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A new thermally-processable aramid/amorphous nylon blend with high heat resistance and high stiffness

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Polymer blends based on a rigid-rod aramid poly (2-chloro-1,4-phenylene terephthalamide) (ClPPTA) and an amorphous nylon poly(hexamethylene isophthalamide) (nylon 6I) were prepared by coprecipitation, and pressed into films by hot-compression. By differential scanning calorimetry (d.s.c.), optical microscopy and dynamic mechanical thermal analysis (d.m.t.a.), formation of a co-continuous superstructure in the blend films was suggested. The blend films exhibited high heat resistance and high stiffness, which are ascribable to the continuous aramid phase characteristic of the co-continuous structure. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Molecular composites[1–7], i.e., miscible rigid-rod/flexible-coil polymer blends, represent an emerging technology in the field of polymer composites for applications as engineering materials. In the concept of molecular composites, the rigid rod polymer is assumed to act as a reinforcing fibre at the molecular scale[1–7].

The reinforcement of random coil matrix polymers by rigid-rod molecules, if achieved, should have several advantages over conventional fibre-reinforced thermoplastics: absence of any problems related to the fibre–matrix interface, high modulus and high strength based on the high aspect ratio of a single dispersed high molecular-weight rigid-rod molecule, etc. Indeed, some successfully prepared molecular composites based on poly(benzbisthiazole)/poly(benzimidazole)[2], poly(*p*-phenylene terephthalamide) (PPTA)/nylon, or rigid-rod polyimide/flexible-coil polyimide blend systems[5–7] displayed the expected performance.

The problem involved in the molecular composite concept is the poor processability of the materials. The rigid-rod/flexible-coil polymer mixtures are inherently immiscible, and hence phase separation is unavoidable when heated above the glass transition temperature (T_g) of the matrix polymer[8]. It means that melt-processing of molecular composites can hardly be performed without phase structure changes[8].

Taking into account the immiscible nature of the components, multiphase blends of rigid-rod and flexible-coil polymers might be interesting to be investigated as a potential high-modulus resin. An aramid/poly(ether sulfone) two-phase blend, as reported by Matsuura *et al.*[9], points in this direction.

Matsuura *et al.*[9] investigated blends of bis(4-aminophenyl) ether/isophthaloyl chloride based aramid with a poly(ether sulfone), and showed that the blends are mouldable through hot-compression. Moreover, an annealed film was found to maintain its stiffness up to the melting point of the aramid ($T_m \approx 420°C$), which is much higher than the processing temperature ($\approx 320°C$). This surprising modulus improvement is due to the highly-crystalline continuous aramid phase formed during annealing.

The aramid employed by these investigators was not a rigid-rod type. Hence no improvement in room-temperature stiffness was observed[9]. However, the above-mentioned mechanism is thought to work with a rigid-rod/flexible-coil polymer system, and might afford a higher room-temperature stiffness of the materials.

These considerations prompted us to study the blending of a rigid-rod aramid with an amorphous matrix resin. A chlorine-substituted PPTA (ClPPTA)/poly(hexamethylene isophthalamide) (nylon 6I) blend system was selected (see *Scheme 1*), and the continuous phase of the aramid was also formed in the present system. As a result, the modulus of the blend films at room temperature as well as the heat resistance were markedly higher than those of the matrix resin. In this paper, the blending procedure, and thermal and mechanical characterization of this system will be reported.

EXPERIMENTAL

Materials

Nylon 6I was supplied by DSM (Geleen, the Netherlands), and used as received. Sulfuric acid salt of 2-chloro-1,4-phenylenediamine (ClP salt) was recrystallized from an aqueous solution. Calcium chloride

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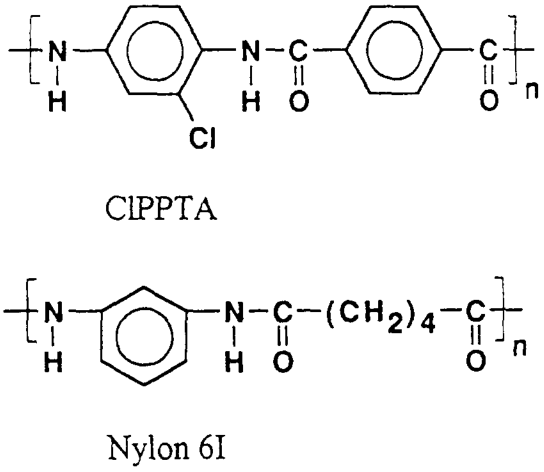


Scheme 1

(anhydrous) was obtained by decomposition of the dihydrate under vacuum above 200°C. Terephthaloyl chloride was purified by vacuum distillation. *N*-methyl-2-pyrrolidinone (NMP) was distilled from CaH_2 under reduced pressure. Sulfuric acid (ca. 97%) was used as received.

Synthesis of ClPPTA

A rigid-rod aramid ClPPTA was synthesized by a low-temperature solution polycondensation method[10]. The procedure can be described as follows.

A three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a drying tube was charged with 8.42 g (35.0 mmol) of ClP salt, 14 g of $CaCl_2$, and 350 ml of NMP. The solution was cooled in an ice-water bath, and 7.11 g (35.0 mmol) of terephthaloyl chloride was added. The mixture was stirred for 15 h at room temperature. Subsequently, the polymer was precipitated by pouring the viscous solution into a water/methanol (50/50) mixture. After immediate neutralization of the non-solvent bath with ammonium hydroxide, the polymer was collected, washed in hot methanol, and dried under vacuum.

The ClPPTA obtained had an inherent viscosity of 1.79 dl g^{-1}, and the yield was 7.5 g (78%).

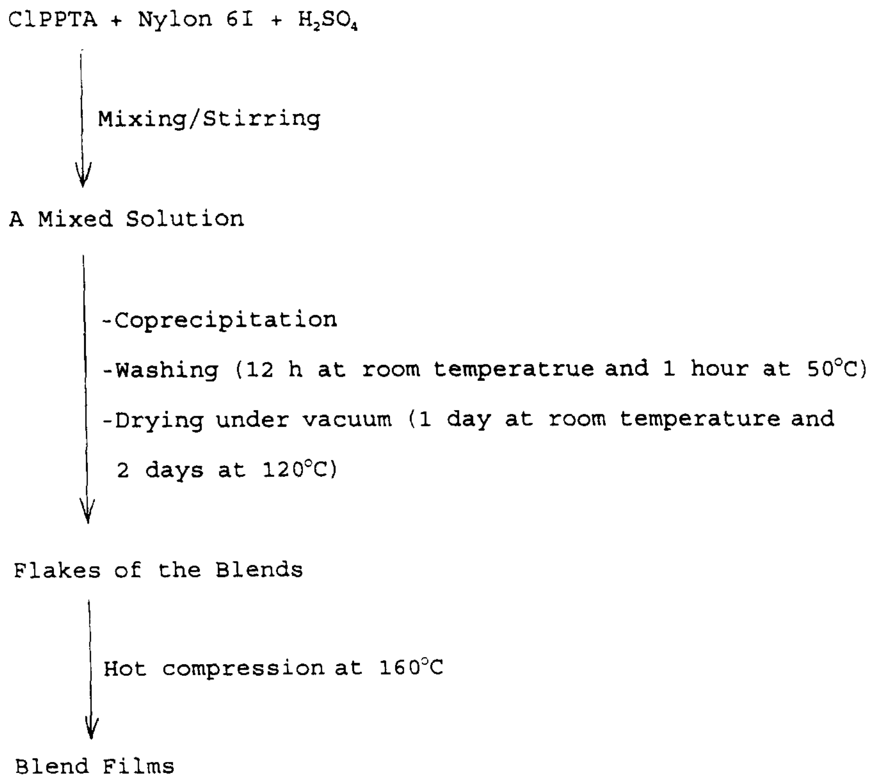
Blending procedure and film formation

ClPPTA and nylon 6I were blended at different compositions by coprecipitation of their sulfuric acid solution into water. The coprecipitates were hot-compressed into films and characterized.

A typical procedure for the blending is as follows. ClPPTA and nylon 6I were dissolved in sulfuric acid to form a 1–2 wt% solution at each composition, and poured into water. The precipitate was washed in water until the pH of the waste became >6, and continuously washed for 12 h at room temperature and 1 h at 50°C, followed by drying under vacuum at room temperature for one day and at 120°C for two days. Films were prepared by hot compression of the flakes at 160°C for 5–15 min.

Scheme 2 and *Table 1* display the conditions employed for blending. The concentration of the solution to be poured into the non-solvent bath should be reduced with ClPPTA content in order to form fine flakes, since the viscosity of the solutions alters with the composition. The time of hot-compression also had to be altered with the composition because of low tractability of the ClPPTA-rich samples.

Translucent blend films were obtained for a ClPPTA content less than 40 wt%.



Scheme 2

Measurements

Inherent viscosities were measured for 0.5 g dl^{-1} solution in sulfuric acid at 25°C with an Ubbelohde viscometer. Differential scanning calorimetry (d.s.c.) measurements were carried out with a Perkin-Elmer DSC7 apparatus at a heating rate of 20°C min^{-1}. Optical microscopy was performed using an Olympus BH-2 apparatus. Wide angle X-ray scattering (WAXS) patterns were recorded on a Rigaku RTP 300 RC using Ni-filtered CuKα radiation (4 kW). Dynamic mechanical thermal analysis (d.m.t.a.) was carried out with a Polymer Laboratory MKII DMTA apparatus in the bending mode at a heating rate of 2°C min^{-1}.

RESULTS AND DISCUSSION

Precipitation behaviour of nylon 6I

Prior to the blending with ClPPTA, the behaviour of nylon 6I during the precipitation from sulfuric acid into water was examined.

Sulfuric acid has been widely used for the preparation of molecular composites, and is considered a good cosolvent of rigid-rod polymers and aliphatic nylons[1,4]. However, one can suppose that the precipitation procedure might cause a decrease in the molecular weight of polyamides, since the acids catalyse the hydrolysis of amides in water as[11]

$$\text{R–NHCO–R}' + \text{H}_2\text{O} \rightarrow \text{R–NH}_2 + \text{R}'\text{COOH}$$

Accordingly, we compared the inherent viscosity of precipitated nylon 6I samples with that of the neat sample. *Table 2* indicates that degradation actually takes place. The decrease in molecular weight (ca. 5%), however, is not very pronounced. Nevertheless, we tried to reduce the degradation by using an aqueous solution of ammonium hydroxide (pH 9) as a nonsolvent, but this was not effective (*Table 2*).

Another effect of precipitation is an induction of crystallization of nylon 6I. The hot-compressed films of precipitated nylon 6I exhibited a small endothermic peak at 215°C during the d.s.c. heating scan (*Figure 1a*). This peak is ascribed to the melting of nylon 6I crystals, since diffraction peaks from the crystals are observed in the WAXS pattern of the same film (*Figure 2A*). The second d.s.c. heating scan after quenching nylon 6I from the melt showed neither a crystallization nor a melting peak (*Figure 1b*). This result indicates that the precipitation process, where high molecular mobility and high supercooling were facilitated, enabled the crystallization.

Table 1 Conditions of blending and hot-compression

Blend composition	Preparation conditions[a]	
ClPPTA content (wt%)	Coprecipitation solution concentration (wt% polymer in H_2SO_4)	Hot-compression time (min)
0	2.5	5
2.5	2.0	5
5	2.0	5
10	1.6	10
20	1.0	15
40	1.0	15

[a] Other conditions are indicated in *Scheme 2*

Table 2 Stability of nylon 6I during precipitation

Condition	Inherent viscosity (dl g^{-1})
Before precipitation	0.77
Precipitated[a]	0.72 ± 0.02
Precipitated (Neutralized)[b]	0.67

[a] A 2.5% solution of nylon 6I in sulfuric acid was poured into water and dried under vacuum

[b] NH_3 aq. (pH 9) was used instead of water

Thermal and morphological characterization of ClPPTA/nylon 6I blend films

D.s.c. thermograms of the ClPPTA/nylon 6I blend films with different ClPPTA contents are represented in *Figure 3*. The features of the thermograms of the blend films are basically identical to those of neat nylon 6I. This blend system does not show any change of T_g with composition, indicating that the blend films have a phase separated structure.

T_g and T_m of ClPPTA were not observed since they are much higher than the temperature range investigated here[13].

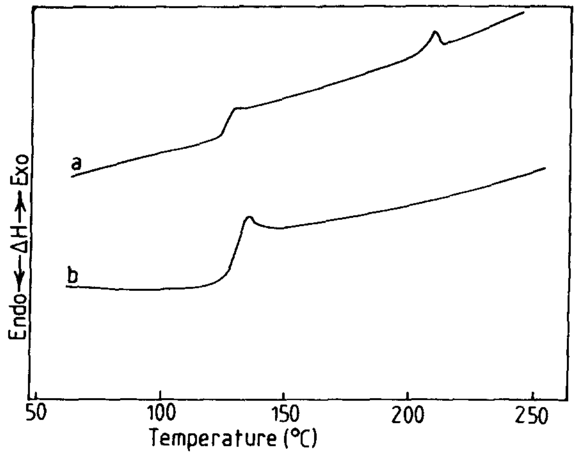


Figure 1 D.s.c. thermograms of precipitated nylon 6I samples: (a) first heating scan; (b) second heating scan

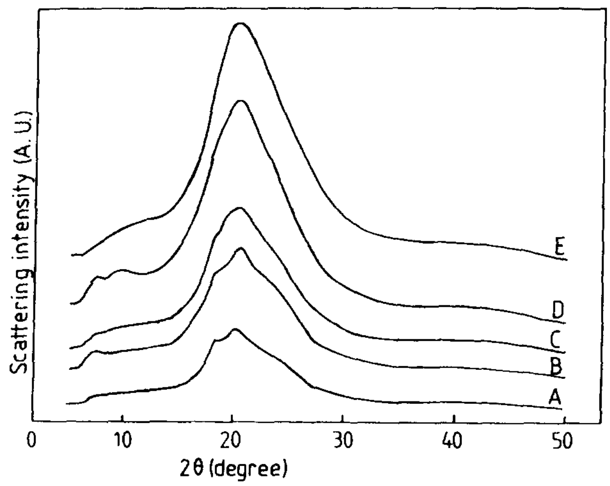


Figure 2 WAXS patterns of (A) nylon 6I and ClPPTA/nylon 6I blend films with a ClPPTA content of (B) 2.5 wt%, (C) 5 wt%, (D) 10 wt%, and (E) 20 wt%

Figure 2 shows the WAXS patterns of nylon 6I and the blend films. In the diffraction pattern of neat nylon 6I, small peaks of nylon 6I crystals can be observed. With increasing ClPPTA content, a new strong peak assigned to ClPPTA appears, and the peaks from nylon 6I crystals become less pronounced. These data indicate an increase in the crystallinity of the blends due to crystallized ClPPTA.

The blend films were examined by optical microscopy in order to determine the morphology. *Table 3* summarizes the observations. At a ClPPTA content less than 10 wt%, no particular structure was found under non-polarized light, but a strong optical anisotropy was seen all over the field under polarized light. This observation indicates that crystals of ClPPTA are mixed in the blends at a scale smaller than a wavelength of visible light.

With increase in a ClPPTA content, some structure at a size of 0.5–1 μm began to emerge.

Dynamic mechanical behaviour of ClPPTA/nylon 6I blend films

Stiffness and heat resistance of the blend films were studied by d.m.t.a. *Figure 4* shows the storage modulus vs. temperature of neat nylon 6I and the blend films.

The d.m.t.a. curve for nylon 6I displays the typical features of semicrystalline polymers; the storage modulus decreases strongly at T_g, however, it increases in the rubbery region because of the secondary crystallization, and strongly decreases again in the melting temperature range[15]. The shape of the storage modulus curves for the blend films is similar to that of neat nylon 6I, but the modulus values are higher. Above T_m of nylon 6I, the modulus of the blends remains high, while that of pure nylon 6I falls quickly.

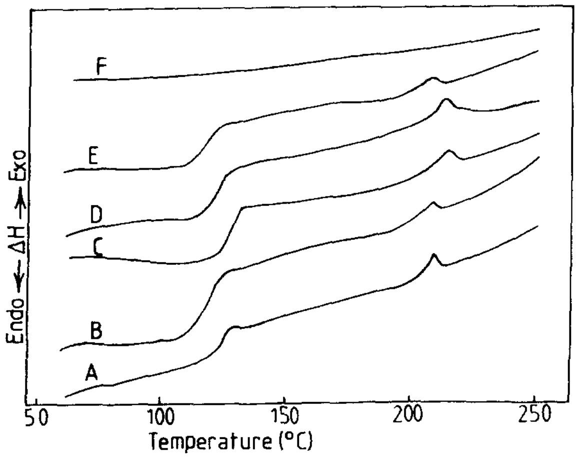


Figure 3 D.s.c. thermograms of (A) precipitated nylon 6I, (F) ClPPTA, and ClPPTA/nylon 6I blend films with a ClPPTA content of (B) 2.5 wt%, (C) 5 wt%, (D) 10 wt%, and (E) 20 wt%

Table 3 Observations by optical microscopy

Blend composition ClPPTA content (wt%)	Optical observations	
	Morphology[a]	Optical anisotropy[a]
0	–	–
2.5	–	+
5	–	+
10	±	+
20	±	+
40	±	+

[a] Under non-polarized light. –, no structure was observed; ±, some heterogeneity was perceived

[b] Under polarized light. –, no anisotropy; +, strong anisotropy all over the field

Table 4 shows the storage modulus values of neat nylon 6I and the blend films at 50°C (below T_g of nylon 6I), 160°C (between T_g and T_m of nylon 6I), and 240°C (above T_m of nylon 6I). As can be seen, the stiffness of the blend films increases with increasing ClPPTA content.

The storage modulus at 50°C is plotted against the blend composition in *Figure 5*. The solid line in the graph corresponds to the best linear plot; the extrapolated bending moduli of nylon 6I and ClPPTA are 2.6 and 20.6 GPa, respectively. The extrapolated modulus value for pure ClPPTA is reasonable. For example, the tensile modulus of a wet-cast PPTA film was reported to be 15 GPa[16], and that of a hot-compressed PPTA/nylon 6 (90/10) blend film was 12 GPa[4].

Providing that ClPPTA phases were randomly dispersed in the blend films, then the modulus of the blend films will be governed by a Halpin–Tsai equation[17]

$$E = (3/8)E_L + (5/8)E_r$$

$$E_L = \frac{1 + 2\xi\eta_L x}{1 - \eta_L x} E_m$$

$$E_T = \frac{1 + 2\eta_T x}{1 - \eta_T x} E_m$$

where E_m and E represent the modulus of the matrix and the blend respectively, x is volume fraction of the dispersed phase, and ξ is the aspect ratio of the dispersed phase. η_L and η_T are parameters depending on the

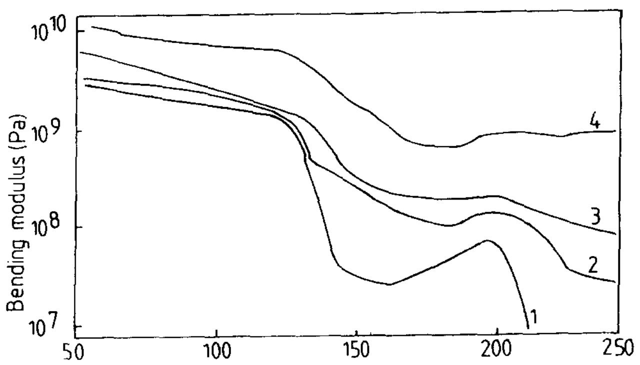


Figure 4 D.m.t.a. storage modulus vs. temperature traces of (1) nylon 6I and ClPPTA/nylon 6I blend films with a ClPPTA content of (2) 5 wt%, (3) 20 wt%, and (4) 40 wt%

Table 4 Bending storage moduli of ClPPTA/nylon 6I blend films

Blend composition ClPPTA content (wt%)	Bending moduli (MPa)[a] at		
	50°C	160°C	240°C
0	2670	60	–
2.5	2570	110	
5	3790	170	30
10	5490	270	120
20	5500	270	100
40	11000	880	800

[a] The values were averaged over two measurements for ClPPTA contents of 0, 5, and 10 wt%

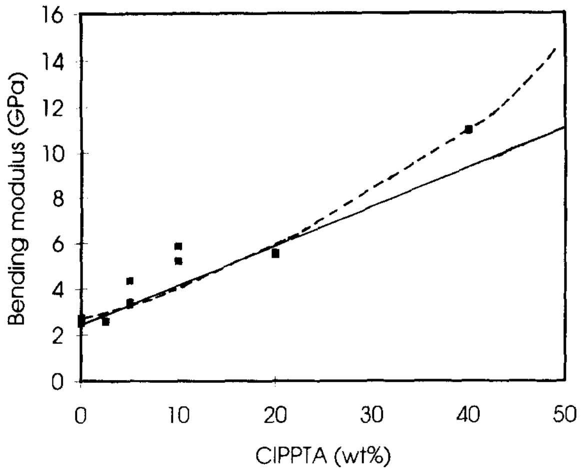


Figure 5 Storage moduli of the ClPPTA/nylon 6I blend films at 50°C as a function of blend composition. See the text for the solid line and the broken line

modulus of the matrix and the dispersed phase. Now, holding the modulus of the dispersed phases to infinity (thereby η_L and η_T become unity), and equating the volume fraction to the weight fraction by neglecting the difference in specific volume of the phases, then we can find an aspect ratio value giving the best fit to the observed moduli of the blends. The calculated aspect ratio value was 3, which corresponds to the modulus curve in *Figure 5* (broken line).

The real aspect ratio of the dispersed phases has to be even larger than 3, since the modulus of the dispersed phases is not infinity. This means that reinforcement of the blend films with ClPPTA is very efficient. Indeed, the linear correlation between the modulus and ClPPTA content, which gave a reasonable extrapolated modulus of ClPPTA, implies that the modulus of the blend films is close to the upper bound predicted by the series model. This conclusion is not significantly affected by the difference in specific volume of the components.

The storage moduli of the blend films at 160°C and 240°C (*Table 4*) indicate that the reinforcement by ClPPTA is still effective above T_g of nylon 6I in spite of its low crystallinity, as well as above T_m.

Morphology and mechanical reinforcement

The d.m.t.a. measurements indicate the high reinforcement efficiency of the matrix by ClPPTA, and the blend films even have a considerable stiffness above T_m of nylon 6I. A way to explain this effective reinforcement is to assume a co-continuous structure in the blend films.

Matsuura *et al.*[9] have suggested that a co-continuous morphology can be constructed in an aramid/poly(ether sulfone) system through a spinodal decomposition, and that the continuous network of the aramid thus formed enhances the heat resistance of the blends.

We think a similar mechanism is working in our system. That is, a co-continuous structure of ClPPTA and nylon 6I could be formed during the hot-compression process through a coarsening of the phases, and afford the heat resistance. The high modulus of the blend films at 50°C can be explained in a similar manner. If the co-continuous structure was formed, stiffness of the blends can be close to the upper bound value expected by the parallel mixing rule.

The other observation is consistent with this idea: optical microscopy revealed that the crystals of ClPPTA are mixed in the matrix at or below the scale of a wavelength of visible lights, instead of forming a coarse segregation.

As can be seen from *Figure 4* and *Table 4*, the storage modulus trace of the blend films with a ClPPTA content higher than 5 wt% displays a plateau above T_m of nylon 6I. In addition, the plateau modulus increases with the ClPPTA content. It means that the continuous network of the ClPPTA phase is already formed at a ClPPTA content of 5 wt%. Around a ClPPTA content of 20 wt%, the bending modulus of the blend films at 240°C reaches a value of 0.8 GPa, usually high enough for a resin.

CONCLUSIONS

A rigid-rod aramid (ClPPTA) was blended with an amorphous nylon (nylon 6I) by coprecipitation of sulfuric acid solutions into water. Blends with a ClPPTA content below 40 wt% could be moulded by the hot-compression technique. The blend films exhibited high heat resistance and high stiffness, which are ascribable to the existence of the continuous ClPPTA phase.

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