Polymer Bulletin 33, 241–247 (1994)

Polymer Bulletin

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Miscibility in molecular composites of polyamide-imide/polyetherimide

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Summary

Compositional dependence of miscibility in molecular composites of polyamide-imide/polyetherimide prepared by coagulation of the blend of the two polymers from dimethyl acetamide solutions has been established by calorimetric and dynamic mechanical thermal studies. This study reports on the thermodynamics of miscibility in the molecular composites.

Introduction

Polymeric materials have been classified (1) into three generations. Homopolymer and copolymer thermoplastics, thermosets and elastomers have been classified as first generation polymers and particulate and fibre reinforced polymer composites and polymer blends, as second generation polymers. Molecular composites of rigid and flexible polymers have been classified as third generation polymers.

A molecular composite (1-7) can be defined as an isotropic synergistic composite of molecularly dispersed, intrinsically rigid and flexible macromolecules, conceptually similar to a fibre reinforced composite, except that the flexible polymer is reinforced by the rigid macromolecule at the molecular level. The objective of molecular composite technology is to process a material which can offer properties similar to those of fibre reinforced composites. Due to reinforcement at the molecular level, molecular composites offer the advantage of an isotropic behaviour over anisotropic fibre reinforced composites. It is well known (8) that the engineering properties of fibre reinforced composites are governed by the aspect ratio (length to diameter ratio) of the reinforcing fibre. Following this reasoning the engineering properties of molecular composites are governed (7) by the aspect ratio of the single intrinsically rigid macromolecule. The second main factor governing the engineering properties of

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*Corresponding author, present address: Centre for Polymers & Composites, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands fibre reinforced composites is the interfacial adhesion between the fibre and the matrix. Similarly for molecular composites, the thermodynamic parameter governing the phase morphology and thereby their properties, is the miscibility of the rigid and the flexible polymer.

Thermodynamically, it is difficult to achieve a miscible molecular composite due to a low combinatorial entropy of mixing and high tendency for self alignment of the rigid polymer (9). However, true thermodynamic miscibility is a critical factor in the processing of molecular composites, as phase separation can adversely affect morphology and mechanical properties.

In this study we report on the miscibility of the molecular composite comprising polyamide-imide/polyetherimide (PAI/PEI) developed as a precursor (10,11) to the processing of oxidation resistant siloxane molecular composite (10,12) of polyamide-imide/polysiloxane-etherimide (PAI/PSI). Miscibility was established by calorimetric and dynamic mechanical thermal measurements.

Experimental

Materials

Polyamide-imide (PAI) (Torlon 4203L, measured T_g=293°C) was provided by Amoco Chemicals, Belgium. The chemical structure as reported in Amoco's Torlon high performance engineering polymer/design manual (13) is shown in figure 1(a). Chemical structures are proprietary and **Ar** consists of m-phenylene and bi-phenylene ether groups, the percentage of which varies with commercial grade of Torlon. Molecular mechanics studies (11) indicate that the molecule is intrinsically rigid and cannot coil easily due to the high rotational energy barriers of the imide and phenylene bonds, and intramolecular bonding between C=O/phenylene and N-H/phenylene.

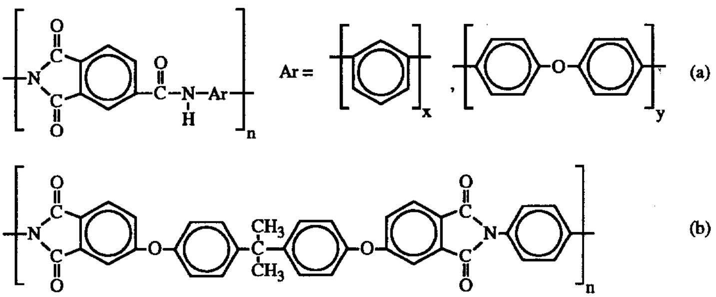

Figure 1 Chemical Structures of (a) PAI and (b) PEI

Polyetherimide (PEI) (Ultem 1000) was provided by General Electric Plastics B.V., The Netherlands and its chemical structure is shown in figure 1 (b). The polymer is relatively more flexible (11) than PAI due to the ether linkages in the chain backbone. The solvent N N' dimethylacetamide (DMAC) was obtained from Aldrich Chemical Co.

Processing of the PAI/PEI molecular composites

Compositions by weight percent for PAI/PEI blends were 15/85, 25/75, 30/70, 40/60, 50/50, 70/30, 75/25 and 85/15. Appropriate amounts of PAI and PEI were separately dissolved in DMAC solvent at 60°C. Solutions were mixed in the required weight ratios to obtain the desired molecular composite compositions in DMAC solutions. Mixed solutions were homogeneous, transparent and isotropic. Coagulation of ternary solutions in water resulted in precipitation of the molecular composites. The precipitates were filtered, washed with water and acetone, and dried under vacuum for two days each at 70°C, 140°C and 200°C. To study the effect of solvent on the thermal and dynamic mechanical thermal properties, the component polymers were also dissolved and precipitated from DMAC.

Characterisation

A Perkin-Elmer differential scanning calorimeter (DSC-4) was used to record changes in heat capacity of component polymers and molecular composites as a function of temperature. All experiments were carried out under nitrogen at a heating and cooling rate of 20°C/min. Samples were repeatedly cycled in the temperature range of 50°C to 310°C to evaluate true miscibility.

Dynamic mechanical thermal measurements were carried out on a Polymer Laboratories Dynamic Mechanical and Thermal Analyser (DMTA). Approximately 1mm thick samples were prepared by compression molding the flakes at 300°C. Data were recorded for a scan in the range of 20°C-310°C at 10Hz at a heating rate of 4°C/min in a flexural mode at a constant strain.

Results and Discussions

Differential Scanning Calorimetry

The change in heat capacity at the glass transition is relatively small for rigid polymers like PAI and consequently the magnitude of the endothermic step is also small. The criterion that miscible polymer blends show a single glass transition intermediate between those of the component polymers, and phase separated blends

Table-1 Glass Transition Temperatures of Components and Molecular Composites

PAI/PEI	Tg (°C) /DSC	Tg (°C)/DMTA
0/100	213	223
15/85	219	227
25/75	221	-
30/70	222	230
40/60	-	231
50/50	217, 280	227, 298
70/30	217, 273	227, 290
75/25	-	228, 303
85/15	279	289
100/0	293	303

show two glass transitions corresponding to individual components (14), was used in this study. PAI shows a glass transition at 293°C and PEI at 212°C. As indicated in Table-1, some compositions show a single reproducible glass transition intermediate between those of the component polymers, whereas others show two glass transitions corresponding to the individual components.

Dynamic Mechanical Measurements

Dynamic mechanical measurements of the polymers, derived by subjecting the polymer blends to a small amplitude cyclic deformation, yield important information on the transitions at the molecular level in a material. In a highly phase separated polymer blend, the transitions observed for the individual components are unchanged and a miscible blend shows a single and unique transition corresponding to the glass transition (14). As shown in figure-2, some of the PAI/PEI molecular composite compositions showed a single tan-δ peak corresponding to their glass transition temperatures and intermediate between those of the component polymers. Other compositions, however, showed two tan-δ peaks corresponding to those of individual component polymers. Glass transition temperatures measured from the tan-δ peak maximum are recorded in Table -1.

The higher Tg values obtained by DMTA relative to DSC are due to the difference in the measuring frequency. The curves also indicate the presence of β relaxations in the 100°C-120°C region in the polyimides arising from rotations of rigid phenylene and imide groups around 'hinges' such as the -O- group. Such β relaxations have been observed in other polyimides (15).

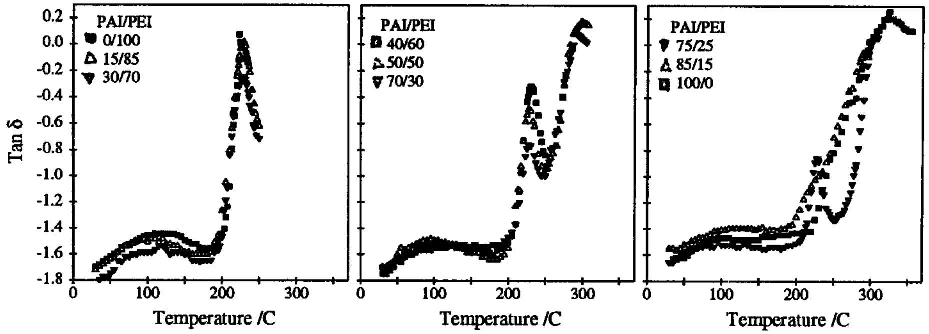

Fig-2 Dynamic mechanical thermal analysis (Tanδ vs Temperature) of components and PAI/PEI molecular composites.

Binary blends of PAI/PEI processed by DMAC solution blending and subsequent solvent casting have been reported to be immiscible (16). PAI used in that study (16) was Torlon 4000T, (T_g=273°C), however, the PAI used in this study is Torlon 4203L (measured T_g=293°C). Hwang et al. (7,17,18) have reported that ternary blends of rigid polymer / flexible polymer / solvent are homogeneous in solution and could lead to miscible homogeneous blends when rapidly coagulated in a non-solvent or to a hetrogeneous phase separated system if solvent cast. The method of rapid coprecipitation used here is partially successful in this system but the miscibility is composition dependent. The PAI/PEI blends with compositions 15/85, 25/75, 30/70, 40/60 and 85/15 are miscible whereas the 50/50, 70/30 and 75/25 blends are immiscible.

Reproducibility of the single Tg values for miscible compositions and two Tg values for phase separated blends in repeated DSC scans, establishes true miscibility in the miscible PAI/PEI molecular composites. The presence of a single relaxation peak intermediate between those of the component polymers observed for each of the miscible compositions and two relaxation peaks corresponding to the two component polymers for phase separated blends in DMTA measurements, is further evidence that there is true miscibility in some of the PAI/PEI molecular composites. The role of specific interactions and similar solubility parameters in polymer blend miscibility (19) is well documented. It may be concluded that miscibility observed in some compositions results from the similar solubility parameters of the imide and the phenylene units in both the rigid and the flexible polymers. This may also be enhanced by intermolecular hydrogen bonding between N-H of PAI and C=O of PEI. Due to the strong intramolecular hydrogen bonding between the N-H, the C=O, and phenylene rings within PAI, it is difficult to confirm intermolecular specific interactions by FTIR spectroscopy.

The Tg values increase with increasing amount of the rigid polymer in the blend and glass transitions of individual miscible molecular composites are intermediate between those of the component polymers and nearer to the glass transitions of the major blend component. The thermodynamic miscibility of PAI/PEI cannot be explained by the Flory theory (9) which has the limitation of being applicable to athermal systems and it would appear that solubility parameters greatly influence the miscibility. Molecular composites based on polyetherimide and several rigid polyimides have been found to be miscible due to similarity of imide units in chain backbone. (20).

It is well known that the rigid polymers have a tendency for self alignment (9). At high concentrations, i.e. PAI/PEI 50/50, 70/30 and 75/25, the rigid PAI molecules reduce the combinatorial entropy of mixing of PAI and PEI due to their tendency of self alignment and lead to a phase separated system. The two glass transitions recorded for each of the immiscible blend do not correspond exactly to the glass transitions of the two component polymers, but are shifted inwards. This indicates a tendency towards miscibility.

Conclusions

Molecular composites of polyamideimide/polyetherimide have been successfully processed by solution blending and a coprecipitation method. Composition dependent miscibility, detected by calorimetric and dynamic mechanical measurements results partly from the similar solubility parameters of the imide and phenylene units in the chain backbones and partly because of hydrogen bonding between the components of the blends. In addition to the thermodynamic miscibility, the critical factors in the processing of the molecular composites are enhanced mechanical properties as compared to those of the flexible polyetherimide polymer which have been evaluated and will be soon be reported in the literature (11).

Acknowledgements

Support of the European Space Agency (ESA) is gratefully acknowledged. We also thank Dr M D Judd (ESA/ESTEC) and Dr D Kassing (ESA/ESTEC) for fruitful discussions and kind support. We are grateful to Amoco Chemicals, Belgium for providing Polyamide-imide (Torlon-4203L) and to G E Plastics B.V. The Netherlands

for providing Polyetherimide (Ultem-1000).

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Accepted November 9, 1993 C