Compatibilization and Property Characterization of Polycarbonate/Polyurethane Polymeric Alloys

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ABSTRACT: Polymeric alloys of bisphenol A polycarbonate and a polyester-type polyurethane were prepared over a complete composition range through melt mixing. The blends were characterized with optical and scanning electron microscopy, tensile testing, dynamic mechanical analysis, thermal analysis (differential scanning calorimetry and thermogravimetric analysis), and spectroscopic techniques (Fourier transform infrared and ^{1}H-NMR). A morphology examination revealed good component dispersion with 30 wt % polyurethane or less and strong interface adhesion. Dynamic mechanical analysis indicated partial component miscibility and tensile testing mechanical behavior typical of a polymeric alloy. Overall, the degree of compatibilization obtained with polycarbonate was lower than that observed previously with poly(ethylene terephthalate) or poly(butylene terephthalate). This was attributed to the lower reactivity of the aromatic —OH of polycarbonate toward the isocyanate groups of polyurethane and the thermal instability of the copolymer–compatibilizer formed. Experimental evidence for the formation of the latter was provided by ^{1}H-NMR and dynamic mechanical analysis of selectively leached blends and by quantitative analysis results for the extraction experiments. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 612–626, 2003

Key words: polycarbonates; polyurethanes; alloys; compatibilization; blends

INTRODUCTION

Polymer blending leading to a miscible system or a polymeric alloy is a useful and more cost-effective route than the synthesis of new polymers for the preparation of materials with unique and tailor-made properties.

In recent work,[1,2] the compatibility of a polyester-type thermoplastic polyurethane (TPU) and crystalline aromatic polyesters [poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET)] was investigated. The binary blends were compatible over the complete composition range, and this was attributed to an in situ PBT–polyurethane (PU) or PET–PU copolymer formed via ester–amide interchange reactions during melt blending.

In this article, we report on the compatibility behavior of TPUs and bisphenol A polycarbonate (PC), an amorphous thermoplastic resin.

TPUs play important roles within the rapidly growing family of thermoplastic elastomers because they possess exceptional properties, such as high tensile strength and elongation, flexibility, and low-temperature impact resistance. However, they have short-term resistance to elevated temperatures, and it would be preferable in some cases to increase their stiffness.

PC is a tough, transparent, impact-resistant thermoplastic engineering polymer with a very wide range of service temperatures. However, it suffers from its high melt viscosity, which causes difficulties in processing (e.g., injection molding), and its low fatigue strength, which generates cracks at points of concentrated residual stress.

For these reasons, blends of TPU and PC are expected to usefully combine the properties of the parent polymers.

A short review of PC blends with polyesters is given in ref. 3. Other studies relevant to this one have dealt with blends of aromatic polyesters and PU. Cyclohexane cast films of PC/PU blends were stated to be incompatible. The PU was a polyether or polyester type.[4] Partial compatibility with pyridine cast films was reported by Ahn et al.[5] The PU component was based on 4,4'-diphenyl methane diisocyanate (MDI) and butanediol-1,4 (BD-1,4) as the hard segment and poly(ethylene adipate) or poly(butylene adipate) as the soft segment. Films annealed in a differential scanning calorimeter between 230 and 270°C for various lengths of time showed a convergence of the main
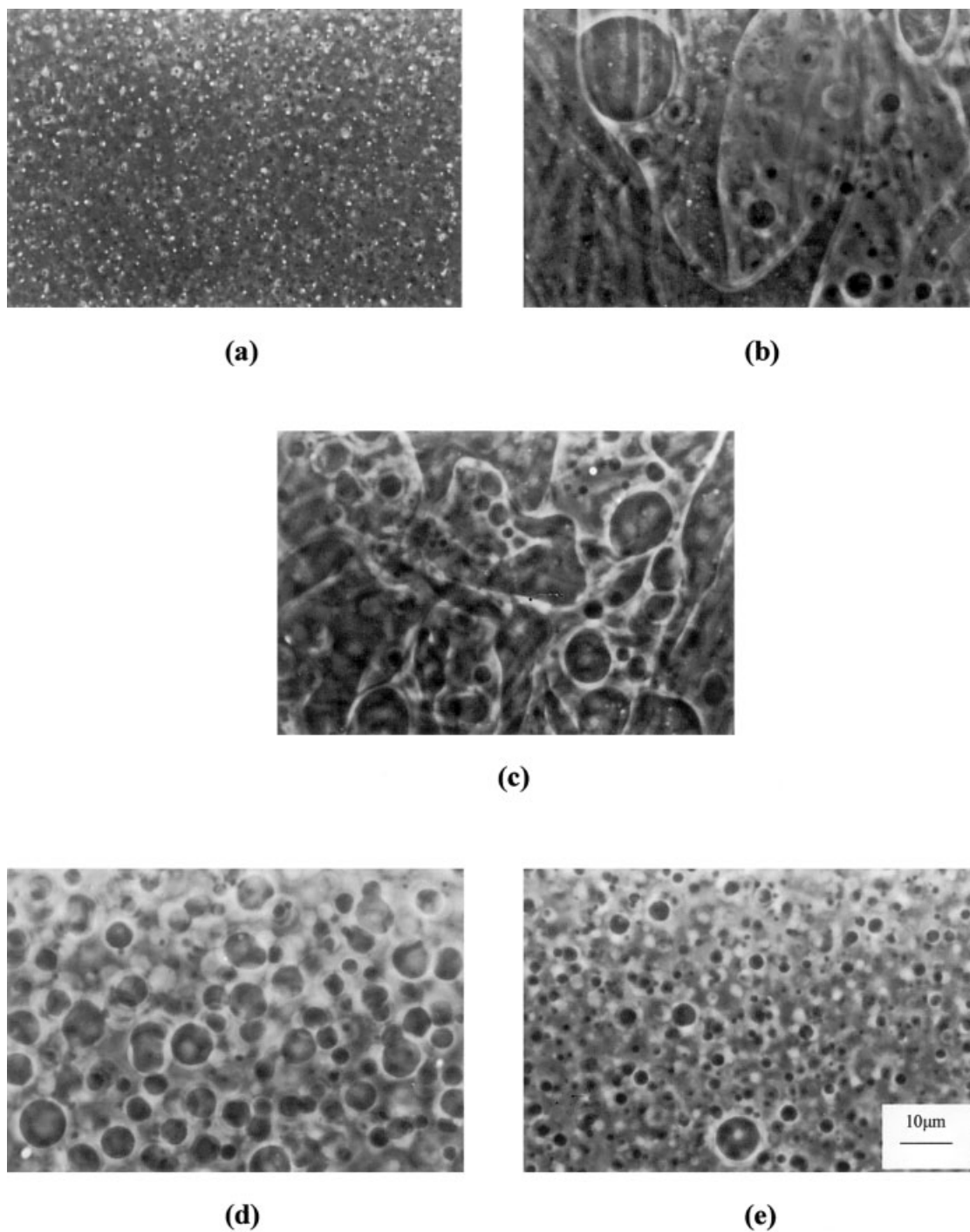
Figure 1 Phase-contrast micrographs of PC/PU blends: (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90 ($t_{mix} = 5$ min).

components' glass-transition temperatures (T_g's). This was taken as evidence for reactive compatibilization attributed to ester–amide interchange reactions. No other characterization techniques were applied. Melt mixing at 235°C was employed by Fabri et al.[6] to obtain PC/PU elastomer blends. The examined compositions were limited to 0–10 wt % PU. On the basis of the T_g shift obtained with dynamic mechanical anal-

ysis (DMA), the system was stated to be miscible. The miscibility was attributed to hydrogen-bonding intermolecular interactions between —NH of the PU groups and —C=O of the PC groups.

In this work, we examined PC/TPU blends prepared by melt mixing over the complete composition range. In addition to static and dynamic mechanical testing, the degree of physical and reactive compati-

bilization was investigated with spectroscopy [NMR and Fourier transform infrared (FTIR)], optical microscopy (phase-contrast), and scanning electron microscopy (SEM) techniques.

EXPERIMENTAL

Materials and specimen preparation

PC was obtained from BDH Chemicals, Ltd., with a number-average molecular weight (M_n) of 29,000 and a density of 1.20 g cm^{-3}. TPU (Desmopan 359) was donated by Bayer A.G. It was a polyester-type PU with hard segments formed by the addition of BD-1,4 to MDI. The soft segment, with $M_n \sim 2000$ g mol^{-1}, consisted of polyester chains formed by the polycondensation of adipic acid onto BD-1,4. The density was 1.23 g cm^{-3}. The polymers were available in the form of pellets. PC was dried at 120°C overnight for the removal of sorbed water because even a low water content could lead to hydrolysis of the polymer, particularly at elevated temperatures.[7] PU was dried at 100°C for 24 h.

The blends were prepared via melt mixing in a version of a mixer more automated than that described previously.[8]

On the basis of the ultimate tensile properties, the optimum mixing temperature and mixing time (t_{mix}) were determined to be 235°C and 5 min, respectively. The compositions of the PC/PU blends prepared were 90/10, 70/30, 50/50, 30/70, and 10/90 (w/w).

The films were obtained via compression molding between Teflon sheets at 235°C and 5 MPa, which was followed by quenching to 0°C. They were conditioned at approximately 25°C and at a relative humidity of approximately 60% for 24 h.

Terminal hydroxyl (phenolic) groups in PC may be important for the compatibilization process. So that their presence could be established,[9] PC was dissolved in methylene chloride and precipitated in acetone. It was filtered, redissolved, and reprecipitated, and this process was repeated several times so that any residual contents of the bisphenol A and oligomers, both soluble in acetone, would be removed. The second stage involved the esterification of the purified PC with an excess of acetyl chloride, in a solution of methylene chloride, by the presence of triethylamine. Finally, it was precipitated in methanol, washed with water, and dried at 60°C in vacuo overnight.

A comparison of the NMR spectra of PC and its acetylated product, obtained from a solution in CDCl$_3$, indicated a new peak at 2.3 ppm in the latter spectrum. The literature[10] confirms that this was due to the methyl protons of the acetyl group. According to the ratio of the new peak to the peak of the aromatic protons or methyl protons of PC as well as its degree of polymerization (DP), the derived number for the

(a)

(b)

10μm
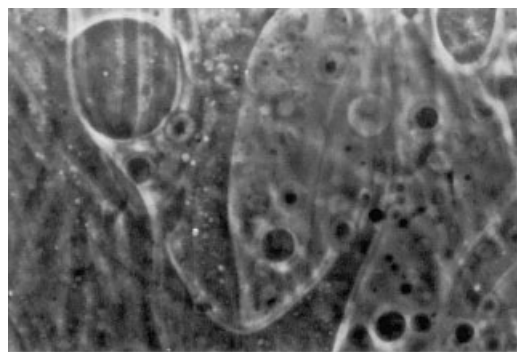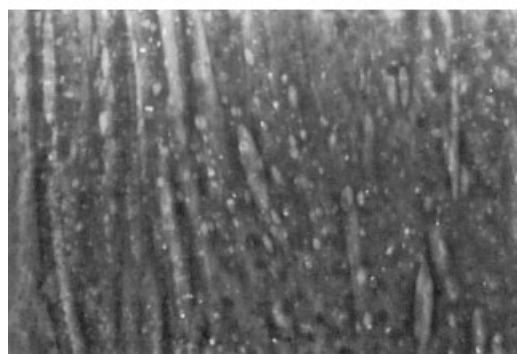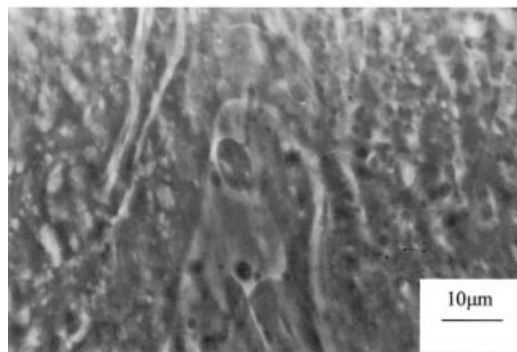
(c)

Figure 2 Phase-contrast micrographs of 70/30 PC/PU blends showing the effects of t_{mix}: (a) 5, (b) 10, and (c) 15 min.

acetyl end groups was in fairly good agreement with the expected number of terminal OH groups.

Apparatus and procedures

Tensile tests were performed at a crosshead speed of 10 cm min^{-1} and at 23°C, according to ASTM D 882, with a J.J. 5001 tensile tester and a film strip measuring $3.00 \times 0.5 \times 0.025$ cm^3.
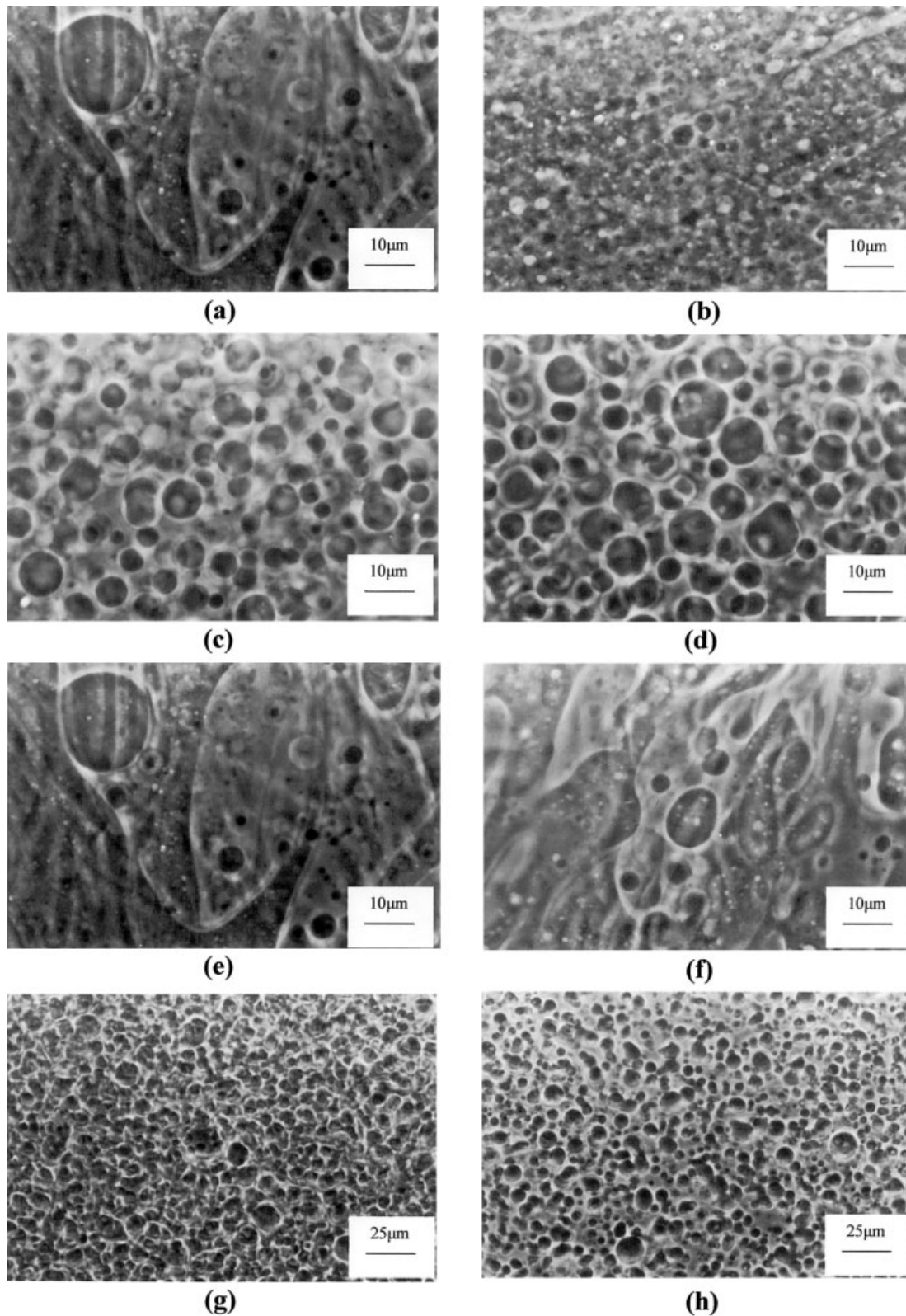
Figure 3 Phase-contrast micrographs showing the effects of annealing for 70/30 PC/PU blends [(a) quenched and (b) annealed] and 30/70 PC/PU blends [(c) quenched and (d) annealed] and the effects of aging for 70/30 PC/PU blends [(e) quenched and (f) aged] and 30/70 PC/PU blends [(g) quenched and (h) aged].

DMA data were obtained with a solid-state RSA II analyzer (Rheometric Scientific Co.) at 10 Hz. The specimen dimensions were $3.0 \times 0.5 \times 0.01$ cm^3.

Differential scanning calorimetry (DSC) analyses were performed with a differential scanning calorimeter (SP+) equipped with the Autocool accessory from
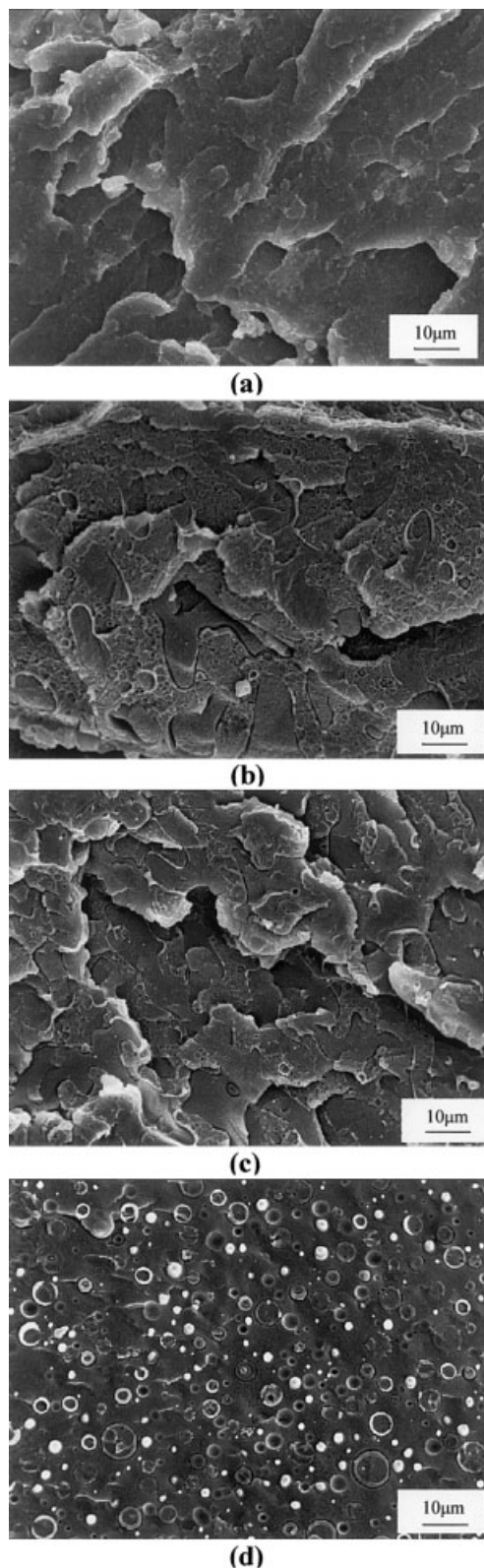
Figure 4 SEM images of cryofractured surfaces of PC/PU blends: (a) 90/10, (b) 70/30, (c) 50/50, and (d) 30/70.

Rheometric Scientific. All the experiments were performed under a constant flow of dry nitrogen. The nominal weight was approximately 10 mg, and the

heating rate was 10°C min^{-1}. The samples were heated from 25 to 250°C.

To examine the effect of t_{mix} on possible decomposition, we performed thermogravimetric analysis (TGA) isothermal scans under a constant flow of dry nitrogen with a DuPont 951 thermogravimetric analyzer equipped with a 990 program recorder. The samples were tested at 235°C for 20 min.

Optical micrographs with a phase-contrast arrangement were obtained with an Olympus BH-2 microscope.

SEM was carried out on a JEOL JSM-500 instrument at a tilt angle of 0° on specimens fractured at cryogenic and ambient temperatures.

Extraction experiments were performed with chloroform for 5 days at ambient temperature. In this solvent, PC was completely soluble, but PU remained practically undissolved (amount dissolved ~ 1 wt %). After extraction, the films were dried in a vacuum oven at 60°C for 3 days.

FTIR spectra were recorded with a PerkinElmer 1600 spectrometer.

^{1}H-NMR spectroscopy was performed with an Avance DPX 400-MHz instrument with a magnetic field strength of 9.4 T. The samples were dissolved in a 2/1 (v/v) mixture of CF_3COOH and $CDCl_3$ so that 2 wt % solutions would be obtained.

RESULTS

Morphology

Optical microscopy

Given the refractive-index difference of PU (n_D = 1.550)[11] and PC (n_D = 1.584),[7] positive phase-contrast dark areas would correspond to PC.

Figure 1 shows the effect of the composition variation on blends quenched at 25°C. Good component dispersion was evident for the 90/10 blend [Fig. 1(a)]. Increasing the PU content led to a phase-separated system [Fig. 1(b–e)]. Figure 1(b,c) shows a characteristic interpenetrating morphology, but at PU compositions greater than 50 wt %, matrix inversion took place. As in previous polyester/PU blends,[1,2] PC separated as spherical domains that were composite in nature; that is, PU was occluded in the PC globules. Note the light gray areas inside the darker PC globules. A larger contrast was observed in the previous blends[1,2] because of the larger refractive-index difference between components. The effect of t_{mix} is shown in Figure 2. Some improvement in the dispersion was observed when t_{mix} was increased to 10 min. However, the interpenetrating nature of the blend morphology persisted. On a macroscale, an improved dispersion was observed after the annealing of the 70/30 and 30/70 blends, which led to a pronounced spherical domain morphology for the latter [cf. Fig. 3(a–d)].
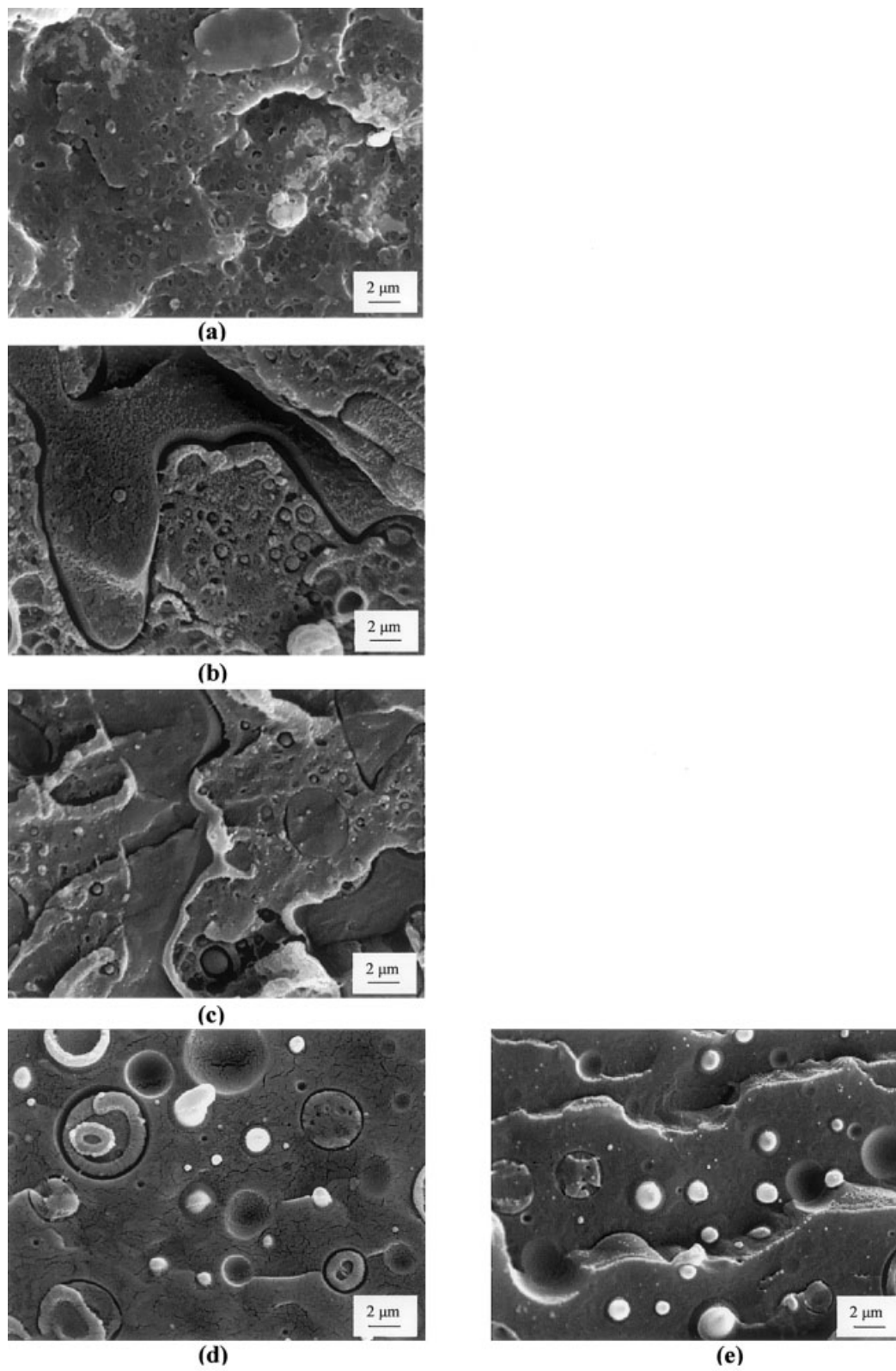
Figure 5 SEM images of cryofractured surfaces of PC/PU blends at a higher magnification: (a) 90/10, (b) 70/30, (c) 50/50, and (d,e) 30/70.
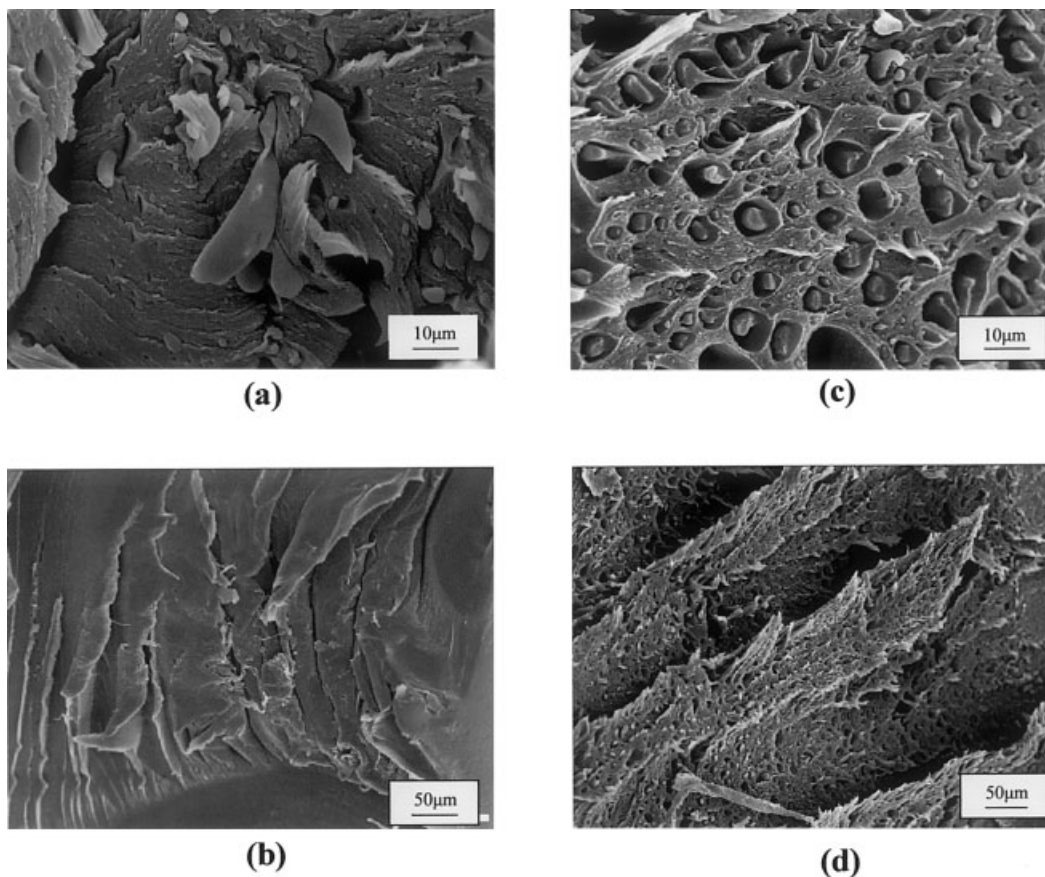
Figure 6 SEM images of PC/PU blends fractured at ambient temperature: (a,b) 90/10 and (c,d) 70/30.

Aging had no effect on the morphology, the high component viscosity preventing any morphological transformation [cf. Fig. 3(e–h)].

SEM

SEM micrographs in Figures 4–6 give additional information on the phase distribution and component adhesion of the fractured surfaces. In Figure 4, the transition from a morphology with a fracture typical of a homogeneously mixed blend [Fig. 4(a)] to an interpenetrating morphology [Fig. 4 (b,c)] to a spherical domain morphology [Fig. 4(d)] is evident. At a higher magnification (Fig. 5), these morphologies are amplified, and in Figure 5(b–e), one can discern the fissures caused by the expansivity mismatch of the two components at cryogenic temperatures. For the 30/70 composition, quite a few of the PC globules were firmly embedded in the PC matrix. In Figure 6, fracturing at the ambient temperature shows a mixed glassy–ductile morphology for the 90/10 composition, the rubbery component being elongated [Fig. 6(a)] but anchored in the glassy matrix [Fig. 6(b)]. In Figure 6(c,d), one can observe that the composite globules of PC, although broken during deformation, remained attached to the PU matrix. Because of matrix

elongation, the dewetting of the PC particles at their equator took place [see the gaps around the inclusions in Fig. 6(c)].

Mechanical properties

Tensile properties

The data and standard deviations for the ultimate properties, including the yield stress (σ_y), are summarized in Table I for blends quenched to 0°C. A large deformation behavior in terms of the tensile strength (σ_b) and, in particular, the elongation at break (ϵ_b), a sensitive indicator of component adhesion in blends, was used to evaluate the mechanical performance and to optimize the mixing conditions. Mixing at temperatures greater than or equal to 260°C resulted in the deterioration of the mechanical properties, and this, as well as the effect of annealing, was discussed in the last section. Annealing led to an enhanced phase separation, which was confirmed by DMA and phase-contrast microscopy. The lower t_{mix} value was adopted because pertinent data showed less scatter and greater t_{mix} values led to higher weight losses in TGA (discussed later). Aging did have an adverse effect on the tensile properties of a PC-rich blend (70/30), possibly the result of phase agglomeration,

TABLE I
Ultimate Tensile Properties of Quenched Blends[a]

PC/PU blend	Mixing temperature (°C)	σ_y (MPa)	σ_b (MPa)	ε_b (%)	Eb (J/cm³)
100/0	—	54 ± 2	63 ± 3	167 ± 16	89 ± 10
90/10	235	47 ± 1	55 ± 7	182 ± 19	82 ± 13
70/30	235	34 ± 3	49 ± 8	200 ± 32	80 ± 12
70/30	240	32 ± 1	43 ± 6	209 ± 77	84 ± 22
70/30	270	32 ± 2	33 ± 2	41 ± 11	14 ± 6
50/50	235	—	33 ± 3	171 ± 15	46 ± 4
30/70	235	—	25 ± 3	243 ± 31	39 ± 6
10/90	235	—	26 ± 3	319 ± 46	37 ± 16
0/100	—	—	56 ± 5	807 ± 130	222 ± 22
70/30[b]	235	34 ± 7	36 ± 7	60 ± 18	18 ± 8
30/70[b]	235	—	18 ± 2	130 ± 44	20 ± 3
70/30[c]	235	33 ± 3	35 ± 3	101 ± 24	30 ± 7
30/70[c]	235	—	26 ± 2	213 ± 52	37 ± 10
70/30[d]	235	33 ± 2	43 ± 4	228 ± 73	92 ± 33
70/30[e]	235	33 ± 2	49 ± 6	211 ± 40	79 ± 8

[a] t_{mix} = 5 min.
[b] Annealed at 150°C for 1 h.
[c] After 40 days of physical aging at 25°C.
[d] t_{mix} = 10 min.
[e] t_{mix} = 15 min.

although microscopy findings did not reveal it. Another possibility is cited later (see the DSC results). In Table I, E_b represents the energy to tensile failure, and it was determined from the area enclosed by the stress–strain curve. It is related to the impact strength, and for a series of similarly prepared blends, it gives the composition dependence of this useful quantity. E_b (or the impact strength) was maintained at a level comparable to that of PC up to approximately 30 wt % PU.

In general, the ultimate properties were characteristic of a polymeric alloy with good component inter-

TABLE II
Viscoelastic and Thermal Properties of Quenched Blends

PC/PU blend	High T_g (°C)	Low T_g (°C)	T_m of PU[h][a] (°C)	T_m of PC (°C)	X_c of PU (%)
100/0[b]	153	—	—	240	—
100/0	155	—	—	—	—
90/10	148	—	—	—	—
70/30	141	25	200	—	10
50/50	147	30	202	—	21
30/70	153	16	175,187,200	—	16
10/90	153	12	177, 188, 203	—	21
0/100	—	3	176, 203	—	22
70/30[c]	148	30	199	—	4
70/30[d]	145	28	—	—	—
70/30[e]	149	−20	201	—	18
30/70[e]	153	−20	203, 218	—	17
70/30[f]	NE	NE	200	—	11
30/70[f]	NE	NE	175, 187, 202	—	21
70/30[g]	132	3	—	235	i
30/70[h]	—	18	202	220	21

NE = not examined.
[a] ΔH_f^0 of (PU) = 5.83 cal/gr.
[b] After treatment with $CHCl_3$.
[c] t_m = 10 min.
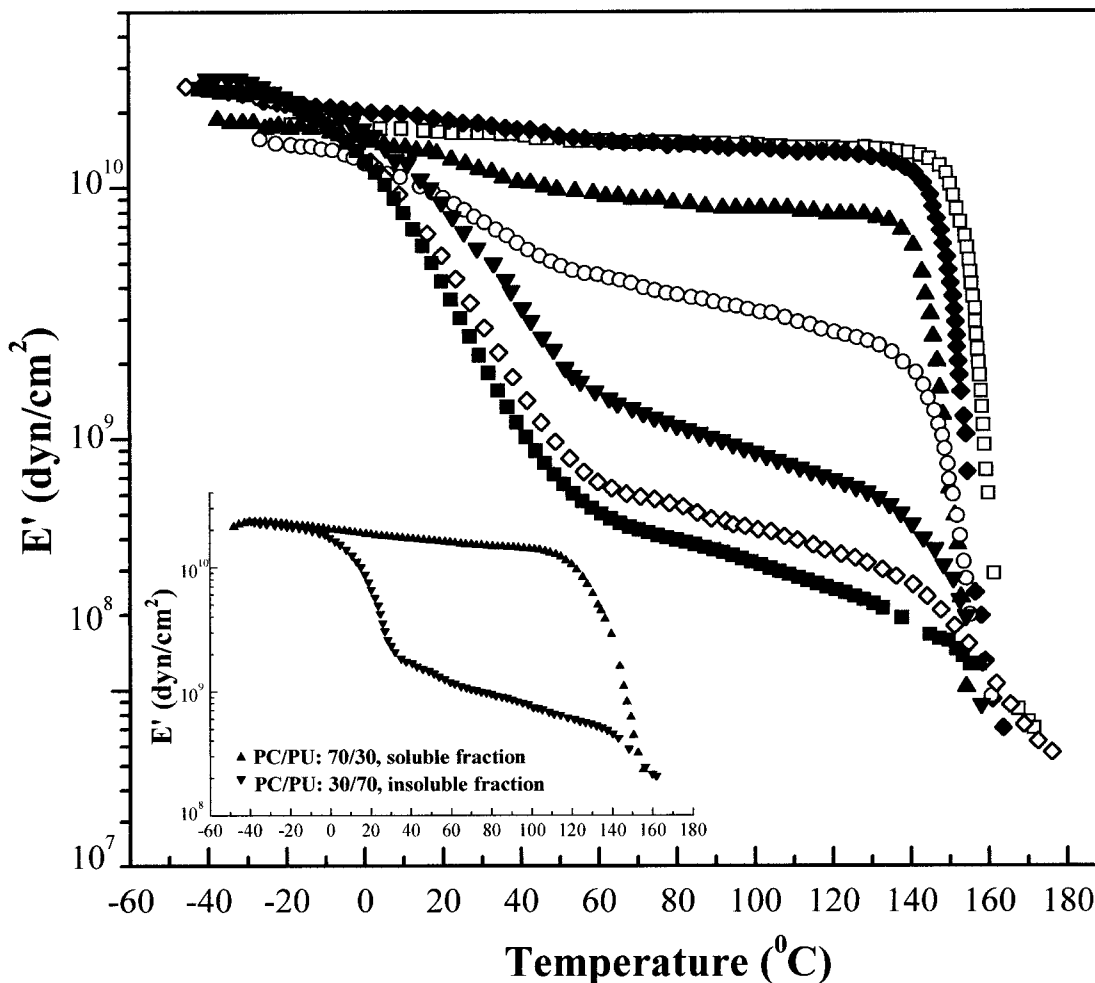[d] t_m = 15 min.
[e] After annealing at 150°C for 1 h.
[f] After 40 days of physical aging at 25°C.
[g] Soluble fraction.
[h] Insoluble fraction.

Figure 7 Temperature dependence of E' for PC/PU blends: () 100/0, () 90/10, () 70/30, () 50/50, () 30/70, ($\diamond$) 10/90, and () 0/100. The inset shows E' for leached blends: ($\blacktriangle$) 70/30, soluble fraction, and ($\blacktriangledown$) 30/70, insoluble fraction.

face adhesion (see the ϵ_b percentage data). The drop at the median compositions was expected for nonmiscible blends and was attributed to matrix inversion.

Dynamic mechanical properties

DMA data for blends may provide information about the degree of polymer–polymer interactions and interphase mixing.

The main relaxations (T_g) of the blends are reported for various compositions in Table II. Figures 7 and 8 give the DMA spectra under isochronous conditions for the storage modulus (E') and loss modulus (E''), respectively, for quenched blends at t_{mix} = 5 min. Both primary relaxations are present, although they converge toward each other as the composition changes. Overall, the spectra are typical of a phase-separated polymeric alloy. In general, the shift in the polyurethane glass-transition temperature ($T_{g,PU}$) is more significant than the shift for the polyester. The addition of PU flexibilized PC at PU concentrations greater than 10 wt % (see Fig. 8). At compositions with greater than

50 wt % PU, the polycarbonate glass-transition temperature ($T_{g,PC}$) reversed its trend, approaching the T_g value of the pure component. This was corroborated by the morphology findings (va), which revealed phase-separated PC domains (see Fig. 1). The insets in Figures 7 and 8 refer to the spectra of blends in which one of the components was removed. The T_g shifts for both components persisted (see also Table II). This is relevant for explaining the compatibilization process (see the Discussion section).

Increasing t_{mix} beyond 5 min did not lead to a further $T_{g,PC}$ decrease. Apparently, the degree of dispersion on the T_g scale was not improved.

Annealing mainly reduced $T_{g,PU}$, and this was possibly the effect of enhanced crystalline–amorphous phase separation of the PU component (see Table II and Figure 9). It is expected that when crystalline blocks are closely intermingled with amorphous segments, the T_g value of the amorphous phase will be raised. This was the case for the quenched specimens for which T_g was approximately 3°C (see Table II). This effect of the thermal history on T_g was also re-
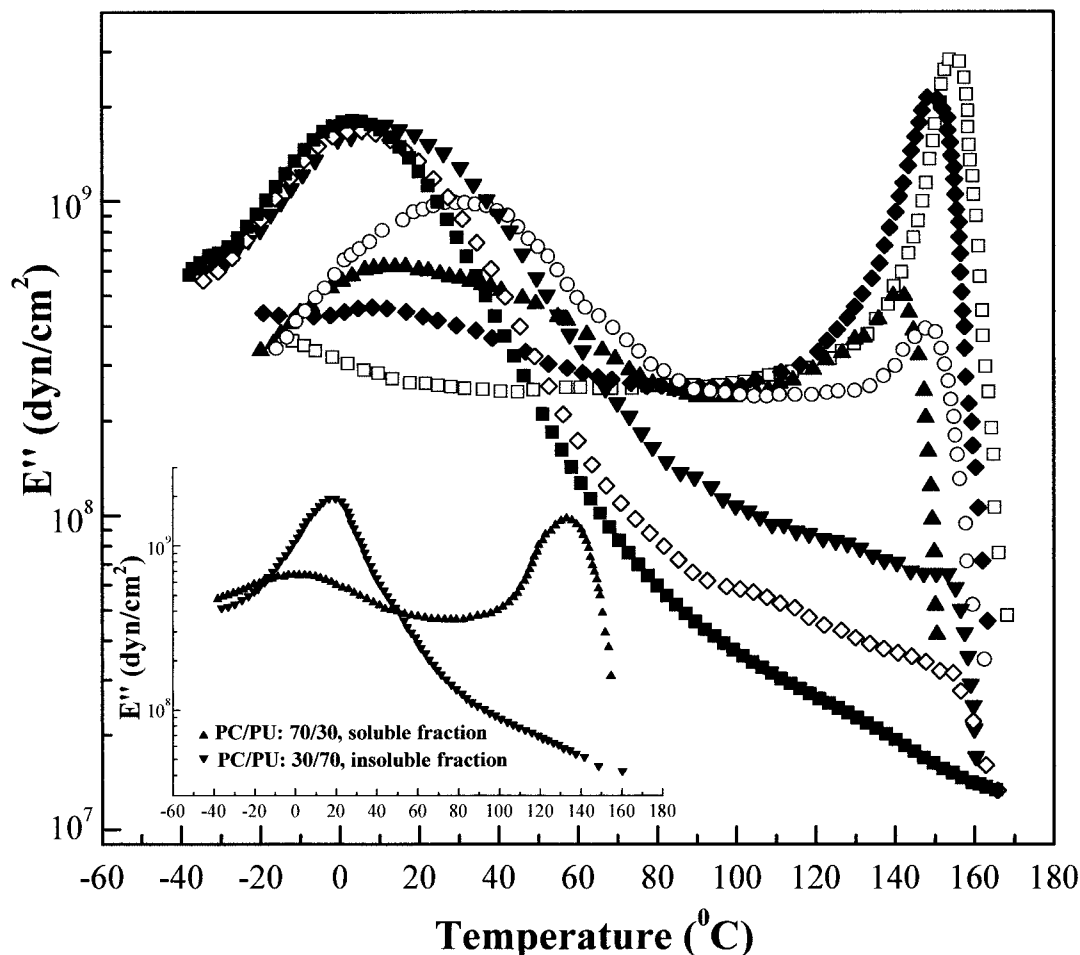
Figure 8 Temperature dependence of E'' for PC/PU blends: () 100/0, () 90/10, () 70/30, () 50/50, () 30/70, ($\diamond$) 10/90, and () 0/100. The inset shows E'' for leached blends: (▲) 70/30, soluble fraction, and (▼) 30/70, insoluble fraction.

ported for PU[12] and poly(ether ester) copolymers that also had short crystalline–amorphous sequences along their main chains.[13]

Thermal properties

DSC results

The DSC results are summarized in Table II and were obtained during the first heating scan. PU crystallized slowly, giving a multiplicity of endotherms depending on the thermal history and rate of heating, the highest melting temperature ($T_m = 203°C$) corresponding to the most perfect crystal. At a high dilution (90/10) in a medium (PC) of high viscosity, crystal formation was suppressed, so no T_m and no bulk crystallinity (X_C) were detected. In compositions in which the phases were separated, crystallinity began to develop, and T_m was slightly depressed; this attested to a lesser degree of crystal perfection (70/30 blends). At higher PU contents, when matrix inversion took place and PC composite domains were formed, crystallinity development was less hindered, but PU

crystallite perfection was less readily attained, endotherm multiplicity being the rule. Physical aging did not affect X_C of a PC-rich blend (70/30), and so its effect on mechanical properties (va) could be attributed to an amorphous-phase densification. The effect of t_{mix} in suppressing crystallinity was significant for the 70/30 blends; no X_C and T_m values were detected after $t_{mix} = 15$ min. The fraction of the blend soluble in $CHCl_3$ gave a $T_{m,PC}$ value caused by solvent-induced crystallization.[7] For the 30/70 blends, the phase separation of PC allowed crystallinity to be developed at a level comparable to that of PU. In general, the multiplicity and overlapping of endotherms did not allow a very accurate determination of X_C of PU. Therefore, the importance of the X_C values cannot be overemphasized.

TGA results

Figure 10 summarizes the results of TGA for the 70/30 blends ($t_{mix} = 5$ or 10 min) under isothermal conditions (235°C).
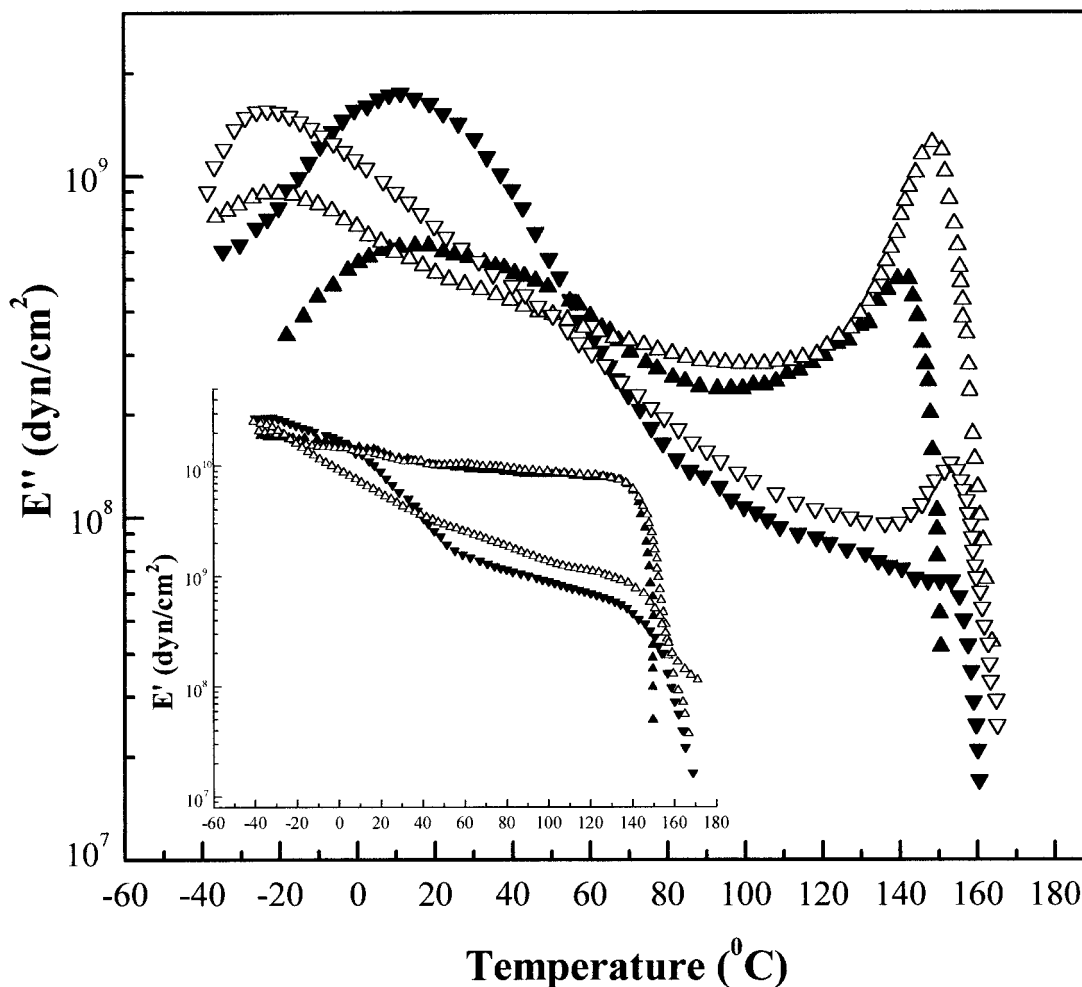
Figure 9   Effect of annealing on E'' for PC/PU blends: () 70/30, quenched; ($\triangle$) 70/30, annealed; () 30/70, quenched; and (∇) 30/70, annealed. The inset shows E''.

PC remained practically stable at this temperature, but there was significant chain scission in PU, as shown by the observed weight loss, which, in principle, could lead to reactive compatibilization. Moreover, the 70/30 blends with $t_{mix} = 5$ or 10 min showed considerably higher weight losses. This indicated that the materials obtained after blending behaved differently than expected for a physical mixture of the two components, supporting the view that interchain reactions occurred during the blending process (see the last section). The higher PU loss in the blends in comparison with pure PU was previously invoked[5] as evidence for reactive compatibilization.

Spectroscopy

1H-NMR

To obtain evidence for possible trans reactions between PC and PU during blending, we compared 1H-NMR spectra of the pure components with the spectra of the 70/30 and 30/70 blends before and after

selectively leaching out one blend component with CHCl3. The spectra of the nonleached blends did not show any additional features or shifts. The spectra of the leached blends were expected to reveal possibly the incorporation of the soluble partner (PC) into the insoluble PU or any chemically formed species (see Fig. 11).

A comparison of the PU and PC spectra with those of the leached blends (70/30 and 30/70, insoluble fractions) indicated that in both compositions, although much of the PC was removed, there were still peaks at 1.73 (methyl protons) and 7.30 ppm (aromatic protons), which were characteristic of its presence.

A quantitative analysis of these spectra showed that for the PU-rich blend (30/70), the insoluble residue after extraction had a 20/80 composition, whereas for the 70/30 blend, the remaining residue had a 50/50 composition. A similar examination of the soluble fraction of the 30/70 blend revealed that a small amount of PU was solubilized together with PC and in excess of the unmodified PU (ca. 1 wt %) determined
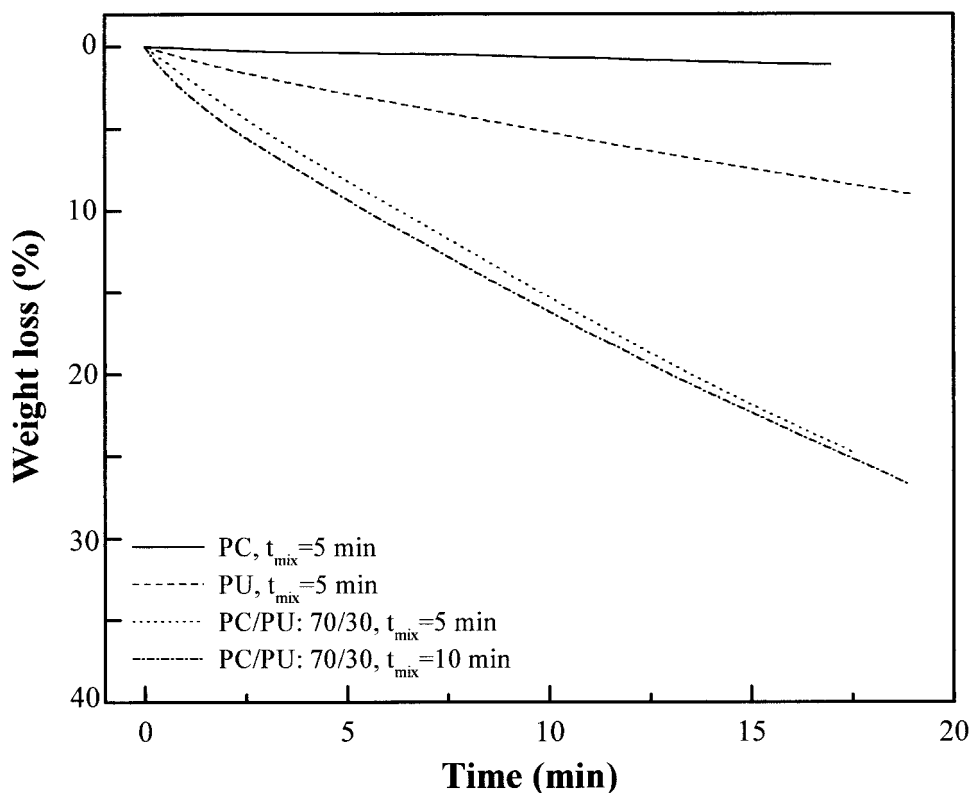
Figure 10   TGA results for (—) PC, t_{mix} = 5 min; (–) PU, t_{mix} = 5 min; (· · ·) 70/30 PC/PU, t_{mix} = 5 min; and (- · -) 70/30 PC/PU, t_{mix} = 10 min (isothermal conditions, 235°C).

by separate experiments. This implied the formation of a PC–PU copolymer corresponding to approximately 3 wt % PU (based on the total amount of the extract).

FTIR

FTIR spectra of blends with various compositions did not reveal any new absorptions or any differentiation in the spectral region associated with intramolecular hydrogen bonding at 3332 cm^{-1} due to the PU imide–ester group interaction.[1] Therefore, the proposition that compatibilization is attained via hydrogen bonding between urethane and carbonate groups is not substantiated by this technique because this intermolecular bonding would also alter the spectrum in the aforementioned region.

As before,[1] to obtain evidence for possible reactive compatibilization via copolymer formation, we freed the 70/30 and 30/70 blends from PU by prolonged extraction with CHCl$_3$ to obtain soluble PC in the extract. In Figure 12, the absorption of the —C=O group of PC films in the range 1760–1790 cm^{-1} is shown to be altered and seems to be coupled with the amide I conformation of —C=O and —NH groups[14] of PU in the range 1690–1745 cm^{-1}. This may support

a chemical modification of the PU chain during mixing or the existence of traces of PU or modified PU in the extract (va).

DISCUSSION

The morphology findings and large deformation mechanical behavior support the view that melt-mixed PC/PU blends form polymeric alloys over the complete composition range. At high PC contents (90/10), both optical microscopy and SEM revealed a high degree of dispersion. Increased amounts of PU ($\geq$50 wt %) gave composite inclusions of PC, as observed previously.[1,2]

In our previous work,[1,2] conclusive evidence was presented to support the view that PET and PBT during melt mixing were reactively compatibilized with TPUs. Both FTIR and ^{1}H-NMR gave evidence for copolymer formation, the result of ~NCO groups reacting with the aliphatic terminal —OH of PET or PBT. In this system, the available —OH of PC was aromatic; its reactivity with the terminal ~NCO groups (obtained by scission of the PU chain) was lower than that with the aliphatic —OH.[15] In addition, the copolymer that formed according to the following reaction

Figure 11   NMR spectra of leached PC/PU blends: (a) pure PC; (b) pure PU; (c) 70/30 PC/PU, insoluble fraction; and (d) 30/70 PC/PU, insoluble fraction.

Figure 12 FTIR spectra of the leached PC/PU blends (soluble fractions).

(1)

was stated to be unstable.[16] Therefore, the low reactivity and thermal instability reduced the amount of the ester–amide copolymer that could form. Moreover, as Table I indicates, an increased temperature of mixing lowered drastically the tensile properties of the blends. Annealing also had an adverse effect on these properties and promoted phase separation, as DMA and optical microscopy indicated. In addition, if reactive compatibilization proceeded via reaction (1), as shown in our previous study,[1] no modification of the spectrum by the aromatic protons was expected because no change in the environment took place on account of the formation of the PC–PU copolymer. However, there was other evidence that suggested that a copolymer might form:

1. ^{1}H-NMR spectra of leached blends showed the presence of the leached-out component (PC) in the insoluble fractions as well as the presence of some modified PU (possibly as a copolymer) in the extract (va).
2. These findings agreed with selective extraction experiments with CHCl$_3$ for the removal of any free (not bonded to PU) PC from the blends. Therefore, in the 30/70 blends, the insoluble residue had a composition of 14/86; ^{1}H-NMR gave a 20/80 ratio. Similarly, for the 70/30 blends, the residue after extraction had a composition of approximately 60/40 versus 50/50 from ^{1}H-NMR. One cannot attach a high degree of accuracy to these determinations because a small percentage of PU homopolymer and some PC–PU copolymer were also leached with the unattached PC (va).
3. More evidence was provided by DMA, which indicated that the main component relaxations converged and that these shifts were maintained even after the extraction and removal of one component (PC; see Table II). The small amount of

PU that might have been mixed with PC in the extract could not account for the $T_{g,b}$ shifts observed. Compatibilization based on intermolecular forces (e.g., hydrogen bonding) could not be adopted because the evidence from FTIR did not substantiate it. Therefore, some chemical modification of the blend partners was involved.

4. As mentioned previously, TGA also provided indirect evidence for enhanced PU reactivity in the presence of PC (va).

The other possibility for PC reacting with PU via a transesterification reaction was not substantiated by FTIR. Had this been the case, the absorbance ratio of the peaks at 1780 and 1760 cm^{-1} would have been altered.[17] This was not observed. However, this is only a tentative conclusion, and further work is needed to arrive at a definite statement.

CONCLUSIONS

PC/PU blends were compatibilized by melt mixing via a route similar to that described previously,[1,2] that is, the formation of a copolymer combining polyester and PU segments. For reasons cited previously, the concentration of this copolymer was quite low. Therefore, a lower degree of compatibilization was attained for the PC/PU blends in comparison with the PET/PU and PBT/PU blends. Although formed at low levels, this copolymer could be effective as a compatibilizer by reducing the interfacial tension of the blend components, thereby facilitating their dispersion and promoting the compatibilization process.

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