Blends of polycarbonate and polyacetal

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Immiscible blends of polycarbonate (PC) and polyacetal (polyoxymethylene, POM) were investigated through rheological measurements, tensile, impact, TEM, SEM, FTi.r. and thermal analysis. The large difference in melt viscosities between these two matrix polymers makes this blending system extremely difficult to process and results in partial thermal degradation of POM. The formation of a strong interpenetrating interface in PC/POM blends significantly raises tensile yield strength, modulus and heat distortion temperature above the average values for the individual polymers. Thermoplastic polyurethane elastomer is not very efficient in toughening PC/POM blends because the elastomer distributes selectively in the PC phase. The rheological morphologies of the blends are interpreted through TEM and SEM photomicrographs.

INTRODUCTION

Research into polymer blends normally involves matrix polymers that are easily available from commercial sources. Polycarbonate and polyacetal are two major engineering thermoplastics which are readily available. Blends of the amorphous polycarbonate and the crystalline polyacetal would appear to be of great interest from both the academic and commercial point of view. However, literature relating to this seemingly attractive pair is unexpectedly scarce. Blends of polycarbonate and polyacetal did appear in an early US patent[1] claiming improved resistance to environmental stress crazing and crack. This patent[1] only mentioned compositions of 50% POM or less and gave limited data on Izod impact, heat distortion temperature and solvent resistance time to failure. This suggests that difficulties were encountered in bringing together this pair of polymers. The present study anticipated some potential problems and did experience some POM degradation, especially during injection moulding. Thermal degradation of polyacetal was encountered during extruder mixing, injection moulding and rheological measurements, with very narrow processable conditions for injection moulding. Thermoplastic polyurethane (TPU) elastomer has been reported[2,3] to improve polyacetal toughness and was selected to toughen the PC/POM blend. This paper presents results for blends of polycarbonate and polyacetal in terms of rheological, morphological and mechanical properties.

MATERIALS AND EXPERIMENTAL PROCEDURES

The materials used in this study were polyacetal (Celcon M 90, Hoechst Celanese), polycarbonate (Calibre 300-22, Dow Chemical Company) and polyurethane elastomer (Elastollan R S90A50, Elastogran). For melt blending a 30 mm single screw extruder ($L/D = 20$) was used and for specimen preparation an Arburg model 270-210-500 injection moulder.

The melt blending was carried out in a specially designed single screw extruder with a temperature range from 180 to 215°C depending upon the compositions. Tensile and flexural (Izod) specimens were prepared by injection moulding under the conditions given in *Table 1*. In order to investigate the deformed phase morphology under tensile stress at break, SEM examination was carried out on the cryogenically fractured specimens at the plane parallel to elongation. An instrumented falling weight impact tester, capable of recording load *versus* time (or displacement), was used to study the impact properties of the Izod type notched specimens; this was essentially identical to the Izod impact test. Microtomed thin sections of the injection moulded specimens perpendicular to the flow direction were stained in osmium tetraoxide (OsO_4) solution prior to TEM examination.

Rheological properties

The flow curves at 230°C for PC, POM and various PC/POM blends are shown in *Figure 1*. The dependence of viscosity on composition of the blends is shown in *Figure 2* for a temperature of 230°C. The presence of 20 and 40% POM significantly decreases PC viscosity to 30 and 20% respectively of its original value at all levels of shear rates. The lubricating effect of the dispersed POM in matrix PC significantly improves the blend processability. The presence of PC in POM up to 50% causes only slight viscosity increase over the POM matrix. Viscosity at 240°C (data not shown) is similar to that at 230°C and the lubricating effect at this temperature is even more pronounced for the blend containing 20% POM. The flow behaviour of the blends is further supported by the morphological structure of the blends determined by later morphological investigations.

Table 1 Injection moulding temperatures[a]

				Temperature (°C)			
	PC	80% PC	60% PC	50% PC	40% PC	20% PC	POM
Zone 1	250	230	220	210	210	195	185
Zone 2	260	260	250	225	225	210	190
Zone 3	260	265	270	235	235	215	200
Die	270	270	265	250	250	220	200
Mould	80	80	80	70	70	70	50

[a]These were temperatures set for operation and not the real temperatures
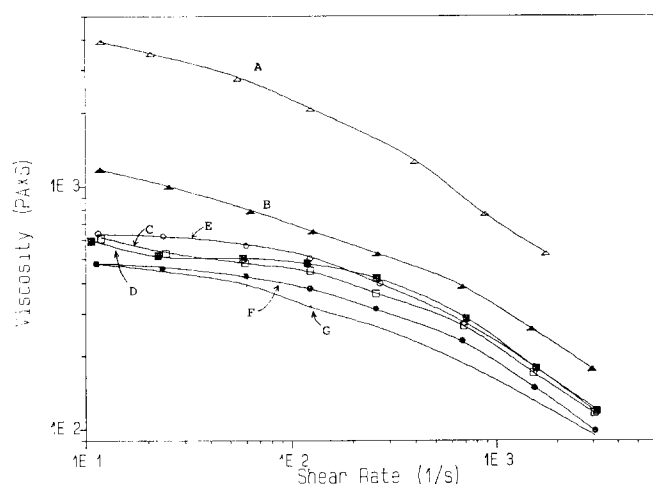

Figure 1 Viscosity *versus* shear rate for PC, POM and PC/POM blends at 230°C. Curve A, PC; B, 80% PC; C, 60% PC; D, 50% PC; E, 40% PC; F, 20% PC; G, POM
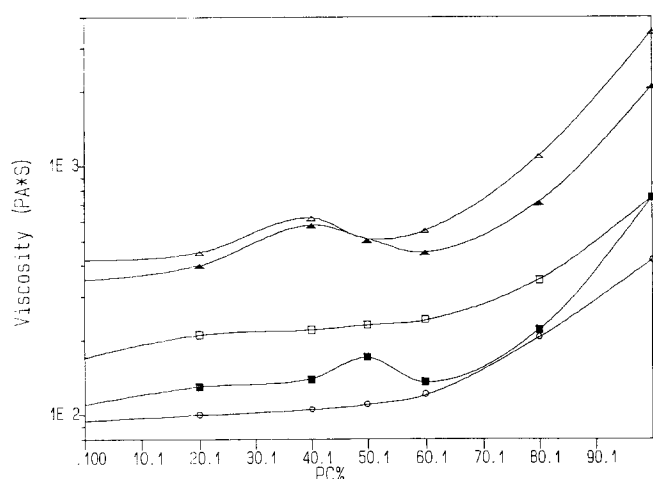

Figure 2 Viscosity *versus* composition at different shear rates at 230°C. Shear rate: △, 20; ▲, 100; □, 1000; ■, 2000; ○, 3000 s⁻¹

Figure 3 Tensile stress *versus* strain curves for PC/POM blends. Curve A, PC; B, PC/POM = 80/20; C, PC/POM = 60/40; D, PC/POM = 50/50; E, PC/POM = 40/60; F, PC/POM = 20/80; G, POM

Tensile and flexural properties

Figure 3 and *Table 2* summarize the tensile and flexural properties for PC, PC/POM blends and POM. *Figure 4* shows the scanning electron photomicrographs parallel to elongation for the tensile specimens at breaking. The SEM morphology of the 80% PC blend (*Figure 4b*) is totally different from the pure PC (*Figure 4a*) showing some fibrillar drawing. The 60% PC blend (*Figure 3*, curve C) has much higher yield stress and modulus than either PC or POM and the corresponding SEM (*Figure 4c*) shows much more fibrillar structure. Such fibrillar
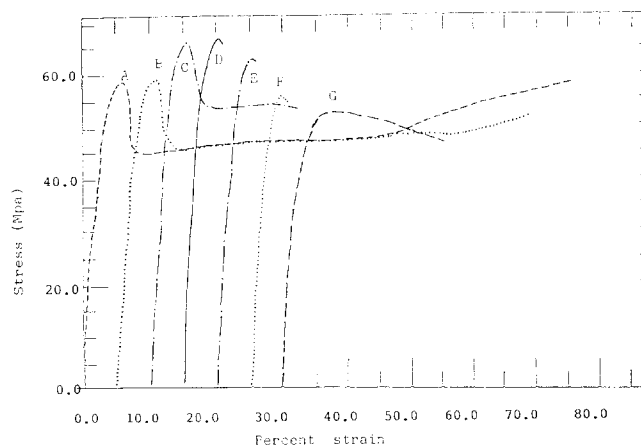
structure occurs most readily when both phases are near cocontinuous. The 50% PC blend is very similar to the 60% PC in yield stress and modulus but shows far less fibrillar structure. The blends with 40 and 20% PC (*Figure 3*, curves E and F and *Figure 4f* and *g*) have higher yield stress and less elongation than POM but no sign of the fibrillar structure. The synergistic effect in yield strength and modulus can be attributed to the formation of a strong interpenetrating interface which is very similar to the strongly reinforcing fibre between two phases. Since both matrix polymers possess different yield stress and yield strain, this strong interface layer will carry maximum shear stress at high elongation, when both matrix phases are cocontinuous. The shear stress finally reaches a point (when the tensile stress is higher than yield stresses of both matrices) at which shear yield of the interfacial layers occurs forming the observed fibrillar structure. Therefore the maximum deviation for the tensile yield stress and modulus is in the composition range of 40–60% PC where both phases are near cocontinuous. Flexural properties of the blends show similar trends to the tensile properties, as shown in *Table 2*.

Izod impact properties

The impact properties as a function of composition (*Figure 5*) show similar trends to the tensile ductility but in general are less than the previously reported values[1]. The lower molecular weight PC (MFR = 22) employed in this study to reduce melt viscosity is responsible for the difference. The lower molecular weight PC has higher
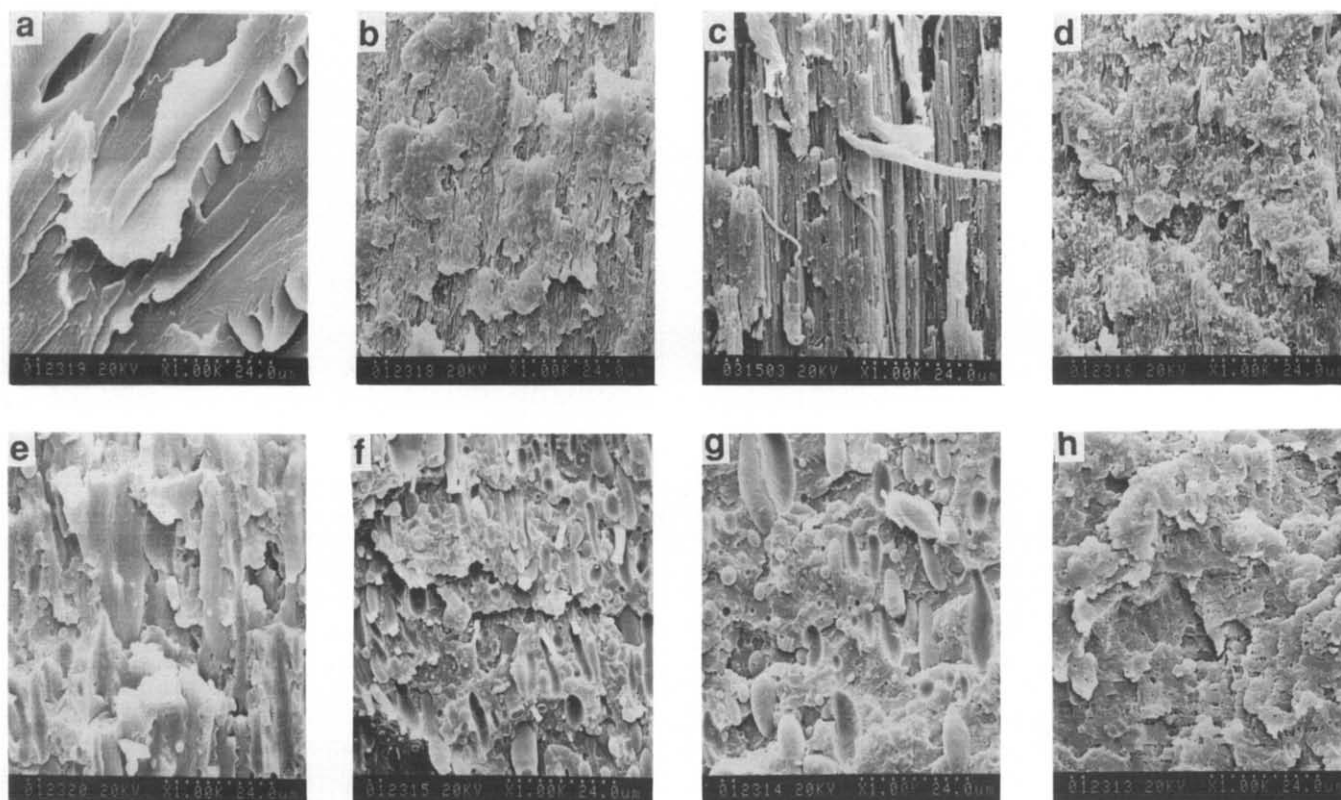
Figure 4 Scanning electron photomicrographs parallel to elongation of the tensile specimens elongated to break. (a) PC; (b) PC/POM = 80/20; (c) PC/POM = 60/40; (d) PC/POM = 50/50; (e) PC/POM/TPU = 45/45/10; (f) PC/POM = 40/60; (g) PC/POM = 20/80; (h) POM

Table 2 Tensile and flexural properties

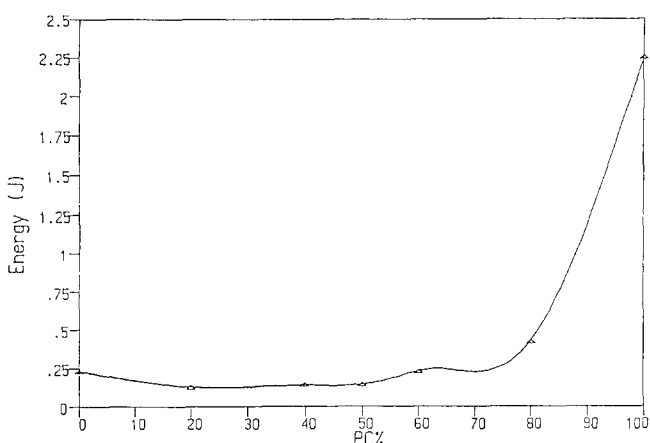| Sample	Tensile			Flexural	
	Yield stress (MPa)	Modulus (MPa)	Elongation (%)	Yield stress (MPa)	Modulus (MPa)
PC	57.10	2437	160.0	80.0	2752
PC/POM = 80/20	59.20	2491	140.4	73.5	2846
PC/POM = 60/40	65.95	2983	47.4	78.4	3108
PC/POM = 50/50	66.59	2940	15.5	89.0	3289
PC/POM/TPU = 45/45/10	52.11	2156	31.3	71.0	2179
PC/POM = 40/60	61.9	2916	13.0	86.8	3525
PC/POM = 20/80	55.8	2812	13.7	77.8	3412
POM	52.1	2818	55.0	69.7	2580

Figure 5 1/8 in Izod impact energy for PC/POM blends in ambient conditions

ductile–brittle transition temperature as previously reported[4]. As the more ductile component in the blends, PC is the key contributor in the blend impact ductility and PC as a continuous phase is important to maintain such toughness. The presence of the brittle POM reduces the PC notched impact strength as expected. The presence of 10% TPU elastomer in the 50/50 PC/POM blend increases the impact energy only slightly, from 0.14 to 0.22 J. Ductile–brittle transition occurs only for the blends in which PC is the continuous phase (*Figure 6*). The notched POM specimen is highly rate sensitive with a ductile–brittle transition rate of less than 1 mm min^{-1} (refs 2, 3). Therefore, the blends with POM as continuous phase are also rate sensitive as expected.

The SEMs of the ambient fractured surfaces for PC, selected PC/POM blends and POM are shown in *Figure 7*. It is interesting to notice that the spheroidal droplets
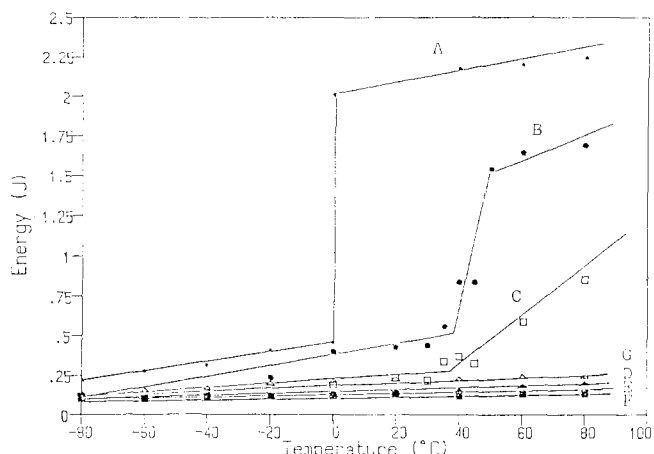
Figure 6 1/8 in Izod impact energy for PC/POM blends at different temperatures. Curve A, PC; B, PC/POM = 80/20; C, PC/POM = 60/40; D, PC/POM = 50/50; E, PC/POM = 40/60; F, PC/POM = 20/80; G, POM
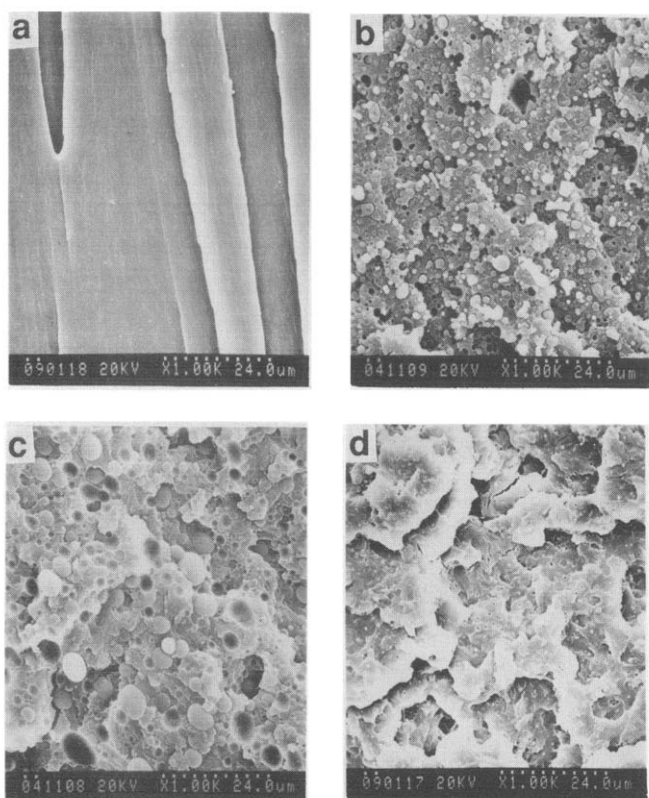

Figure 7 Scanning electron photomicrographs of the Izod impact fractured surfaces at ambient conditions for PC/POM blends. (a) PC; (b) PC/POM = 40/60; (c) PC/POM = 20/80; (d) POM

from the 20% PC blend (*Figure 7c*) are significantly larger than from the 40% PC blend (*Figure 7b*). The injection moulding temperature of the 40% PC blend was about 20°C higher than the blend with 20% PC as shown in *Table 1*. The viscosity ratios of PC/POM at shear rates of 3000 s^{-1} are 3.1 and 4.5 at 240 and 230°C respectively. Wu[5] studied in detail the formation of dispersed phase in blends of incompatible polymers and found that the dispersed drop size is directly proportional to the interfacial tension and to the + 0.84 power of the viscosity ratio. The interfacial tension can be assumed to be equal in this study since the same pair of matrix polymers has been used. Therefore, the unexpected dispersed drop size

can be attributed to the change in viscosity ratio by processing at different temperatures.

Instrumented falling weight impact

The commonly used standard Izod (or Charpy) test gives a single composite fracture energy and the energies required for crack initiation and propagation cannot be isolated. The load *versus* time (displacement) curves obtained from the instrumented falling weight impact tests for the PC/POM blends and POM are shown in *Figure 8*. All the blends fracture in brittle mode as seen from the impact energy and a nearly triangular shaped load–unloading form with insignificant propagation energy. The matrix PC (curve not shown) fractures in ductile mode with much greater impact energy and with both initiation and propagation energies. The impact energies obtained from the instrumented falling weight impact are fairly consistent with the results previously obtained from Izod impact testing. It is interesting to notice that the relative moduli of PC and 80% PC, derived from the load displacement (which is necessary to calculate K_c from G_c through $K_c^2 = G_c E$) are higher than POM, while the tensile modulus reverses the order. The strain rate at the notch tip is considerably higher and has been estimated[6] to be 1000 times greater than the impact rate. The local strain rates involved in the notched impact test are highly complex and vary according to the location of the specimen. The modulus and yield stress of polymeric matrices in response to different strain rates are the fundamental properties of the viscoelastic materials.

Thermal properties

Most blends significantly raise the heat distortion temperature above the line of additivity (*Table 3*). These results show very similar trends to the tensile modulus, with the maximum increase occurring in the range of 40–60% PC where the blends are near or in cocontinuous structure. This is probably due to the strong interpenetrating interfacial layers acting like reinforcing fibres, as previously described for the tensile properties.
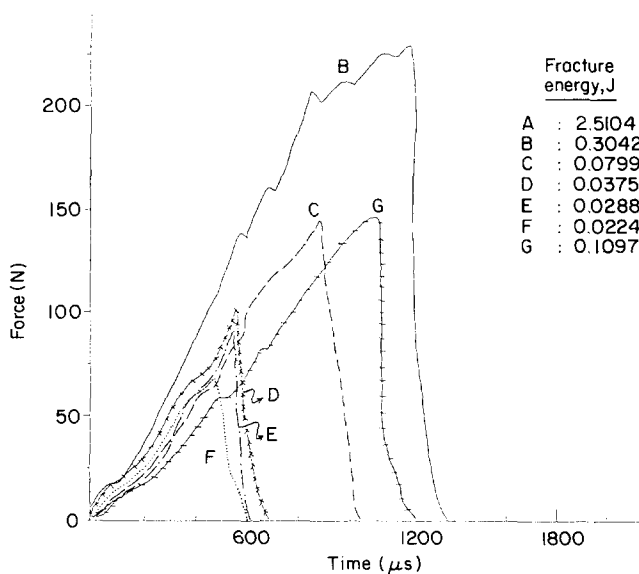

Figure 8 Plots of load *versus* time from the instrumented falling weight impact tests for PC/POM blends. Curve A, PC; B, PC/POM = 80/20; C, PC/POM = 60/40; D, PC/POM = 50/50; E, PC/POM = 40/60; F, PC/POM = 20/80; G, POM

Table 3 Density and thermal properties of PC/POM blends

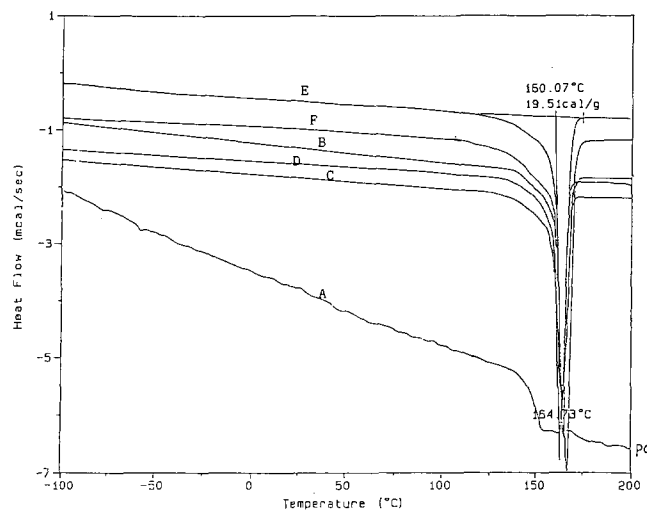| Sample	Density (g ml^{-1})	HDT, 264 psi (°C)	T_m or T_g (°C)	Melt heat (cal g^{-1})
PC	1.385	130.7	149.7 (T_g)	–
PC/POM = 80/20	1.337	123.8	164.1	5.88
PC/POM = 60/40	1.306	124.6	164.4	13.88
PC/POM = 50/50	1.276	131.8	165.3	18.48
PC/POM/TPU = 45/45/10	–	112.7	–	–
PC/POM = 40/60	1.240	124.0	164.7	19.50
PC/POM = 20/80	1.215	119.4	165.2	25.83
POM	1.191	107.1	167.4	35.79

Figure 9 D.s.c. thermograms for PC/POM blends. Curve A, PC; B, PC/POM = 80/20; C, PC/POM = 60/40; D, PC/POM = 50/50; E, PC/POM = 40/60; F, POM
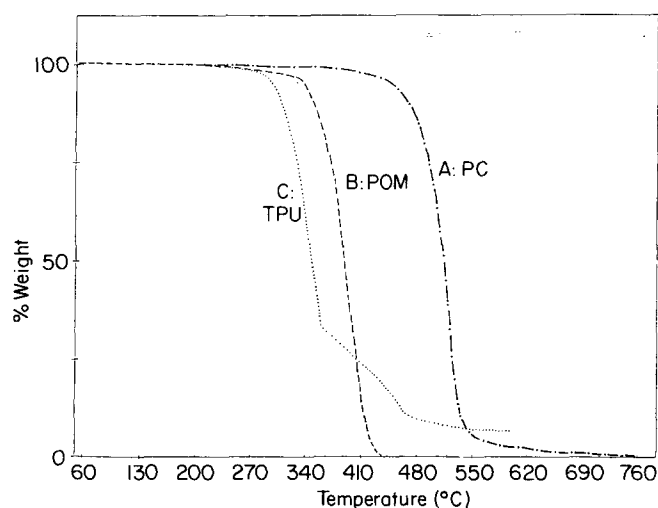
Figure 10 Weight loss *versus* temperature in air. (A): PC; (B): POM; (C): TPU

Figure 9 illustrates the d.s.c. thermograms of PC, POM and various PC/POM blends. The shift of POM melting temperature of the blends is in the range of 2–3°C and the heat of melting based on POM content is unchanged (*Table 3*). Thermogravimetric data on PC, POM and TPU are illustrated in *Figure 10*. The thermal decomposition temperature for PC is about 120°C higher than that for POM which explains the decomposition of the POM component during melt processing.

Density

The density *versus* composition plots for the phase-separated blends would be expected to exhibit linear behaviour. Many miscible polymer blends, however, show greater densification than that expected from an additivity relation. Density data for the PC/POM blends of the injection moulded products are given in *Table 3* and show an additivity relation.

Transmission electron microscopy

Due to the high spatial resolution and the small scale morphological structure, transmission electron microscopy (TEM) has become an essential tool to investigate the morphology of multiphased polymer systems. OsO$_4$ is often employed to stain rubbers containing double bonds and is normally applicable only to polymers containing double bonds[7] or other reactive sites. However, in this study of the PC/POM multiphase system, staining with OsO$_4$ solution resulted in satisfactory contrast in phase resolution even in the three-component blend (*Figure 11*). Due to their differential chemical structures, PC and POM stain at different rates thus enabling the phases to be distinguished. As in the PC/PBT blending system previously reported[8], PC is stained at a faster rate than POM because the aromatic rings substituted by electron-donating groups are readily oxidized. *Figure 11a* illustrates the TEM morphology of PC/POM = 80/20 where the POM phase exists in the form of elliptical droplets. As the POM content in the blend is increased to 40% (*Figure 11b*), the POM phase, although still a minor component, exists as near cocontinuous with the more viscous PC phase. The component with the lower viscosity tends to encapsulate the more viscous component during mixing[9], since this reduces the rate of energy dissipation.

The TPU elastomer distributes exclusively in the PC phase in the three-component blend. Relative affinity between PC/TPU and POM/TPU dictates the final location of the TPU elastomer in the blend. TPU is an excellent toughening agent for POM[2,3] but is less effective for polycarbonate[10]. The TPU elastomer selectively distributing in the PC phase instead of the brittle POM phase probably explains why it is inefficient as a toughening agent for the PC/POM blend. The phase distribution of an elastomer in a two-matrix blending system is very important in studying the rubber-toughening mechanism, but only a few studies have been reported. It has recently been reported[11] that impact modifier distributes exclusively in the PC phase in a PC/PBT blend. As pointed out earlier, the blend with higher PC content (*Figure 11e*) has a smaller droplet size
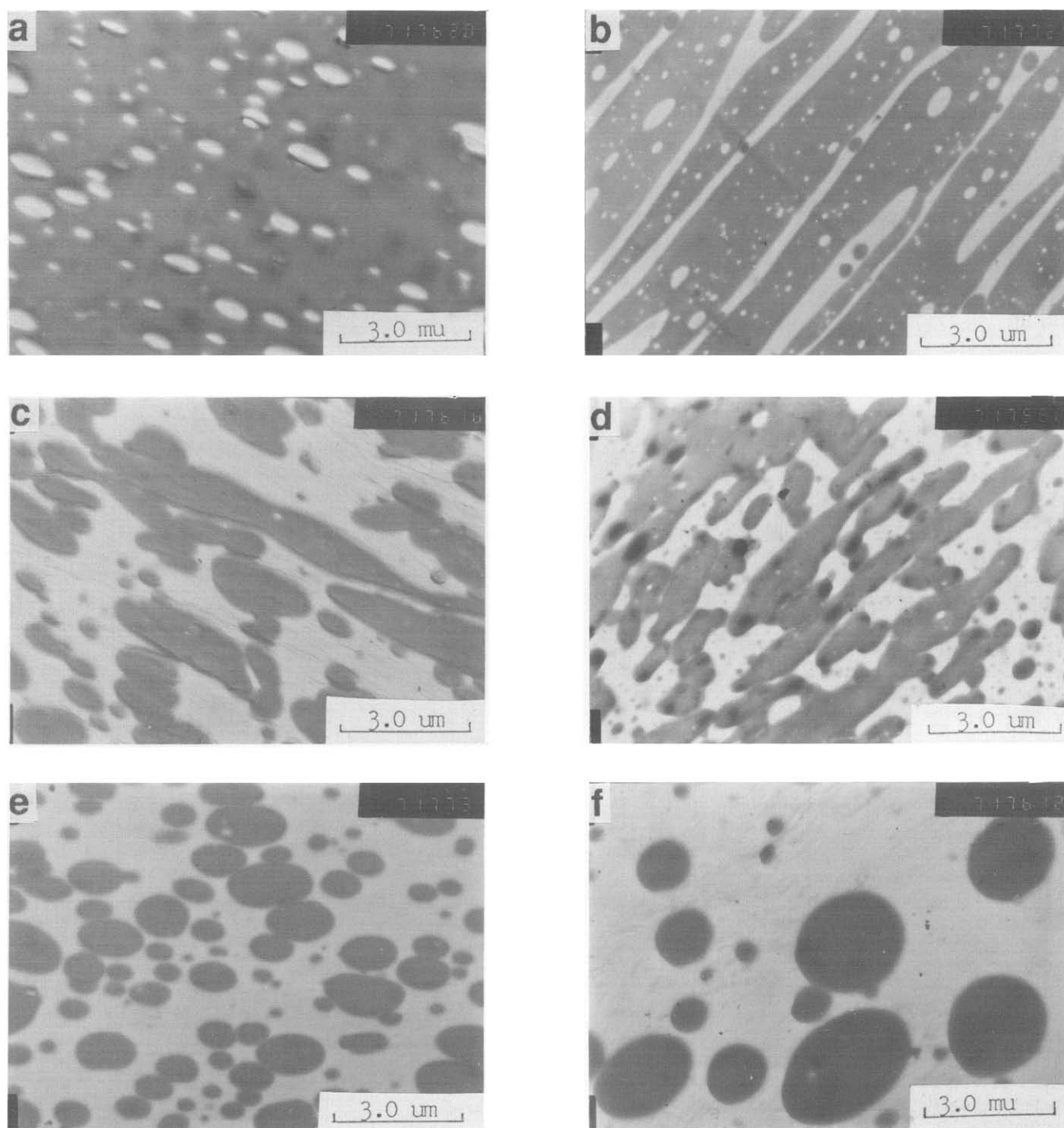
Figure 11 Transmission electron photomicrographs for PC/POM and PC/POM/TPU blends normal to flow direction. (a) PC/POM = 80/20; (b) PC/POM = 60/40; (c) PC/POM = 50/50; (d) PC/POM/TPU = 45/45/10; (e) PC/POM = 40/60; (f) PC/POM = 20/80

than the blend with lower PC content (*Figure 11f*) due to a change in viscosity ratio by processing at different temperatures (*Table 1*). The size of the dispersed phase is determined by the drop breakup[12] and coalescence[13], which are governed by the deformation field imposed by the mixing device, interfacial tension, and the rheological characteristics of the components.

Fourier transform infra-red spectroscopy

FTi.r. has become a powerful tool to study polymer blend miscibility. If immiscible, the absorption spectrum of the blend will be the sum of those for the components. If the blend is miscible or partially miscible, specific

interactions between the two components disrupt the bonding between atoms, and a difference is seen in the spectrum of the blend compared to the sum of those for the components. The *FTi.r.* investigation of a miscible blend not only reveals the presence of an interaction, but also provides information on which groups are involved in interaction. Since POM is very difficult to dissolve in solvents for film casting, multiple internal reflection attachment (a.t.r.) was employed (*Figure 12*). The surface of an injection moulded specimen may deviate from true composition quite significantly for some matrix pairs, due to the viscosity difference during injection moulding. By comparing the blend PC/POM = 50/50 (*Figure 12*,
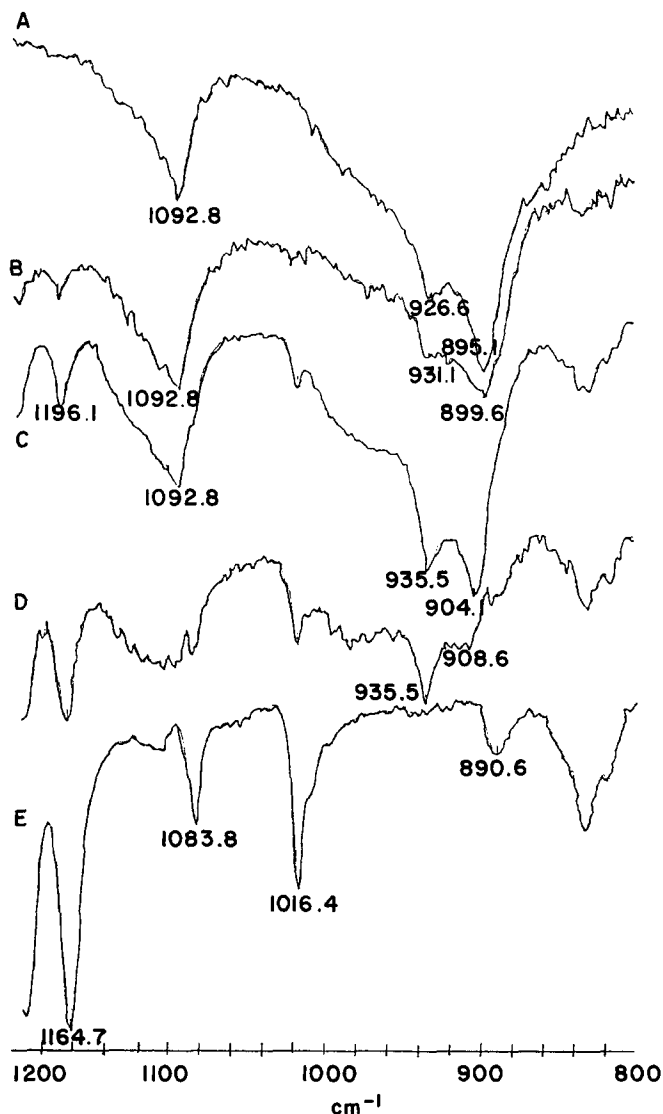
Figure 12 *FT*i.r.–a.t.r. spectra for PC, POM and PC/POM blends. Curve A, POM; B, PC/POM = 20/80; C, PC/POM = 50/50; D, PC/POM = 80/20; E, PC

curve C) with the two matrices (*Figure 12*, curves A and E), this blend appears more like that containing 20% PC. Lower viscous matrix tends to migrate to the surface in a typical injection moulded specimen. Three major peaks, at 1092.8, 926.5 and 895.1 cm^{-1}, are present in POM: the latter two relate to the ether bonding as previously reported[14]. The peak from POM at 895.1 cm^{-1} shifts to 899.6, 904.1 and 908.6 cm^{-1} for the blends containing 20, 50 and 80% PC respectively, while the peak at 926.6 cm^{-1} shifts to 931.1, 935.5 and 935.5 respectively for these blends. The peak from PC at 1164.7 cm^{-1} shifts to 1196.1 for the blend with 50% PC.

All these peak shifts are considered very significant regarding interaction between two matrices. Therefore, the PC/POM blend is considered partially miscible.

CONCLUSIONS

The great difference in melt viscosity between PC and POM makes it necessary to process at a temperature above that typical for POM and makes the PC/POM blend system extremely difficult to process with very narrow processable conditions.

The PC/POM blends significantly increase modulus, yield strength, and heat distortion temperature above the average of the matrices. This synergistic effect probably comes from the formation of the strong interpenetrating interface similar to reinforcing fibres.

The TPU elastomer selectively distributes in PC phase instead of POM phase where TPU is known as an efficient toughening agent. Therefore TPU is not an ideal toughening agent for the PC/POM blends.

Contrary to the common belief that OsO_4 can only be used to stain rubbers containing double bonds, this study demonstrates that OsO_4 can also be used to stain PC/POM and PC/POM/TPU blends.

*FT*i.r. spectra of the PC/POM blends significantly shift the major peaks due to the ether group in POM, indicating strong interactions between these two matrices.

ACKNOWLEDGEMENT

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