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Melt blends of poly(methyl methacrylate) with a phenoxy

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Melt blends of poly(methyl methacrylate) (PMMA) with a phenoxy (polyhydroxy ether of bisphenol A) have been prepared over the complete composition range using a single-screw extruder. Injection-moulded specimens of the blends were transparent, and differential scanning calorimetry and rheological measurements gave a single glass transition temperature (T_g), indicating miscibility of the blends. The plot of measured T_g *versus* composition showed negative deviation from additivity, except for the 10/90 (PMMA/phenoxy) blend which showed a positive one. Fourier transform infra-red spectroscopy showed that the maximum peak around 3400 cm^{-1} moved towards a higher frequency in the blends, suggesting that intercomponent hydrogen bonding exists. Tensile properties (modulus, strength and elongation at break) of the blends showed a negative deviation for PMMA-rich compositions, and a positive deviation or followed simple additivity in phenoxy-rich blends. The blends were also miscible in the melt state, and a viscosity rise over log additivity in phenoxy-rich compositions strongly suggested chemical reactions between the ester groups of PMMA and hydroxy groups of the phenoxy polymer in these compositions.

(Keywords: blend miscibility; poly(methyl methacrylate); phenoxy)

INTRODUCTION

It is well known that miscible polymer pairs are usually obtained by means of specific attractive forces. These forces between molecules or segments can be due to dipolar interactions, ionic interactions and hydrogen bondings[1,2]. Poly(methyl methacrylate) (PMMA) has previously been shown to exhibit miscibility with poly(vinyl chloride) (PVC)[3], styrene–acrylonitrile copolymer (SAN)[4,5], poly(vinylidene fluoride)[6] and poly(α-methyl styrene-*co*-acrylonitrile)[7]. In PMMA/PVC blend, the carbonyl group in PMMA acts as an electron donor and the α-hydrogen in PVC as an electron acceptor, which induces specific interaction between the polymers.

PMMA is not miscible with polystyrene or polyacrylonitrile, and miscible with SAN containing 9–29 wt% acrylonitrile due to the relatively strong intramolecular repulsion between styrene and acrylonitrile units in SAN.

Phenoxy, which is a polyhydroxy ether of bisphenol A, is a relatively tough and ductile thermoplastic with excellent oxygen barrier property. It is reported that phenoxy is miscible with aromatic or aliphatic polyesters such as poly(butylene terephthalate)[8,9] and polycaprolactone[10], and with polyethers such as poly(ethylene oxide)[11]. The miscibility is mainly due to strong hydrogen bonding between the component polymers. That is, the hydroxyl group in phenoxy acts as a proton donor while the ester or ether group of the other polymers acts as a proton acceptor, and their combinations result in thermodynamically miscible blends. Interchange reactions between the polyesters and the phenoxy, leading to grafting or crosslinking, have also been observed following melt processing[12].

It is known that phenoxy is immiscible with most thermoplastics. However, for PMMA/phenoxy blends, Chiou and Paul[13] reported a single glass transition temperature and lower critical solution temperature (*LCST*) behaviour. Nazabal and co-workers[14] reported that the injection moulding process could also produce transparent samples.

The objective of this work was to investigate the miscibility of PMMA/phenoxy blends, prepared by melt extrusion using a single-screw extruder. Since PMMA has similar a glass transition temperature (T_g) to phenoxy, an enthalpy relaxation method has been used to elucidate the glass transition behaviour of the blends. Fourier transform infra-red (*FT*i.r.) spectroscopy measurements were made to examine interactions between PMMA and phenoxy. Tensile and rheological properties of these blends were also studied to study the solid- and melt-state miscibility.

EXPERIMENTAL

Materials and blending

Commercial grades of PMMA (Lucky IG 840; $M_n = 35\,000$, $M_w = 66\,000$) and phenoxy (Union Carbide PKHH; $M_w = 50\,700$) were used for blending after drying for 3 days at 80°C in vacuum. Blending was

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performed using a Brabender Plasticorder with $L/D = 30$ at 50 rev min^{-1} and temperature profile of 230, 235, 240, 235°C (die). Specimens for mechanical tests were prepared by injection moulding (BOY 22SVV Dipronic), with the same temperature profile as the extruder.

Thermal analysis

Thermal properties were measured by differential scanning calorimetry (d.s.c.; Du Pont 9900 instrument) following the enthalpy relaxation method[15–17]. Extrudates were sealed in d.s.c. pans using a crimping and welding press (Du Pont). First, samples were kept for 5 min at 180°C, following by quenching in liquid nitrogen, and then were aged for 15 days at 75°C. The d.s.c. thermograms were taken from 40 to 150°C at a heating rate of 10°C min^{-1}.

FT*i.r. analysis*

Thin films of the blends were obtained by solvent casting from chloroform at room temperature. After most of the solvent had evaporated, films were transferred to a vacuum desiccator to completely remove the residual solvent. I.r. characterization of the samples was performed using a Perkin–Elmer 1330 spectrophotometer.

Mechanical properties

Samples were obtained by injection moulding under similar conditions to those during extrusion. Tensile properties were determined following the standard procedure described in ASTM D638 with type IV specimens. A tensile tester (Tinius Olsen Series 1000) was operated at a crosshead speed of 5 mm min^{-1}. Notched Izod impact testing was carried out in accordance with ASTM D256. Tests were made at room temperature, and at least five runs were made to report the average.

Rheological and dynamic mechanical measurements

Rheological properties of the melts were measured using a parallel-plate rheometer (Rheometrics Dynamics Spectrometer, RDS II). Discs measuring 12.5 mm (radius) × 1.2 mm (height) were compression moulded and measurements were carried out isothermally at 235°C, 15% strain level. The strain level was determined from a strain sweep which gives the maximum torque value within the linear viscoelastic limit. The dynamic mechanical properties above room temperature were determined employing a Rheometrics Mechanical Spectrometer and a sample of dimensions 73 × 13 × 3 mm, prepared as described above.

RESULTS AND DISCUSSION

Thermal properties

Direct visual observation is a useful method to determine polymer–polymer miscibility. Upon extrusion and injection moulding miscible polymer pairs form transparent melts and specimens. Injection-moulded specimens of our PMMA/phenoxy blends were transparent over the full composition range. Since the difference in refractive index (n) is sufficiently large ($\Delta n = 0.1$), phase separation on a scale larger than the wavelength of visible light should lead to translucent samples.

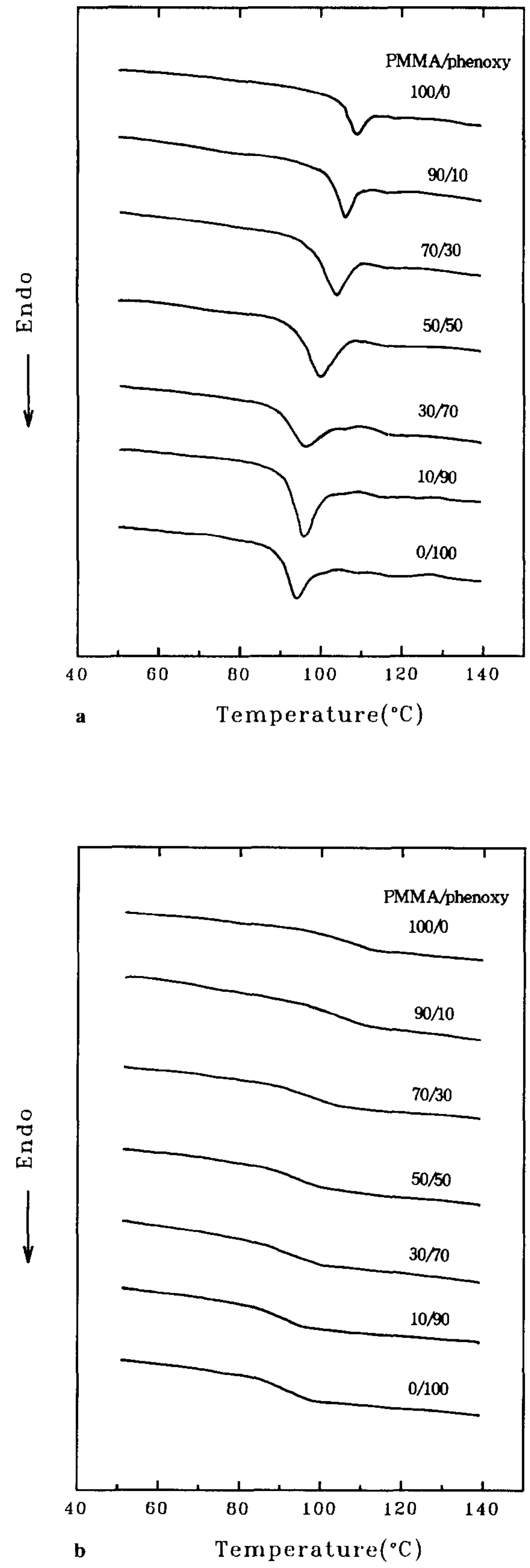


Figure 1 D.s.c. thermograms of PMMA/phenoxy blends: (a) with ageing, (b) without ageing

The enthalpy relaxation method[15] has been developed to identify the T_gs of blend components, and the technique is especially useful when the T_gs of the two component polymers are close to each other. When the

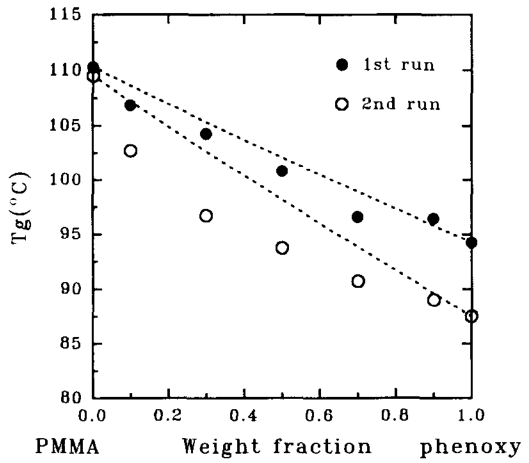


Figure 2 T_g of PMMA/phenoxy blends

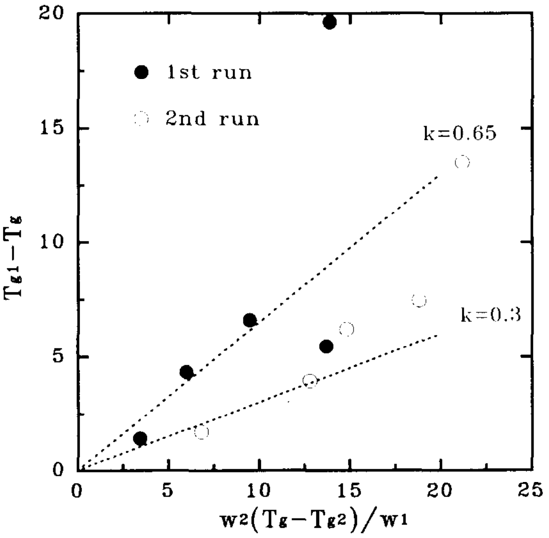


Figure 3 $(T_{g1} - T_g)$ *versus* $w_2(T_g - T_{g2})/w_1$ for PMMA/phenoxy blends

blends are immiscible with similar T_g, two distinct endothermic peaks can appear in this method. *Figures 1a* and *b* show the d.s.c. thermograms of PMMA/phenoxy blends obtained with (first run) and without (second run) annealing, respectively. The second-order transition is a point of inflection in *Figure 1b*, and it is a peak in *Figure 1a*. It seems that PMMA/phenoxy blends are miscible because only a single enthalpy recovery peak appears.

The T_g of PMMA/phenoxy blends showed a negative deviation from additivity, except for the 10/90 blend (*Figure 2*). Manson and Sperling[18] reported that when there are strong intermolecular interactions (for example hydrogen bonding) between two components, T_g shows a positive deviation from additivity. It seems that the intermolecular interaction between the -OH group in phenoxy and the COO group in PMMA is relatively weak. The Gordon–Taylor equation can be rewritten as[19,21]:

$$T_{g1} - T_g = \frac{kw_2}{w_1}(T_g - T_{g2}) \qquad (1)$$

where w_i and T_{gi} are the weight function and T_g of component i, respectively. A plot of $(T_{g1} - T_g)$ *versus* $w_2(T_g - T_{g2})/w_1$ gives the value of k as the slope (*Figure 3*). Except for the 10/90 blend, k values lie in the region 0.3–0.65. The Gordon–Taylor equation tests for a correlation between T_g data over the composition range. However, from *Figure 3* it is clear that the correlation is poor, since k is far from constant owing to the reactions between the components. It is reported that k of phenolphthalein poly(ether ether ketone) (PEK-C)/phenoxy blend is 0.87 and that for PVC and many polymethacrylates is >1 (ref. 18). A higher value of k (ref. 22), represents a stronger intermolecular interaction. The interaction between PMMA and phenoxy seems relatively weak compared with the interaction in PEK-C/phenoxy and PVC/polymethacrylate blends.

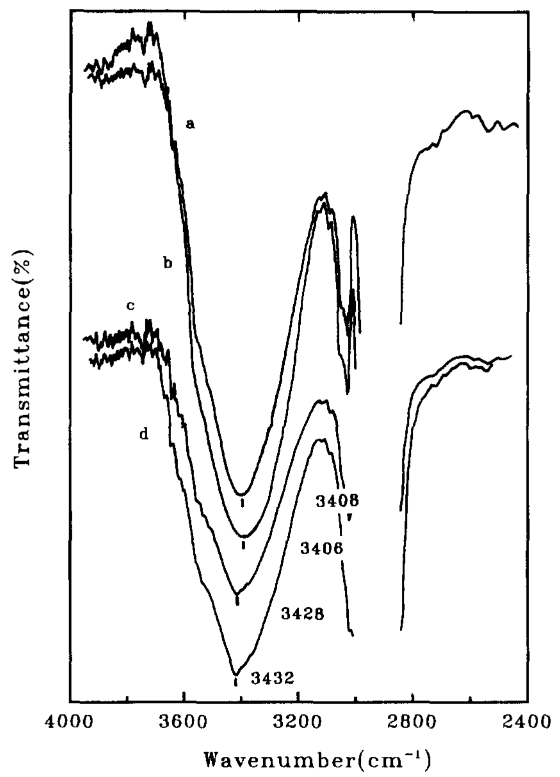


Figure 4 *FT*i.r. spectra of PMMA/phenoxy blends: (a) 0/100; (b) 10/90; (c) 30/70; (d) 50/50

FT*i.r. analysis*

When polymer blends have a strong interaction such as hydrogen bonding, shifting of peaks is often observed in i.r. spectra[1,12]. *Figure 4* shows i.r. spectra in the 3000–4000 cm^{-1} region of pure phenoxy and PMMA/phenoxy blends containing 10, 30 and 50% PMMA. With increasing PMMA content up to 50%, the maximum peak around 3400 cm^{-1} moves towards a higher frequency, suggesting the presence of hydrogen bonding in the blends. Saito *et al.*[23] showed that the OH band in phenoxy consists of a free OH band at 3560 cm^{-1}, an intermolecularly H-bonded OH band at 3520 cm^{-1} and a self-associated OH band at 3400 cm^{-1}. For PEK-C/phenoxy (50/50, w/w) the free OH peak at 3400 cm^{-1} was shifted by about 60 cm^{-1} to higher frequencies (in this blend, $k = 0.87$). The shift of peak position ($\Delta\nu$) is a barometer of the strength of intermolecular hydrogen bonding[24]. The $\Delta\nu$ of 50/50 (PMMA/phenoxy) blends is 24 cm^{-1}, indicating relatively weak hydrogen bonding.

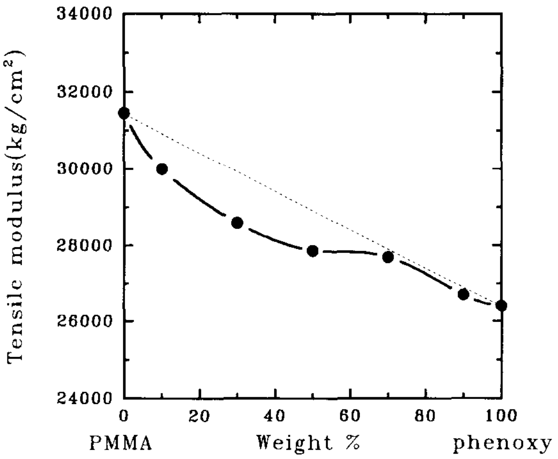


Figure 5 Tensile modulus of PMMA/phenoxy blends

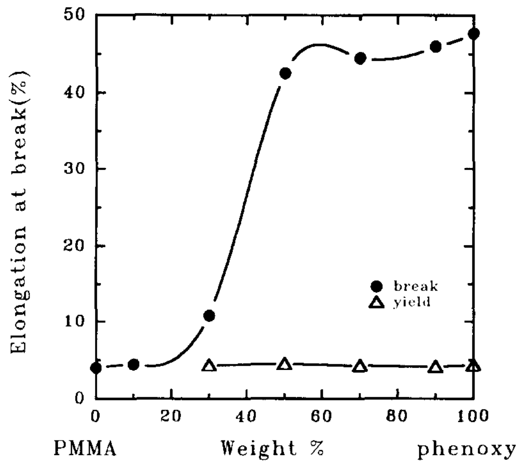


Figure 7 Elongation at break of PMMA/phenoxy blends

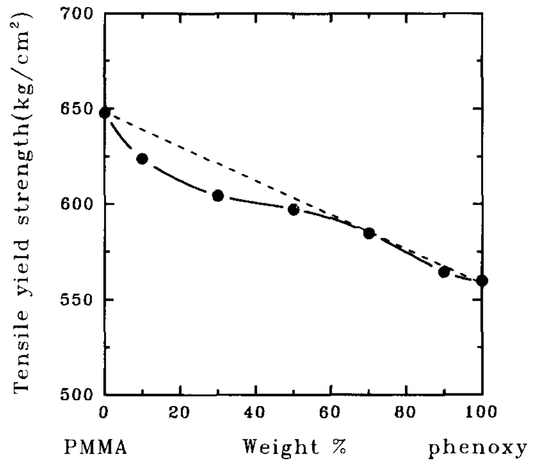


Figure 6 Tensile strength of PMMA/phenoxy blends

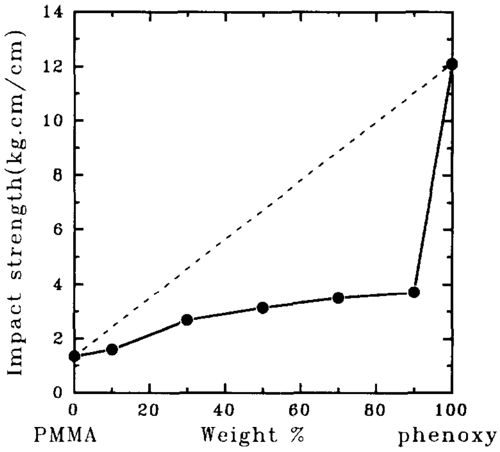


Figure 8 Impact strength of PMMA/phenoxy blends

Mechanical and dynamic mechanical properties

The modulus of miscible blends generally follows the rule of mixtures or shows positive deviation from additivity. It can be predicted by using simple models, a parallel model for miscible blends and a series model for immiscible blends[2,20].

Figures 5 and *6* show tensile modulus and strength, respectively, as a function of composition. Both modulus and strength show a small negative deviation from additivity at PMMA-rich compositions, and linearity in phenoxy-rich compositions. This may be attributed to the relatively weak hydrogen bonding for PMMA-rich blends and the strong interactions for phenoxy-rich blends. PMMA is brittle, whereas phenoxy is a ductile thermoplastic. Thus PMMA shows brittle fracture without yielding, and phenoxy exhibits shear yielding and cold drawing. Ductile fracture was observed experimentally with blends containing more than 30% phenoxy.

Figure 7 shows elongation at break as a function of composition. It shows an S-shaped curve, with the brittle–ductile transition occurring at about 40% phenoxy. Such behaviour is sometimes observed when brittle polymer particles are dispersed in a ductile polymer matrix, including polycarbonate (PC)/SAN[25], PC/PMMA[26] and SAN/phenoxy[27] systems. In immiscible blends, the brittle–ductile transition depends on the interfacial adhesion[28]. For example, the elongation at break of the PC/phenoxy system (partially miscible), which otherwise shows negative deviation, has been greatly improved by reaction between the components in a mixing chamber[29].

The notched Izod impact strength of the blends (*Figure 8*) stays more or less at the level of PMMA, indicating that the PMMA is not toughened by the phenoxy. The different effects of elongation and impact toughening of the blends seem to be due to the different time scales of each test and different toughening mechanisms.

Figure 9 shows the shear storage modulus (G') and $\tan\delta$ curves of the blends. The rubbery plateau is hardly seen for PMMA and phenoxy, but it is generally defined for the blends, indicating more entanglements to exist for the blends. This may be due to the miscibility of the blends and/or chain extension by the chemical reactions between the component polymers. The $\tan\delta$ curves of the blends show a single peak, temperature of which varies monotonically with composition, indicative of miscible blends.

Rheological properties

Figure 10 shows melt viscosity (η^*) *versus* frequency (ω) for PMMA/phenoxy blends measured at 235°C. Plateau-like behaviour for $\omega < 10^0\,\mathrm{rad\,s^{-1}}$ turns into typical shear thinning behaviour at the high frequency region. At low frequency the viscosity of PMMA is several times higher than that of phenoxy.

Figure 11 shows the viscosity–composition curve of

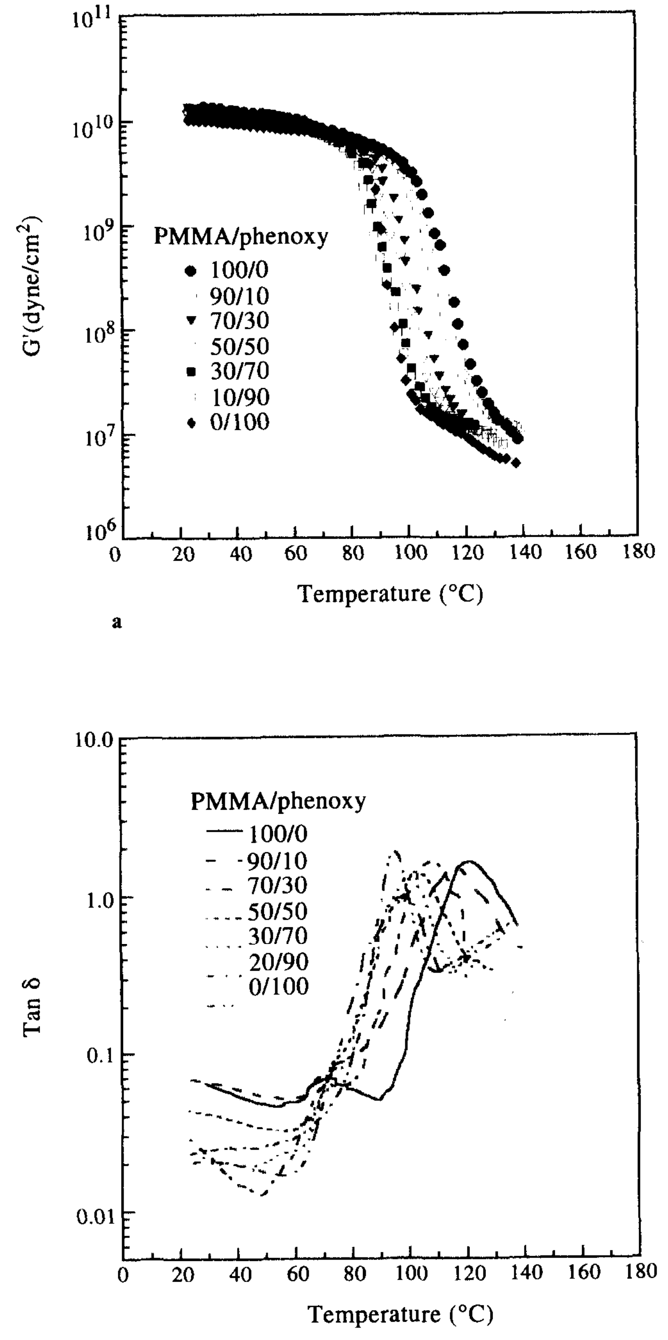


Figure 9 Dynamic mechanical properties of PMMA/phenoxy blends: (a) shear storage modulus; (b) loss tangent

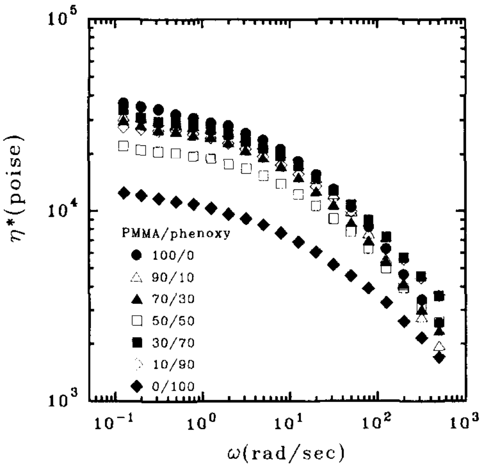


Figure 10 η^* *versus* ω for PMMA/phenoxy blends at 235°C

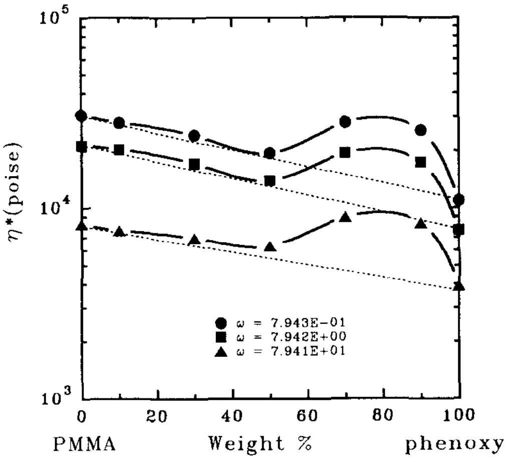


Figure 11 η^* *versus* phenoxy content for PMMA/phenoxy blends at 235°C

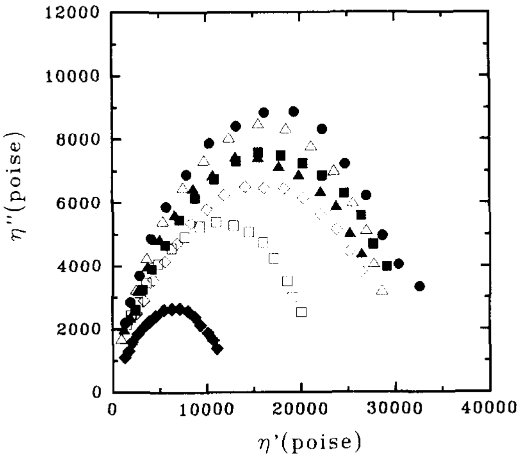
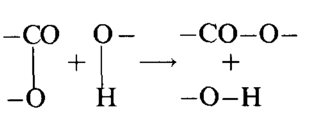


Figure 12 Cole–Cole plot for PMMA/phenoxy blends at 235°C (same symbols as in *Figure 9*)

the blends, which follows additivity in PMMA-rich blends, and a positive deviation in phenoxy-rich blends (on the grounds of d.s.c. analysis it is assumed that the 10/90 PMMA/phenoxy blend also shows a positive deviation of T_g). The viscosity increase in phenoxy-rich blends may be due to interchange reactions between PMMA and phenoxy. The formation of grafting and/or crosslinking should contribute to the viscosity increase, which is more pronounced at phenoxy-rich compositions. It is well known that phenoxy could react with polyester in the following manner[30]:



$$\begin{array}{c}-CO\\ |\\ -O\end{array} + \begin{array}{c}O-\\ |\\ H\end{array} \longrightarrow \begin{array}{c}-CO-O-\\ +\\ -O-H\end{array}$$

Crosslinking is dominant for phenoxy/poly(butylene terephthlate) and phenoxy/poly(ethylene terephthlate) blends, and grafting occurs in phenoxy/polycaprolactone by means of the above reaction scheme. Viscosity increase is probably due to the presence of interchain reaction between the ester group of PMMA and the pendent hydroxy group of phenoxy, since grafting or crosslinking should give rise to higher viscosity of the blends than simple additivity[12,29–32]. It is noted that the extent of deviation is not so great, meaning that there is a small amount of grafting or crosslinking in PMMA/phenoxy blends. More studies should be conducted to elucidate the nature of chemical reactions between PMMA and phenoxy.

Since the η'' (loss part) *versus* η' (dynamic viscosity) curve (Cole–Cole plot) gives information about the relaxation time distributions[30,33], it is often used to determine the miscibility of blends. It is known that the Cole–Cole plot of miscible blends is necessarily semicircular while immiscible blends show a drift from the semicircle. The drift indicates the presence of a longer relaxation time, which reflects a build-up of structure in the blends in the melt state. The PMMA/phenoxy blends show a semicircle independent of composition (*Figure 12*). This reflects rheological miscibility of the blends, and single-phase behaviour in the melt state.

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