# Miscibility studies of polyimide/poly(ether imide) molecular composites

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A new group of miscible mixtures (molecular composites) has been studied by means of differential scanning calorimetry, dielectric relaxation and dynamic mechanical techniques. Three kinds of rigid aromatic polyimides (PI) and a commercial-grade poly(ether imide) (PEI) were mixed by dissolving them in *m*-cresol and subsequently coagulating in methanol. The mixtures show a single glass transition temperature ($T_g$) in all compositions in which the $T_g$ increases with increasing PI content. These $T_g$ values are reproducible in repeated heating cycles, suggesting the true miscibility of the blends. This miscibility may be attributed to the similarity of imide structure between the rigid PI and PEI matrix. The bulk PI/PEI indeed shows improved modulus and tensile strength as compared to the pure PEI matrix.

**(Keywords: miscibility; molecular composites; polyimide; poly(ether imide); differential scanning calorimetry; dielectric relaxation; dynamic mechanical analysis)**

## INTRODUCTION

Molecular composites[1–3] have received considerable attention owing to their potential for development of new polymeric materials that may be employed in the area traditionally dominated by metals and ceramics. Conceptually, a molecular composite is a mixture of rigid-rod and flexible-coil molecules, in which rigid-rod molecules reinforce a flexible matrix in a manner similar to a chopped-fibre-filled composite. The optimum reinforcement would occur in composites if rigid rods and flexible coils were mixed at a molecular level. According to Flory[4], such a molecular-level dispersion is very difficult to achieve because of the small entropy of mixing and high orientability of rigid-rod molecules. Most studies on molecular composites also indicate the immiscible character of the mixtures[3,5,6].

In this study, rigid aromatic polyimides synthesized in our laboratory are used as the reinforcing molecules[7]. These polyimides, having excellent chemical and thermal stabilities, could be dissolved in a limited type of solvents such as *m*-cresol. Considerable attention has been directed to the synthesis of polyimides[7,8], but there are limited studies addressing polyimide-based molecular composites[9]. Three kinds of aromatic polyimides (PI) of different chemical moieties were mixed with a commercial-grade poly(ether imide) (PEI). PEI was chosen as a matrix material primarily because of its similarity in chemical structure to rigid-rod polyimides and also because of its availability on a commercial basis. The miscibility behaviour of PI/PEI has been explored based on differential scanning calorimetry (d.s.c.), dynamic mechanical and dielectric realxation methods. Subsequently, tensile properties of these molecular composites are evaluated.

## EXPERIMENTAL

The chemical structures of the three polyimide moieties and their corresponding inherent viscosities are shown in *Table 1*. The synthesis procedure of the PIs was reported elsewhere[7]. These polyimides contain a common diphenylpyromellitic dianhydride (DPPMDA) unit, the other units being different in chemical structure, namely 4,4'-diaminodiphenyl ether (oxydianiline) (ODA), 6,6'-perfluoromethylbenzidine (PFMB) and 3,3'-dimethoxybenzidine (DMB). The polyimide DPPMDA-ODA has an ether bond in the main chain, and therefore it probably has greater chain flexibility relative to the other two. There is no identifiable $T_g$ in all three PIs owing to their chain rigidity. Degradation is suspected to occur before $T_g$ could be detected via thermal analysis. The flexible matrix used in this study is poly(ether imide) (PEI), namely poly(2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane-2-phenylenebisimide) (Ultem 1000, General Electric), which is an amorphous thermoplastic with a $T_g$ around 215°C. The number- and weight-average molecular weights were 12 000 and 30 000, respectively[10].

Various blends were prepared by dissolving PI/PEI in *m*-cresol at 130°C for 5 h. The concentration of polymer solutions was 2 wt%. The solutions of various PI/PEI compositions were coagulated in methanol. The precipitates were washed copiously with methanol to remove residual solvent and then dried at 150°C in a conventional vacuum oven for over a week. Additionally, PI/PEI films were made by casting the ternary solutions

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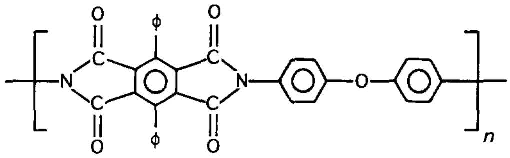
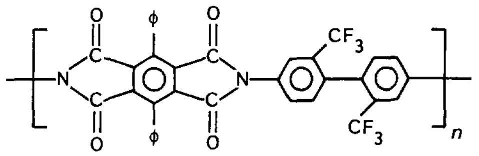
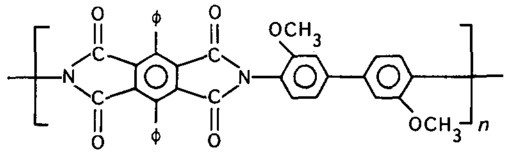
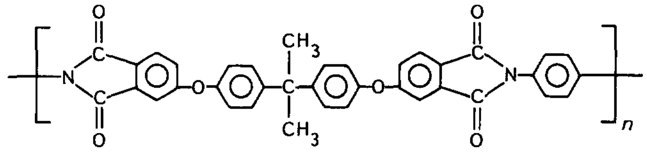
**Table 1** Material characteristics

| Polyimide | Chemical structure | Inherent viscosity[a]<br>molecular weight[b] |
|---|---|---|
| DPPMDA-ODA<br>(diphenylpyromellitic dianhydride 4,4′-diaminodiphenyl ether) |  | $\eta = 2.2$ dl g$^{-1}$ |
| DPPMDA-PFMB<br>(diphenylpyromellitic dianhydride 6,6′-perfluoromethylbenzidine) |  | $\eta = 2.4$ dl g$^{-1}$ |
| DPPMDA-DMB<br>(diphenylpyromellitic dianhydride 3,3′-dimethoxybenzidine) |  | $\eta = 2.63$ dl g$^{-1}$ |
| Poly(ether imide)<br>(Ultem 1000; General Electric) |  | $M_n = 12000$<br>$M_w = 30000$ |

[a] Inherent viscosity of polyimide was determined in *m*-cresol at a concentration of 0.5% w/v
[b] General Electric, Ultem Resin Material Safety Data, November 1985

in Petri dishes at 120°C under vacuum. The cast films were washed with methanol repeatedly and subsequently dried at 150°C for a week, as the precipitates.

Precipitated powders were used for thermal studies. The d.s.c. experiments were carried out on a Du Pont 9900 thermal analyser system at a heating rate of 20°C min$^{-1}$ under nitrogen. Cast films were used in dielectric studies using a dielectric thermal analyser (d.e.t.a., Polymer Laboratories). Data were collected at 1 and 100 kHz at a heating rate of 4°C min$^{-1}$. For dynamic mechanical experiments and tensile tests, precipitated powder samples were compression moulded into flat sheets at about 300°C. The thickness was about 0.5–1.0 mm. Dynamic mechanical experiments were carried out using a dynamic mechanical thermal analyser (d.m.t.a., Polymer Laboratories) equipped with a high-temperature chamber (500°C). Data were collected at 1 Hz at a heating rate of 4°C min$^{-1}$ in the flexural mode at a constant strain. Tensile tests of compression moulded samples were conducted using a Monsanto tensometer (T-10) with a cross-head speed of 5 mm min$^{-1}$. In the case of solution-cast specimens, tensile modulus measurements were taken using a Seiko thermal mechanical analyser (TMA/SS 100). The gauge length was 10 mm and the cross-head speed was 2 mm min$^{-1}$.

## RESULTS AND DISCUSSION

### *DPPMDA-ODA/PEI*

The moulded DPPMDA-ODA/PEI sheets are slightly yellowish owing to the inherent colour of DPPMDA-ODA, but transparent. *Figure 1* shows the d.s.c. traces as a function of composition. The single glass transitions are evident at most DPPMDA-ODA contents up to 70 wt%. These $T_g$ values are reproducible in repeated d.s.c. heating cycles. However, in the mixtures with higher DPPMDA-ODA content, the heat capacity change at the glass transition temperature reduces appreciably because DPPMDA-ODA has no identifiable glass transition. Consequently, no $T_g$ was observed in the compositions beyond the 70 wt% DPPMDA-ODA content.

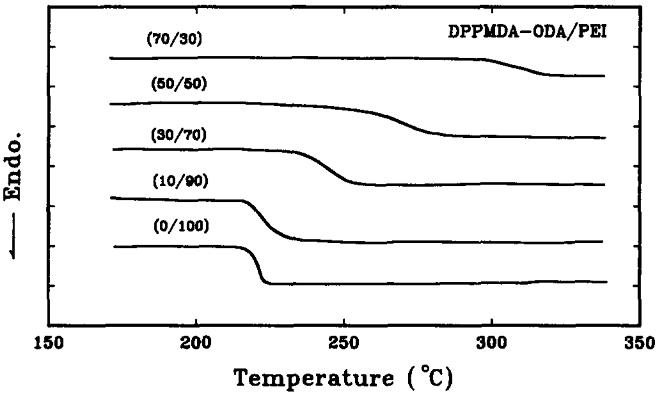


**Figure 1** D.s.c. traces of various DPPMDA-ODA/PEI mixtures as a function of temperature. The heating rate was 20°C min$^{-1}$

*Figure 2* illustrates the tan $\delta$ curves obtained by dynamical mechanical methods. A single relaxation peak is evident in all compositions, suggestive of a single-phase blend, which is in good accord with the d.s.c. results. A similar trend could be witnessed in the dielectric relaxation studies (*Figure 3*).

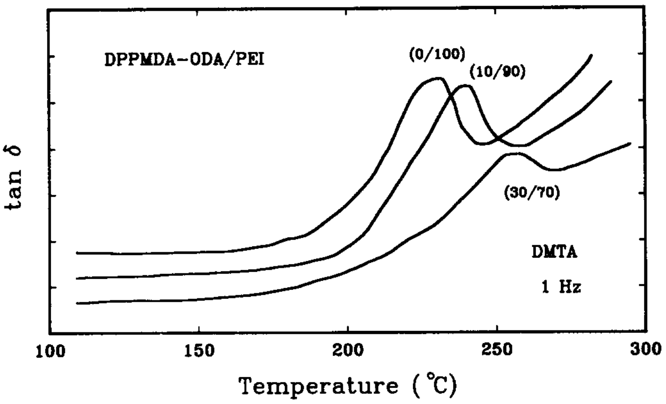


**Figure 2** Tan $\delta$ relaxation curves of DPPMDA-ODA/PEI (0/100), (10/90) and (30/70) mixtures obtained by dynamic mechanical thermal analysis (d.m.t.a.) at a heating rate of 4°C $min^{-1}$ and at the frequency of 1 Hz

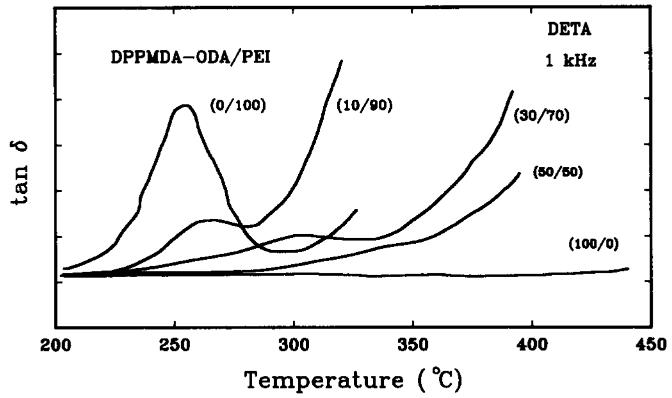


**Figure 3** Tan $\delta$ relaxation curves of various DPPMDA-ODA/PEI mixtures obtained by dielectric thermal analysis (d.e.t.a.). The heating rate was 4°C $min^{-1}$ and the frequency was 1 kHz

*Figure 4* shows the plot of the glass transition temperature *versus* composition in which the $T_g$ increases progressively with increasing polyimide content, indicative of miscible character. Higher $T_g$ values in the d.e.t.a. and d.m.t.a. relative to the d.s.c. studies are simply due to the frequency effect. It is concluded that the blend of DPPMDA-ODA and PEI is truly miscible as evident in the d.s.c., d.e.t.a. and d.m.t.a. studies.

*Figures 5* and *6* show the modulus and tensile strength of various DPPMDA-ODA/PEI molecular composites, respectively, as obtained by the Monsanto tensile tester. The modulus and tensile strength of the bulk molecular composites appear to improve as compared to the pure PEI. As mentioned earlier, the stiffness of DPPMDA-ODA may not be sufficiently high, because the ether bond in the main chain of DPPMDA-ODA provides some chain flexibility. From such a point of view, one would not expect significant enhancement in the mechanical properties of the bulk molecular composites. However, the 30% DPPMDA-ODA molecular composite shows approximately 50% improvement in modulus and about 10% improvement in tensile strength relative to the neat PEI. Such improvement is more remarkable in the oriented molecular composite fibres[11].

### *DPPMDA-PFMB/PEI*

*Figure 7* shows d.s.c. curves for various compositions of solution-cast DPPMDA-PFMB/PEI. A single glass transition was observed in all compositions. The reproducibility of the $T_g$ values in repeated d.s.c. heating runs is a signature of the true miscibility in the DPPMDA-PFMB/PEI. The miscibility between DPPMDA-PFMB and PEI can further be verified by a dielectric relaxation method, in which a single loss tangent peak is observed for all compositions and increases systematically with increasing PI content (*Figure 8*). As mentioned previously, the chemical structure of DPPMDA-PFMB is believed to be more rigid than that of DPPMDA-ODA, and hence the miscibility is expected to be reduced. However, no evidence of thermally induced phase separation was found in the repeated d.s.c. runs. A systematic movement by the $T_g$ values with composition (*Figure 9*) suggests that rigid polyimides and PEI are truly miscible, beyond

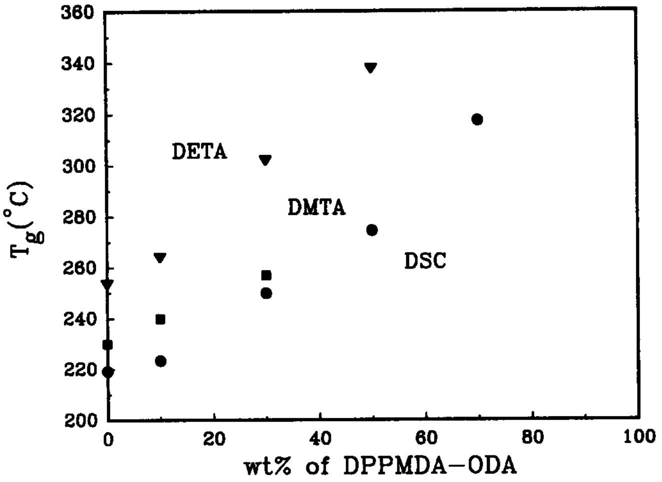


**Figure 4** The $T_g$ *versus* composition plot for the DPPMDA-ODA/PEI mixture based on the d.s.c., d.e.t.a. and d.m.t.a. results

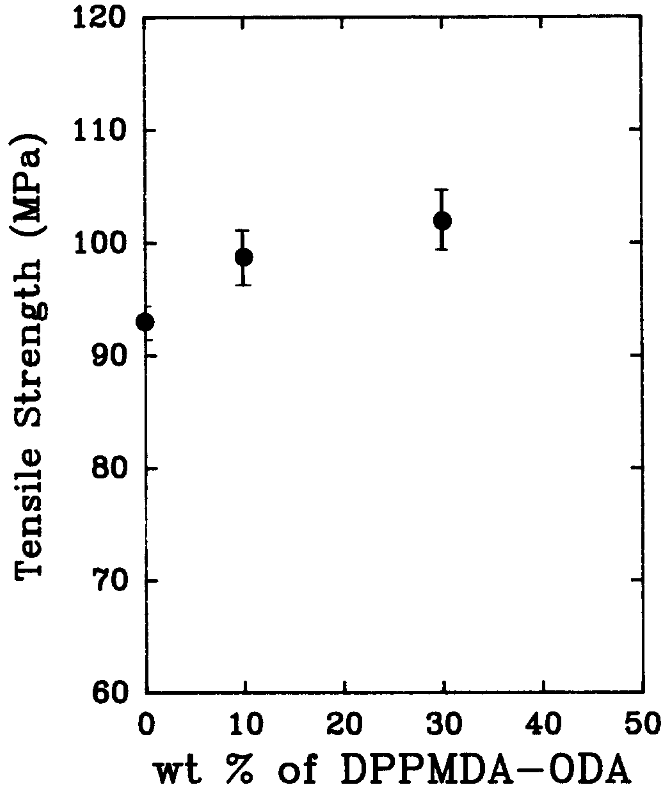


**Figure 5** The relationship between tensile modulus and composition of the DPPMDA-ODA/PEI molecular composite

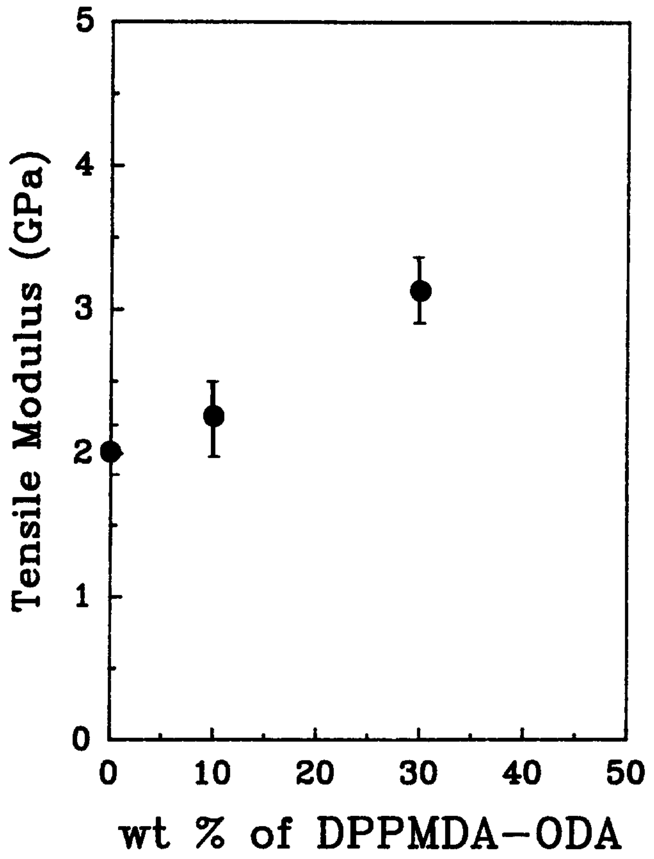


**Figure 6** The relationship between tensile strength and composition of the DPPMDA-ODA/PEI molecular composite

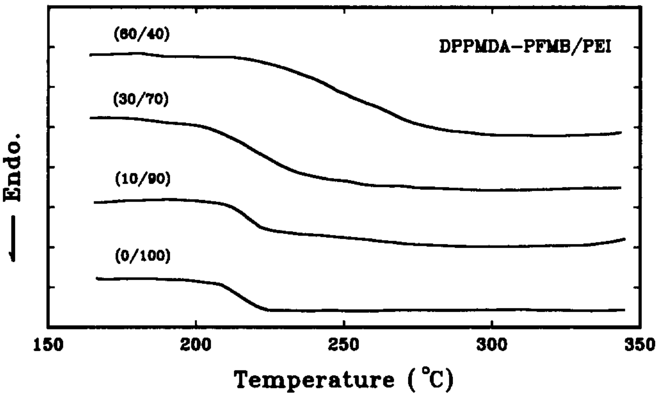


**Figure 7** D.s.c. traces of various DPPMDA-PFMB/PEI mixtures as a function of temperature. The heating rate was 20°C min$^{-1}$

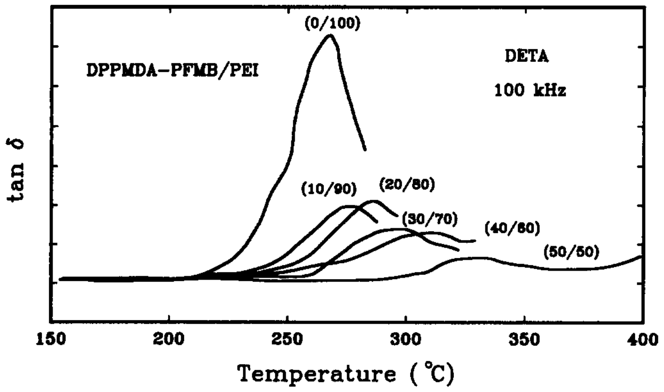


**Figure 8** Tan δ relaxation curves of various DPPMDA-PEMB/PEI mixtures obtained by dielectric thermal analysis (d.e.t.a.). The heating rate was 4°C min$^{-1}$ and the frequency was 100 kHz

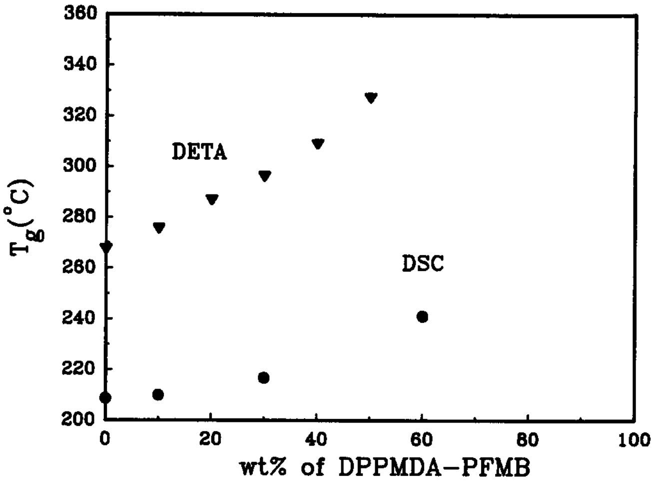


**Figure 9** The $T_g$ *versus* composition plot of various DPPMDA-PFMB/PEI mixtures obtained by d.s.c. and d.e.t.a.

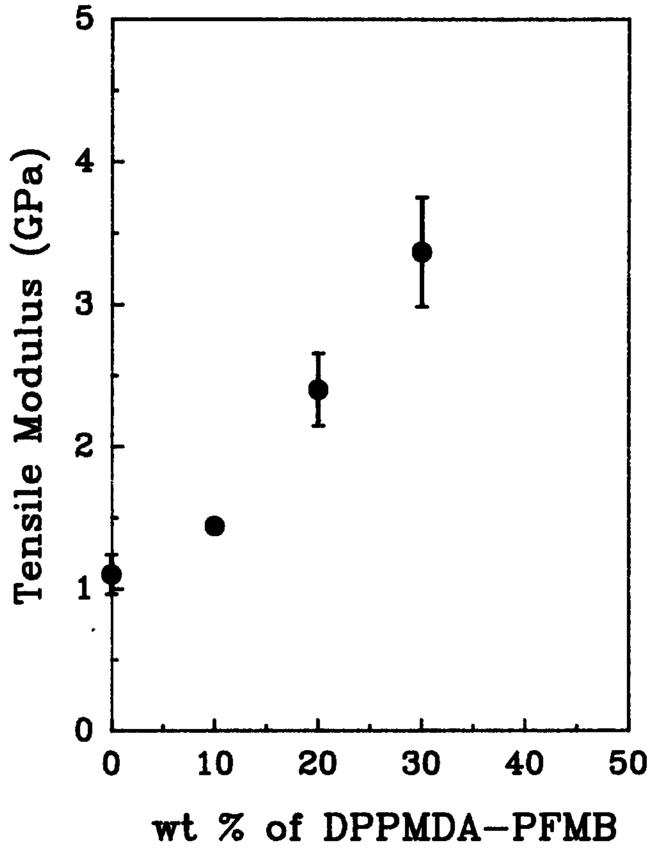


**Figure 10** The relationship between tensile modulus and composition of the DPPMDA-PFMB/PEI molecular composite

general expectation. Besides, the addition of 30% DPPMDA-PFMB into flexible polymer matrix shows approximately a three-fold improvement in modulus over the neat PEI (*Figure 10*). These modulus values were obtained by a Seiko thermal mechanical analyser, which was designed for drawing thin films or fine fibres. The present study shows that the modulus of solvent-cast film is always lower than that of the compression-moulded PEI (*Figure 6*). We suspect that the residual *m*-cresol in such large cast films is difficult to remove completely, and therefore the plasticization effect would lower the modulus. Owing to a shortage of DPPMDA-PFMB specimens, compression moulding of the composites was not feasible. However, the relative comparison between the solvent-cast composites and the neat PEI should be valid.

### *DPPMDA-DMB/PEI*

Next, we examined another kind of polyimide, i.e. DPPMDA-DMB, to establish further the miscibility between polyimides and PEI. As can be seen in *Figure 11*, a single $T_g$ appears in all intermediate compositions. The movement of $T_g$ with increasing polyimide content (*Figure 12*) is relatively small compared to the DPPMDA-ODA/PEI system. The reproducibility of the $T_g$ values in the repeated d.s.c. heating cycles strongly suggests that DPPMDA-DMB and PEI are miscible, and the system shows no indication of phase separation. It should be pointed out that our results are based on the d.s.c. experiments only. A shortage of DPPMDA-DMB does not permit confirmation by other techniques such as d.m.t.a. and d.e.t.a. Hence, our conclusion for the DPPMDA-DMB/PEI case should be regarded as tentative. However, there is no doubt that the similarity of imide structures would promote polymer miscibility between various polyimides and PEI.

Again, tensile measurements were undertaken for solution-cast DPPMDA-DMB/PEI composites using the Seiko thermal mechanical analyser. *Figure 13* shows the plot of modulus *versus* composition. As pointed out previously, the modulus of solvent-cast PEI turns out to be lower than that prepared by compression moulding (*Figure 6*). However, the relative comparison of solvent-cast molecular composites and solvent-cast PEI specimens should still be meaningful. At 30% DPPMDA-DMB composition, the tensile modulus increases four-fold relative to the neat PEI.

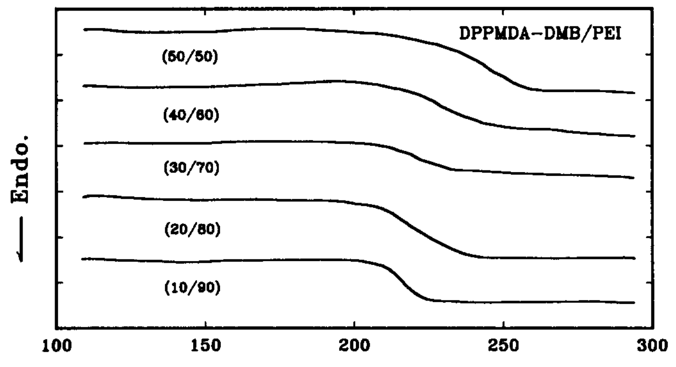


**Figure 11** D.s.c. traces of various DPPMDA-DMB/PEI mixtures as a function of temperature. The heating rate was 20°C min$^{-1}$

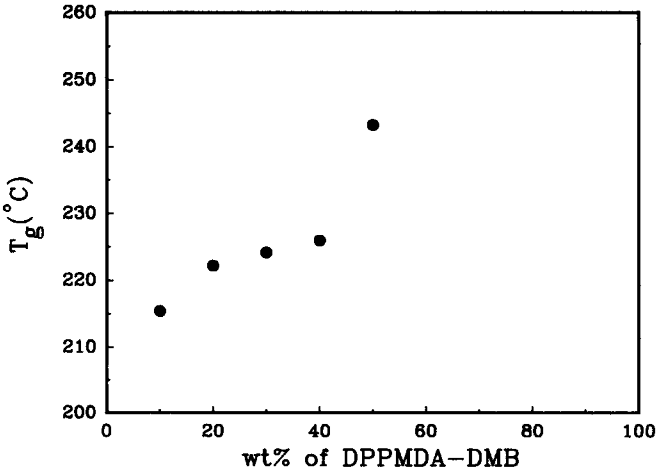


**Figure 12** The $T_g$ *versus* composition plot of various DPPMDA-DMB/PEI mixtures obtained by d.s.c.

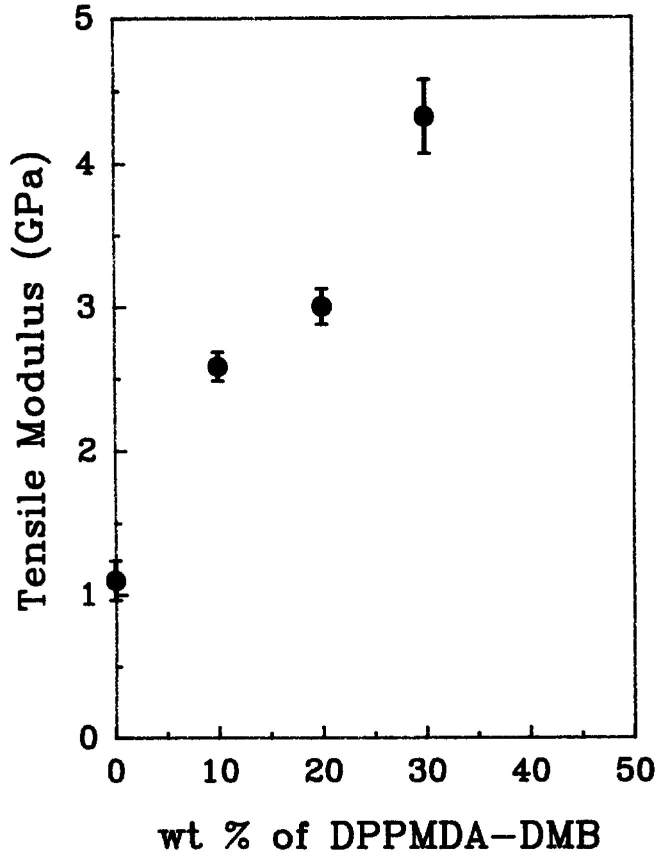


**Figure 13** The relationship between tensile modulus and composition of the DPPMDA-DMB/PEI molecular composite

The true miscibility between rigid PIs and flexible PEI is contradictory to Flory's theory$^4$, which predicted unfavourable thermodynamics of mixing for dissimilar polymer pairs such as rigid rods and flexible coils. Flory's prediction is calculated for an extreme case where the molecular topology of the rigid rods and flexible coils is vastly different and interparticle attractions are deliberately disregarded in the formulation. Moreover, the structural similarity such as imide moieties in the present case would favour miscibility; such an effect was not taken into consideration in Flory's theory.

It should be pointed out that the DPPMDA-ODA polyimide used in this study can be regarded as a stiff molecule, but it is by no means a rigid rod because of the ether linkage in the main chain. However, the latter two polyimides, viz. DPPMDA-PFMB and DPPMDA-DMB, should be sufficiently rigid to comply with the idea of molecular composites despite the steric hindrance due to the side groups in the PFMB and DMB segments. Hence, it seems reasonable to conclude that the latter two PI/PEI systems are truly molecular composites.

## CONCLUSIONS

Miscible mixtures (molecular composites) comprising rigid-rod polyimides and poly(ether imide) were successfully prepared by solvent casting and/or co-precipitation. DPPMDA-ODA/PEI mixtures are completely miscible, i.e. a signature of molecular-level mixing. The good dispersion of rigid DPPMDA-ODA in the PEI matrix considerably enhances the modulus and tensile strength of the bulk mixtures relative to the pure PEI. DPPMDA-PFMB/PEI and DPPMDA-DMB/PEI mixtures reveal true miscibility. The significant improvement in tensile strength and modulus of these miscible rigid/flexible molecular composites is attributed to the reinforcement effect at a molecular level.

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