Some studies on polyblends of poly(*p*-phenyleneterephthalamide) and nylon-6

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Polyblends of poly(*p*-phenyleneterephthalamide) (PPTA) and nylon-6 have been prepared by coprecipitation from solutions of the polymers in concentrated sulphuric acid. The behaviour of solutions of the polyblends in concentrated sulphuric acid was investigated. The polyblends were characterized by differential scanning calorimetry, X-ray diffraction and density measurements. The polymers were found to form a miscible blend with the composition 62.7 wt% nylon-6 and 37.3 wt% PPTA. The blends could be compacted to hard dense solids by high pressure compaction.

Keywords Polyblends; nylon-6; poly(*p*-phenyleneterephthalamide); coprecipitation; miscibility; characterization

INTRODUCTION

The concept of physically blending two or more polymers to obtain new products or for solving the processing problems is attracting widespread interest. Miscible blends of poly(phenylene oxide) and polystyrene have been formulated to overcome the processing problems of poly(phenylene oxide)[1-3]. Multiphase blends of brittle polymers and elastomers have significantly higher toughness than the brittle polymers and higher dimensional stability than the elastomers[4]. Various blends of commercial utility have been described by Dunn[5] and Corish and Powell[6].

Polyblends, in which one of the constituents is a rigid chain polymer, offer interesting possibilities. Such polyblends are expected to have properties similar to those of fibre composites with the additional advantage of absence of interfaces[7,8]. These materials are isotropic and are better suited to fabrication of three-dimensional components than the fibre composites, which are normally used in the form of thin plates or shells.

Here the results of the investigation on polyblends of poly(*p*-phenyleneterephthalamide) (PPTA) and nylon-6 will be presented. The method of obtaining miscible blends by a coprecipitation technique and characterization of the blend powders by differential scanning calorimetry, X-ray diffraction and density measurements have been reported. Preliminary results of pressure compaction of the blend powders have also been reported.

PPTA, with aromatic units linked through amide linkages at the *para* position, is a rigid chain polymer. The molecules of PPTA exist in extended chain conformation both in solid state and in solution. Owing to the extreme rigidity of the molecules, PPTA does not melt but decomposes without melting above 550°C. PPTA can therefore be processed only from solution to form fibres or films, and fabrication of strong three-dimensional components is not possible. Nylon-6 is a thermoplastic melting at around 210°C and can be processed by conventional methods. A blend of PPTA and nylon-6 may overcome the processing problems of PPTA and enhance the thermal and mechanical properties of nylon-6. Nylon-6 was selected as the flexible chain component because both nylon-6 and PPTA have monoclinic crystal structures and both are known to form intermolecular hydrogen bonds.

THERMODYNAMIC ASPECTS OF PPTA–NYLON-6 SYSTEM

The free energy of mixing of a total volume of two polymers is given by[9]:

$$\Delta G_{\mathrm{mix}} = \frac{RTV}{V_{\mathrm{r}}}\left(\frac{\varphi_{\mathrm{A}}}{x_{\mathrm{A}}}\ln \varphi_{\mathrm{A}} + \frac{\varphi_{\mathrm{B}}}{x_{\mathrm{B}}}\ln \varphi_{\mathrm{B}} + \chi_{\mathrm{AB}}\varphi_{\mathrm{A}}\varphi_{\mathrm{B}}\right) \qquad (1)$$

where V_{r} is a reference volume, ϕ_{A} and ϕ_{B} are volume fractions of the two polymers, x_{A} and x_{B} are the degrees of polymerization of the two polymers in terms of the reference volume and χ_{AB} is the Huggins interaction parameter.

The equation for the spinodal (at constant P and T) is calculated from:

$$\frac{\delta^2(\Delta G_{\mathrm{mix}})}{\delta\phi_{\mathrm{A}}^2} \qquad (2)$$

and is equal to:

$$(\chi_{\mathrm{AB}})_{\mathrm{sp}} = \tfrac{1}{2}[x_{\mathrm{A}}^{-1}\phi_{\mathrm{A}}^{-1} + x_{\mathrm{B}}^{-1}\phi_{\mathrm{B}}^{-1}] \qquad (3)$$

The condition for the formation of a single-phase, miscible blend is given by[10]:

$$(\chi_{\mathrm{AB}})_{\mathrm{sp}} \geqslant \chi_{\mathrm{AB}}$$

The Huggins parameter χ_{AB} for nylon-6–PPTA system is given in *Table 1*.

The $(\chi_{\mathrm{AB}})_{\mathrm{sp}}$ for PPTA–nylon-6 system with nylon having

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Table 1 The Huggin's parameter χ_{AB} for nylon-6–PPTA system at various temperatures

Temperature (K)	χ_{AB}
300	0.3325
480	0.2028
600	0.1662

Table 2 $(\chi_{AB})_{sp}$ for different volume fractions of nylon-6

Volume fraction	$(\chi_{AB})_{sp}$
0.1	0.01767
0.98	0.1555
0.985	0.2068
0.99	0.3065

a molecular weight of 40000 and PPTA a molecular weight of 25000 are listed in *Table 2*.

From *Tables 1* and *2* it can be seen that a miscible blend is formed only when the PPTA volume fraction is less than 0.02. Blends with PPTA volume fraction greater than 0.02 will form only incompatible blends.

However, both nylon and PPTA are soluble in conc. H_2SO_4 and can be regenerated without significant degredation by precipitation in water. The dissolution of both the polymers proceeds through protonation of lone-pair electrons of the nitrogen atoms of the amide groups. Because of the strong electrostatic interactions between the polymer molecules and H_2SO_4, it is possible to prepare single-phase homogeneous solutions of nylon and PPTA in conc. H_2SO_4. When the two polymers are precipitated from such a solution, a metastable, miscible blend of PPTA and a nylon-6 can be prepared. This procedure was used to prepare blends of PPTA and nylon-6.

EXPERIMENTAL PROCEDURE

PPTA was prepared in the laboratory by low temperature polycondensation of terephthaloyl chloride and *p*-phenylenediamine. The PPTA prepared had an $\eta_{inh} = 2.3\,\mathrm{dl\,g^{-1}}$ in conc. H_2SO_4 (98 %) at concentration 0.5 g/100 ml. Nylon-6 was obtained commercially and had a molecular weight of 38000. The mixtures and PPTA and nylon-6, with PPTA weight fractions from 0.9 to 0.1, were dissolved in 98 % H_2SO_4. The total polymer content in H_2SO_4 was varied from 10 g per 100 ml of acid to 40 g/100 ml. Some of the solutions, particularly those with high total polymer content, were turbid multiphase liquids at room temperature. These solutions on heating to higher temperatures transformed into a clear single-phase liquid. The cloud points (or the temperatures of the transition from turbid to clear solutions) were measured by observing the solution under a microscope. The cloud point–composition diagrams have been obtained. The cloud points were measured during both heating and cooling and the average values were recorded. Clear, single-phase liquids were poured into flowing water with constant stirring to precipitate the blends. The temperature of the water was always maintained above the cloud point of the polymer solution being precipitated. The precipitated blend was wet ground, filtered and washed free of acid. The washed blend powder was dried under vacuum at 80°C.

The glass transition temperature of the powders were measured using Perkin–Elmer DSC II differential scanning calorimeter. The densities of the powders were measured using a specific gravity bottle with xylene as the liquid medium. A cross-check on the density measurement was made by making compacts under a pressure of 8000 psi and the densities of the compacts were measured by weighing them in air, water and xylene, taking care to see that the compacts were completely impregnated with the liquid medium. The average of the three density values was taken.

X-ray diffraction patterns were recorded on a Philips powder diffractometer from the following samples: (a) nylon-6; (b) PPTA; (c) a physical mixture of nylon-6 and PPTA in the ratio 62.7:37.3; (d) a blend of nylon-6 and PPTA in the same ratio, precipitated from concentrated solution; and (e) a blend as in (d) but precipitated from dilute solution. Cu Kα radiation was used in the analysis. The samples were in the form of compacted discs. Identical conditions were employed for recording data from the different samples.

The blend powders were compacted at a temperature of 175°C and a pressure of 4.1 kbar. The density and the Shore-D hardness of the compacts have been measured.

RESULTS AND DISCUSSION

The cloud point–composition curves are presented in *Figures 1* and *2*. *Figure 1* shows the cloud point as a function of relative quantities of PPTA and nylon-6 at total polymer contents of 20, 25 and 30 g of polymer per 100 ml of H_2SO_4. *Figure 2* gives the cloud points as a

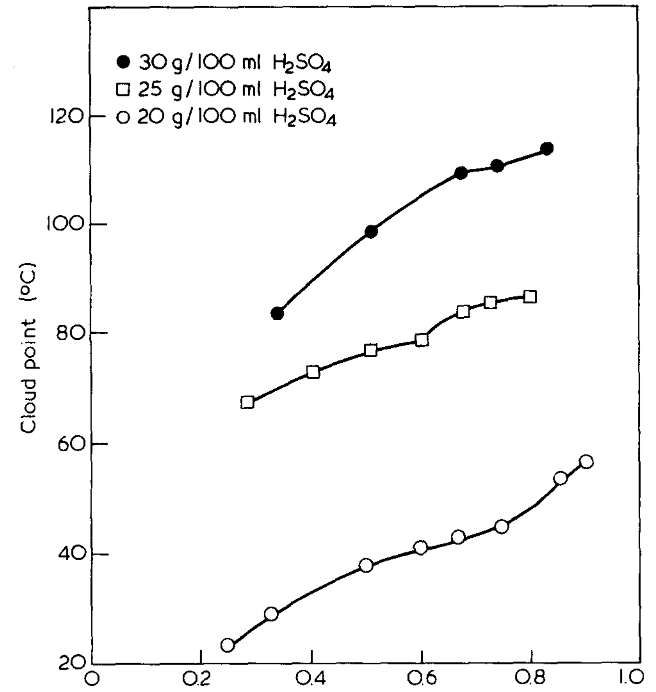

Figure 1 Cloud point as a function of blend composition

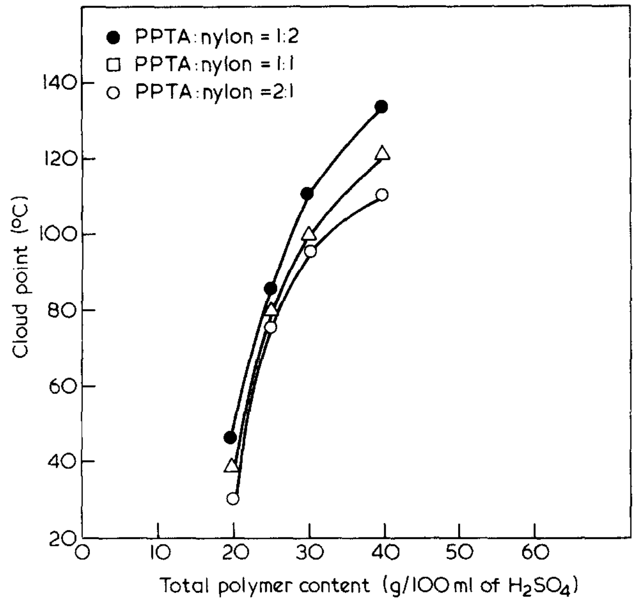

Figure 2 Cloud point as function of total polymer content in H_2SO_4

function of total polymer content in H_2SO_4. The solutions are clear single-phase liquids in the regions above the curves and are turbid multiphase liquids in the region below the curves. It is observed that the cloud point increases as the nylon-6 content increases at a given total polymer content in the solution. Also the increase in the cloud point with increase in nylon content is larger in the case of higher total polymer content solutions, as can be seen from *Figure 2*. Solutions with a total polymer content less than 18 g per 100 ml of H_2SO_4 are clear single-phase liquids at room temperature irrespective of PPTA:nylon ratio. To obtain miscible blends, the blends were precipitated from clear single-phase liquids.

The d.s.c. scans showed that the blends have a glass transition temperature of 420K. The T_g did not depend on the composition of the blends. Nylon-6 has a T_g of 330K and PPTA does not exhibit a clear T_g. But T_g of PPTA is estimated to be 806K based on group contributions. Using these values of T_g for nylon-6 and PPTA and the relationship for T_g of miscible blends, viz.:

$$\frac{1}{T_g}=\frac{w_{\mathrm{nylon}}}{T_{g(\mathrm{nylon})}}+\frac{w_{\mathrm{PPTA}}}{T_{g(\mathrm{PPTA})}} \qquad (4)$$

the composition of the phase which shows a T_g of 420K works out to be 62.7 wt% nylon and 37.3 wt% PPTA. The blends with nylon content higher than 62.7 wt% are thus made up of a blend of composition 62.7 wt% nylon and 37.3 wt% PPTA and free nylon. Blends with nylon content less than 62.7 wt% are composed of a blend of composition 62.7 wt% nylon and 37.3 wt% PPTA and free PPTA. A nylon melting peak was observed in all the blends at 480K even when the blend had a nylon content of less than 62.7 wt%, except when the nylon content was below 20 wt%. This indicates that phase separation takes place between 420K (the T_g of miscible blend) and 480K.

The results of the density measurements are shown in *Figure 3*. The experimental values are shown as points. The full curve is the additive density as a function of composition calculated using the densities of pure nylon and pure PPTA, assuming the blend to be a physical mixture of PPTA and nylon. The broken curve is the additive density as a function of composition calculated assuming that the blends are made up of a miscible blend with a composition of 62.7 wt% nylon/37.3 wt% PPTA and free nylon in the nylon-rich composition range and with free PPTA in the PPTA-rich composition range. It can be seen from the figure that the experimental points lie close to the broken curve, indicating that the blends are made up of a miscible blend with 37.3 wt% PPTA and 62.7 wt% nylon and one of the components.

X-ray diffraction patterns provided further evidence for the formation of miscible blends. The diffraction patterns from nylon-6 and PPTA were remarkably similar, although the peaks in the former were sharper than those in the latter. The most striking feature of both the patterns was the occurrence of two intense reflections in the 2θ range 22–28°. Diffractometer records for the different samples in this region are given in *Figure 4*. The 2θ values for the peaks are also marked in the same figure. The diffraction maxima occurring outside the 2θ range 22–28° were not considered in the present work as their intensities were more than an order of magnitude lower than those of the two maxima occurring in this range. The patterns from all the samples faded completely beyond $2\theta = 55°$.

The intensity distribution in the pattern from the physical mixture corresponded approximately to the

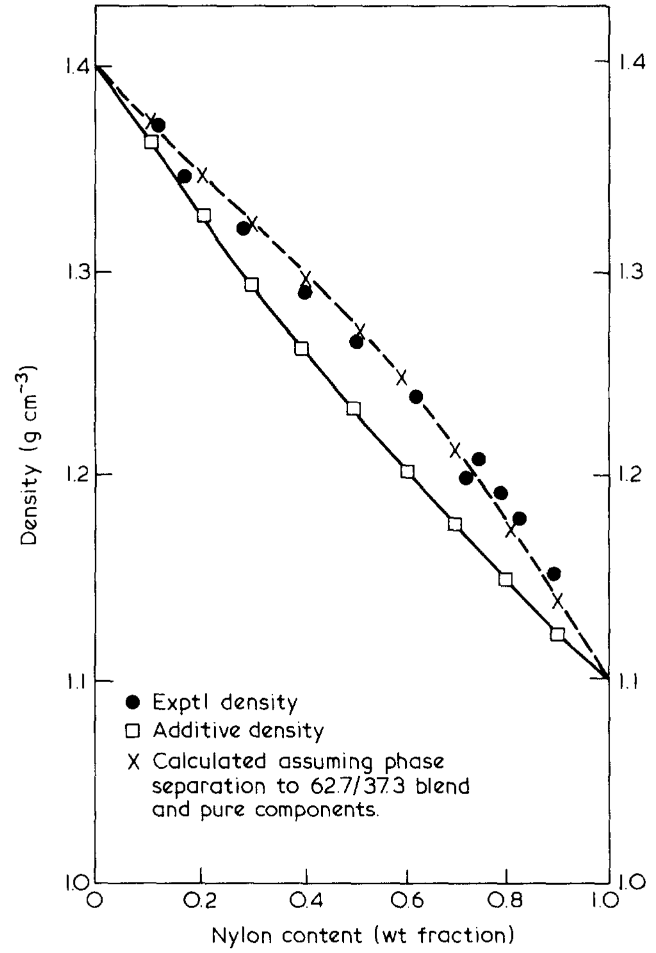

Figure 3 Variation of density of the blends with composition

weighted sum of the distributions in the patterns from the individual components. The diffraction patterns from the blends were different from those from the physical mixture in two important respects. First, the 2θ values for both the maxima were lower than those for the corresponding maxima in the pattern of the physical mixture. Secondly, the diffraction maxima were substantially more intense in the former than in the latter. Both these features can be explained satisfactorily if the blend is considered as a substitutional solid solution in which some of the molecules of nylon-6 have been replaced by those of PPTA. This substitution, while materially not altering the arrangement of the rest of the nylon molecules, could be expected to alter the cell dimensions slightly. Hence the small shifts in the peak positions.

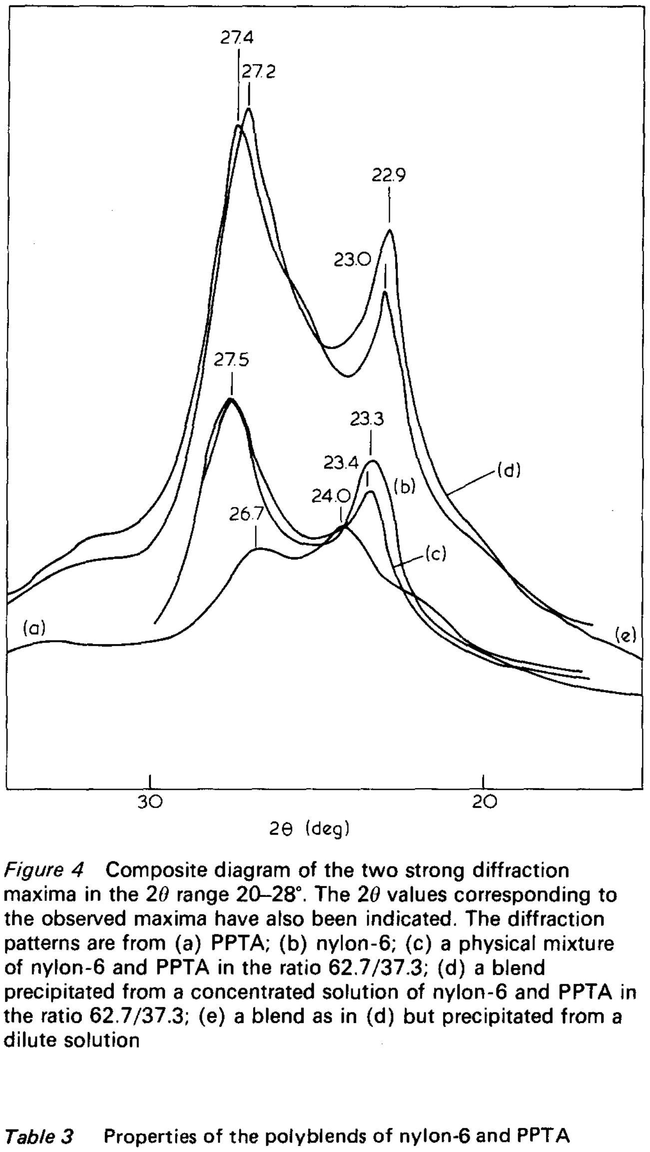

Figure 4 Composite diagram of the two strong diffraction maxima in the 2θ range 20–28°. The 2θ values corresponding to the observed maxima have also been indicated. The diffraction patterns are from (a) PPTA; (b) nylon-6; (c) a physical mixture of nylon-6 and PPTA in the ratio 62.7/37.3; (d) a blend precipitated from a concentrated solution of nylon-6 and PPTA in the ratio 62.7/37.3; (e) a blend as in (d) but precipitated from a dilute solution

While the intensity of a diffraction maximum in a physical mixture is proportional to:

$$w_1F_1^2+w_2F_2^2 \tag{5}$$

that in a blend is proportional to:

$$(w_1F_1'+w_2F_2')^2 \tag{6}$$

Here $w_1:w_2$ is the ratio of the two components in the sample and F_1 and F_2 the corresponding structure factors in the respective lattices. F_1' and F_2' correspond to the structure factors of component 1 and component 2 respectively in the lattice of the blend. The intensities of the diffraction maxima from the physical mixture and the blend are therefore expected to be different. The fact that the maxima from the blend have higher intensities indicates that the molecules of one or the other of the components or those of both the components are better ordered in the blend than in their individual lattices. Considering that one is dealing with powdered samples of poorly ordered fibrous molecules, the above explanation, though admittedly qualitative, strongly indicates that nylon-6 and PPTA form a fibrous blend.

Diffraction patterns have also been recorded from blends heated to 423K and 523K respectively and then pressed at 4.1 kbar. Based on the criteria of shift in 2θ values and the intensity of the diffraction maxima, it was found that these two samples corresponded to phase-separated physical mixtures. This feature supports the conclusion derived earlier from the measurement of T_g values.

In *Table 3* the conditions of compaction, the density of compacts and Shore-D hardness of the compacts have been listed. It can be seen that compaction at 175°C under a pressure of about 4.1 kbar yields compacts with good densities and high hardnesses. The hardnesses of the

Table 3 Properties of the polyblends of nylon-6 and PPTA

Composition (wt%)		Compaction conditions			Density of compact (g cm^{-3})	Density of the powder (g cm^{-3})	Compact density / Powder density	Shore-D hardness
PPTA	Nylon-6	Pressure (kbar)	Temperature (°C)	Pressing time (min)				
90	10	2.7	150	10	1.228	1.365	0.8996	62
90	10	4.1	175	10	1.34	1.365	0.98	68
90	10	4.1	175	15	1.351	1.365	0.99	82
90	10	4.1	175	20	1.354	1.365	0.992	80
80	20	2.7	150	10	1.255	1.336	0.94	64
80	20	4.1	150	10	1.250	1.336	0.93	68
80	20	4.1	175	10	1.31	1.336	0.98	76
80	20	4.1	175	20	1.328	1.336	0.99	86
70	30	4.1	175	20	1.344	1.324	1.015	85
70	30	4.1	175	20	1.335	1.324	1.008	84
60	40	4.1	175	20	1.297	1.294	1.002	88
*0	100	–	–	–	1.102	–	–	68

* The sample is an extruded rod

compacts are significantly greater than the hardness of pure nylon. A Shore-D hardness of a blend compact with a value in the region of 85 is comparable to the hardness of glass fibre–epoxy composites which have a Shore-D hardness of 80–85.

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