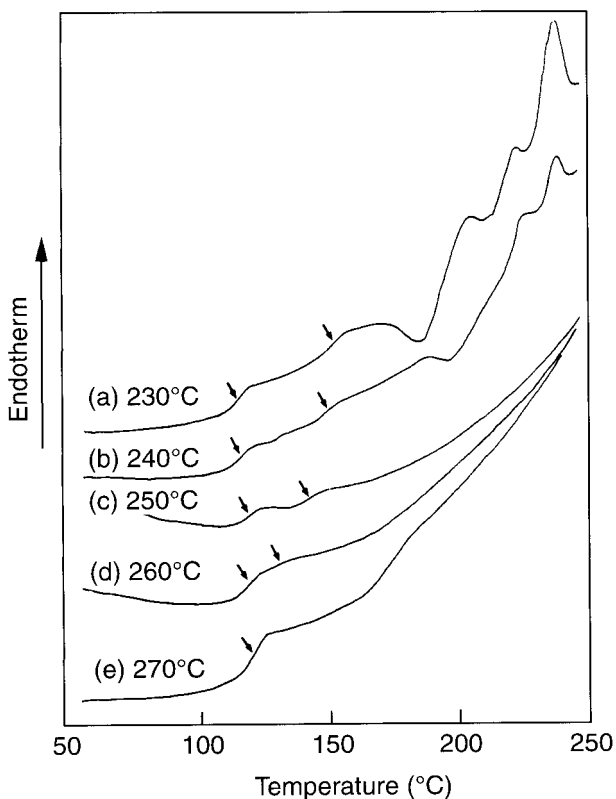The blended film of TPU and PC showed differ-

Figure 3 DSC thermograms of poly(MDI-BD)/PC(5/5) blend annealed at various temperatures for 10 min: (a) 230°C; (b) 240°C; (c) 250°C; (d) 260°C; (e) 270°C.

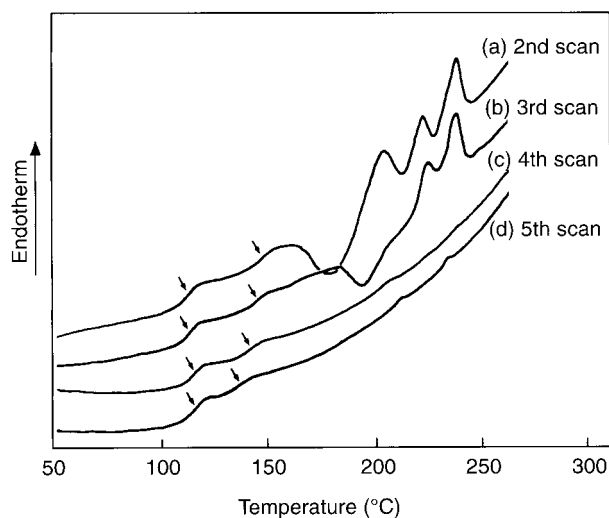**Figure 4** DSC thermograms of poly(MDI–BD)/PC (5/5) blend obtained on repeated scans (scanning range: 30–270°C, heating rate: 20°C/min, cooling rate: −150°C/min).
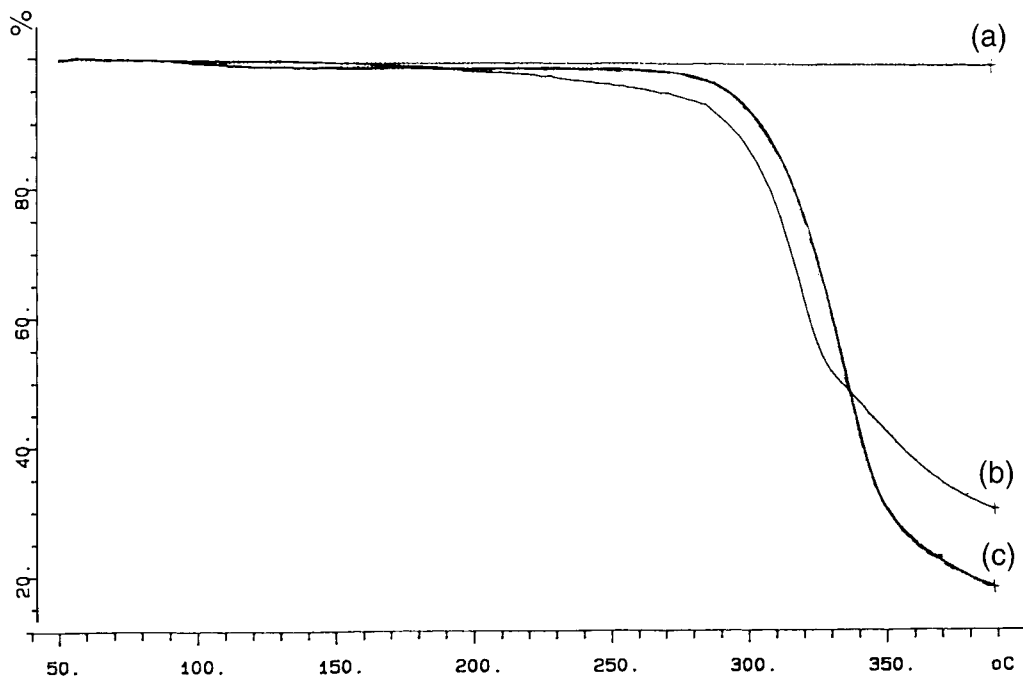
Figure 5 TGA results of (a) PC, (b) poly(MDI–BD), and (c) poly(MDI–BD)/PC (5/5) blend.

ent phase behaviors according to the annealing conditions as with poly(MDI–BD)/PC blend. In Figures 6 and 7 are shown DSC thermograms of PBA-based TPU/PC (5/5 by weight) binary blends annealed 3 min at 230 and 270°C, respectively. When annealed at 230°C, the blends generally showed two distinct T_g's at the -10 to 50°C range and the 150–155°C range, corresponding to those of TPU and PC domains, respectively. The T_g's of the TPU domain for PBA-based TPU with a hard-segment content of 40–80% shifted about

6–7°C from those of TPU, implying a limited compatibility with PC. For PBA-based TPU with a hard-segment content of 24%, however, the partial miscibility with PC was significantly higher than for other TPUs with a lower soft-segment content. The difference of TPU T_g values before and after the blending was 27°C in this case. The crystallization of PC was facilitated in this sample as shown by the large PC melting peak at 240–250°C.
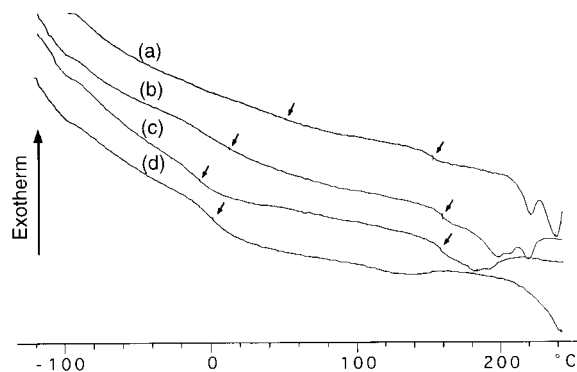
When the blends were annealed at 270°C, a

Figure 6 DSC thermograms of PBA-based TPU/PC (5/5) blends annealed at 230°C for 3 min: (a) PBA–PUH80/PC; (b) PBA–PUH60/PC; (c) PBA–PUH40/PC; (d) PBA–PUH24/PC.
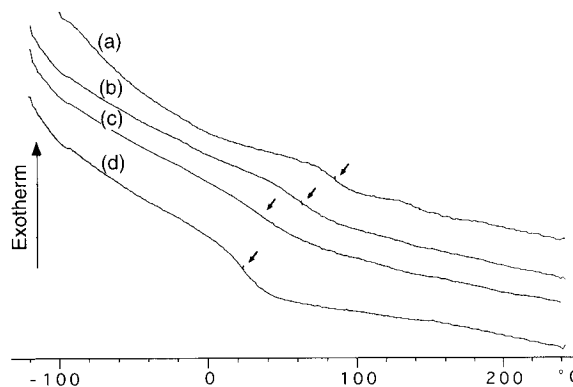

Figure 7 DSC thermograms of PBA-based TPU/PC (5/5) blends annealed at 270°C for 3 min: (a) PBA–PUH80/PC; (b) PBA–PUH60/PC; (c) PBA–PUH40/PC; (d) PBA–PUH24/PC.
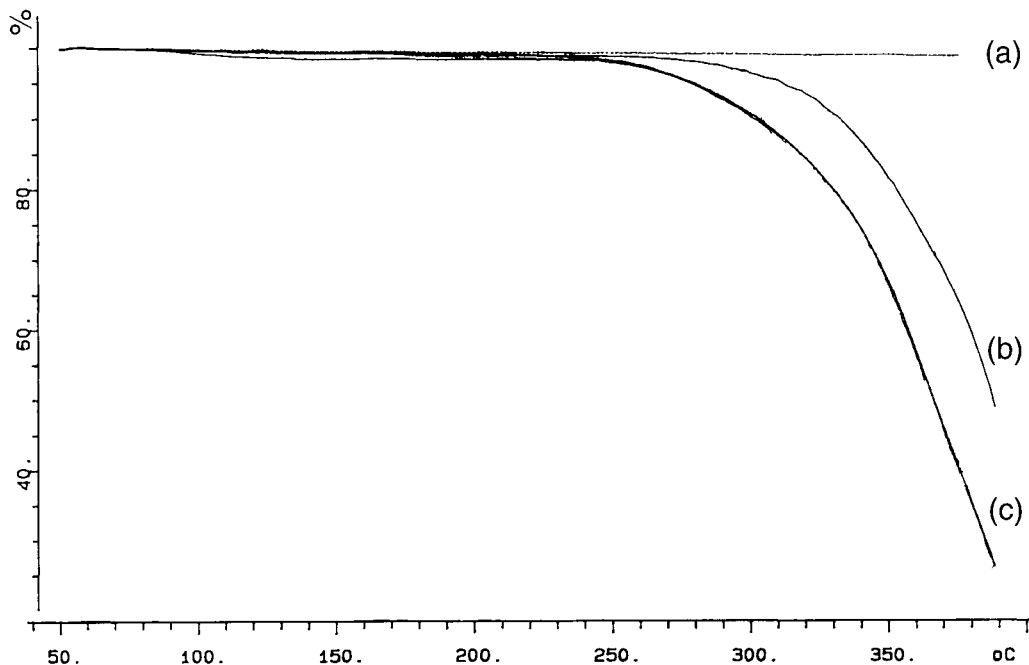
Figure 8 TGA results of (a) PC, (b) PBA–PUH24, and (c) PBA–PUH24/PC (5/5) blend.

single T_g was observed for all the blends, showing enhanced miscibility. Melting peaks were not observable. In Figure 8 are shown the TGA thermograms of PC, PBA–PUH24, the PBA–PUH24/PC 5/5 blend. It is evident from this result that the thermal stability of the PBA–PUH24/PC (5/5 by weight) blend is significantly lower than that of either one of the polymers. This implies that a certain reaction occurred between the two polymers. Comparison between the TGA curves of the PBA–PUH24/PC blend and the poly(MDI–BD)/PC blend (Fig. 5) shows that the initial thermal degradation begins at lower temperatures in the PBA-based TPU blend than in the poly(MDI–BD) blend. It suggests that the presence of PBA facilitates the reaction with PC at lower temperatures. The extent of weight loss for the PBA–PUH24/PC blend is not thorough, however, as with the poly(MDI–BD)/PC blend, implying that a different mechanism is at work. The specific mechanism and the products of the reaction were not studied in this current stage. However, the above results suggest that the reaction between the ester functional group in the PBA segment and the carbonate group in PC is involved in this case.

A very similar behavior was observed for PEA-based TPU/PC binary blends. DSC thermograms of PEA-based TPU/PC (5/5 by weight) binary

blends annealed for 3 min at 230 and 270°C are shown in Figures 9 and 10, respectively. As with PBA-based TPU/PC blends, two distinct T_g's were observed for the blends annealed at 230°C for 3 min. The T_g of TPU shifted 10–20°C by blending with PC, suggesting partial miscibility of the polymers to a certain extent. When annealed at 270°C for 3 min, PEA-based TPU/PC blends showed a single T_g and no melting peak. For both PBA-based TPU/PC and PEA-based TPU/PC blends, samples after the DSC scans showed a bubble for-
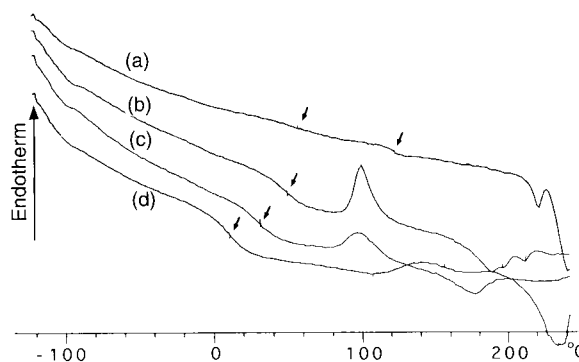

Figure 9 DSC thermograms of PEA-based TPU/PC (5/5) blends annealed at 230°C for 3 min: (a) PEA–PUH80/PC; (b) PEA–PUH60/PC; (c) PEA–PUH40/PC; (d) PEA–PUH24/PC.
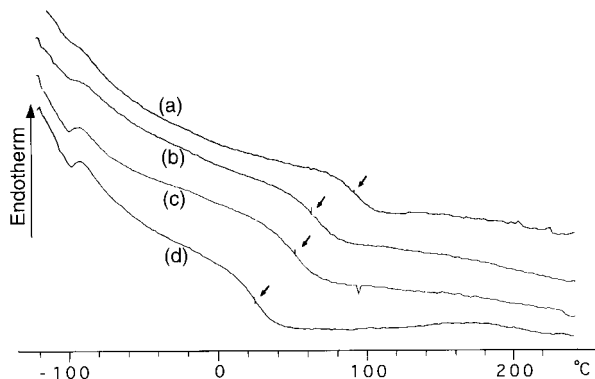
Figure 10 DSC thermograms of PEA-based TPU/PC (5/5) blends annealed at 270°C for 3 min: (a) PEA–PUH80/PC; (b) PEA–PUH60/PC; (c) PEA–PUH40/PC; (d) PEA–PUH24/PC.

mation in the solid and the embrittlement of the material.

CONCLUSION

The miscibility between PC and poly(MDI–BD) or TPU containing a polyester soft segment was enhanced by interchange reactions. The TGA results suggested that the interchange reaction mechanism of the PC and poly(MDI–BD) blend might be different from that of the PC and TPU blend.

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