

# Polyimide films from linear and network precursors

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Pyromellitic anhydride–4,4'-diaminodiphenyl ether (PMDA-DDE) polyimide precursor was blended with mellitic acid hexamethyl ester–4,4'-diaminodiphenyl (MAHE-DDE) precursor to obtain polyimide films. The films from blends required higher temperatures for complete imidisation than those necessary for either of the pure constituents. Storage moduli and secondary glass transition temperatures improved with increase of imidisation temperature and amount of the network constituent, indicating that the latter provided some reinforcement to the mixed films. Differential thermal analysis (DTA) of the blends and the changes in morphology with composition observed by scanning electron microscopy suggested that the two constituents may be cross-linked.

## Introduction

During the past three decades, polyimides have been widely used because of their excellent properties such as thermal-oxidative stability, high strength and modulus, and excellent chemical resistance. An important consideration in the successful preparation and application of polyimides is the design of proper composition and processing conditions/parameters so that the useful properties are exploited to the fullest.

Improvements in polyimide properties have been made in a variety of ways. High modulus, high strength polyimides have been successfully prepared by high temperature treatment of polyimide fibres under tension.<sup>1</sup> Cold drawing of polyamic acid films followed by thermal imidisation has yielded high modulus and high strength polyimide films.<sup>2,3</sup> Chemical methods including synthesis of copolymers<sup>4–6</sup> to improve the mechanical and thermal properties have also been reported. Recently, an increase in storage modulus and secondary glass transition temperature has been reported after cross-linking in AFR 700B polyimide.<sup>7</sup>

Since the commercialisation of the PMDA-DDE polyimide, a variety of pyromellitic anhydride-based polyimides have been synthesised and characterised because of scientific and commercial interests.<sup>8–10</sup> However, there have not been many reports about multifunctional reactants, despite the potential for creating robust network structures. The preparation and properties of a mellitic acid-based polyimide were only recently reported.<sup>11</sup>

In this article, we discuss the preparation of MAHE-DDE (mellitic acid hexamethyl ester–4,4'-diaminodiphenyl ether†) polymer precursor solution and of films by blending MAHE-DDE with PAA-DDE (pyromellitic dianhydride–4,4'-diaminodiphenyl ether based poly(amic acid)) followed by post-polymerisation treatment. The mechanical and thermal properties as well as the morphology were studied and the results are discussed in terms of the effects of curing temperature and composition.

## Experimental

### Materials

4,4'-Diaminodiphenyl ether (DDE) was obtained from TCI (Japan) and purified by recrystallisation from distilled ethanol followed by vacuum drying at 60–80 °C for 4 h.<sup>12</sup>

†IUPAC name: bis(4-aminophenyl) ether.

Pyromellitic dianhydride (PMDA) from TCI was purified by recrystallisation from acetic anhydride followed by vacuum drying at 150–180 °C for 4 h.

Mellitic acid hexamethyl ester (MAHE) from TCI was used as received.

**Linear polymer precursor solution.** Polyamic acid (PAA) precursor was prepared by dissolving DDE in *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidin-2-one (NMP). Subsequently solid PMDA was added in stoichiometric amounts to this solution and the solution was stirred for two hours at 25 °C under a stream of argon or nitrogen to obtain a lemon-yellow, viscous solution.<sup>13</sup>

**Network polymer precursor solution (MAP).** Mellitic acid polymer (MAP) precursor was prepared by dissolving DDE and MAHE in the ratio (MAHE: DDE) of 2:3 in DMAc or NMP. The solution was stirred for 2 h under a blanket of Ar or N<sub>2</sub> while the temperature was raised from room temperature to a final value in the range 120–200 °C. A dark brown solution was obtained. This procedure is similar to that reported by Nagata *et al.*<sup>11</sup> except for the temperature and duration of heating.

Schematic formulae of monomers and polymers used in this study are shown in Fig. 1.

### Film formation

The precursor solutions containing the linear and network constituents were mixed in different proportions and cast as films in petri dishes. The films were dried at 80 °C in a vacuum oven for 1 h and imidised at temperatures in the range 250–400 °C for 1 h. The final products were coloured reddish brown and were insoluble in organic solvents.

### Characterisation

Infrared spectra were recorded on a Shimadzu DR-8101 FTIR spectrophotometer. The samples were prepared in the form of pellets together with KBr.

Storage modulus and loss modulus were measured with a TMA 2940 Thermomechanical Analyser (TA Instruments) at a ramp rate of 3 °C min<sup>-1</sup> and a frequency of 1 Hz. The samples were heated from ambient to 400 °C.

Differential thermal analysis (DTA) was performed on a Setaram Labsys instrument by using an open aluminium TG-DTA crucible in a flow of nitrogen. The samples, previously

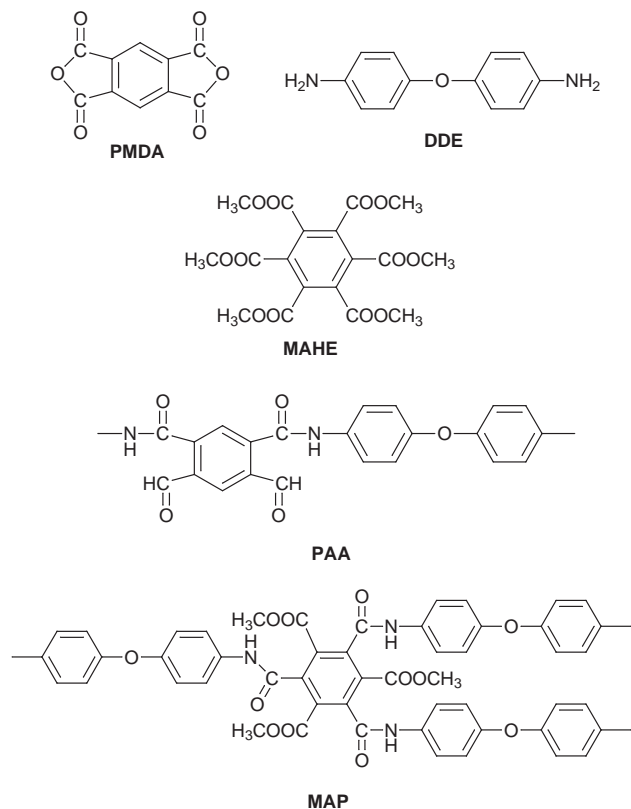


Fig. 1 Structures of monomers and polymer precursor units.

heated to 350 °C, were heated from ambient to 1000 °C at a rate of 5 °C min<sup>-1</sup>.

Thermogravimetric analyses were performed on a TA Instruments SDT 2960 simultaneous DTA-TGA under a nitrogen atmosphere. The samples were heated from 40–1000 °C at a rate of 10 °C min<sup>-1</sup>.

The cross-sectional morphology of the films was examined on a JSM-T220A scanning electron microscope. The specimens were coated with gold with a JFC-1100 ion sputterer at 10 kV and 10 mA for 5 min before examination.

## Results and discussion

### Preparation of the mixed films

Polyamic acid was prepared in the form of a viscous solution by a procedure similar to methods widely used in the literature.<sup>8</sup> Upon heating MAHE in NMP to obtain MAP, the solution was converted to a gel at a certain temperature. The gel did not re-dissolve upon adding more solvent. The transformation took place at progressively lower temperatures with increasing concentration of the reactants. A similar dependence of transformation temperature on concentration was observed when DMAc was used as the solvent. These observations are in accordance with the expected behaviour of monomers with more than two functional groups. Fig. 2 shows the relationship between reactant concentration and the transformation temperature. The point 'L' represents the conditions under which the MAP precursor solution was prepared.

The films were imidised at temperatures ranging from 250–400 °C. The colour of all the films became deeper after the heat treatment, with a greater intensity observed for higher fractions of the MAP. Also, the films became increasingly brittle with increase in MAP content. We chose two different compositions (PAA75 and PAA50 containing 75 and 50% respectively, of PAA) for investigation of thermal and mechanical properties of composite films.

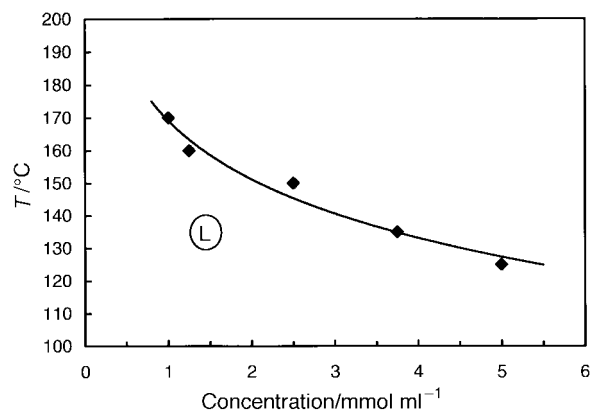


Fig. 2 Influence of monomer concentration on the temperature of solution-to-gel transformation for MAP. Position of 'L' corresponds to the conditions for preparing the MAP precursor solution.

### Infrared spectroscopy

Fig. 3 shows the scans for films containing 50% of PAA for comparison of partially ('A') and completely ('B') imidised films. Incomplete imidisation is indicated by the presence of the amide absorption peak at about 3400 cm<sup>-1</sup> for the NH stretch, and at 1655 and 1550 cm<sup>-1</sup> (weak) for the carbonyl (CONH) stretch. The imide absorption also appears at 1750 and 1780 cm<sup>-1</sup> (weak), indicating the formation of the five-membered group. Indeed, the imide absorption was present for all films containing MAP that were vacuum-dried at 80 °C, indicating that imidisation had taken place even in the solution state. The CH absorption (from the OCH<sub>3</sub> group of MAP) appears at about 2900 cm<sup>-1</sup> (weak) and at 1380 cm<sup>-1</sup>. The NH and CH absorption bands weakened with increasing temperature of imidisation and disappeared completely as in 'B'. Scan 'A' was typically obtained from MAP-PAA blend films heated to 300 °C, while scan 'B' was obtained from PAA samples heated to 250 °C, MAP heated to 350 °C, and MAP-PAA heated to 400 °C. As their structures indicate, apart from the methyl absorption for the MAP precursor, it was not possible to differentiate between the various kinds of samples based on their infrared spectra. When imidisation was complete, the pure PAA, MAP and the blends have similar spectra (as in 'B').

While the PAA is completely imidised at 250 °C, a temperature of at least 350 °C is required for complete imidisation of MAP. However, as mentioned earlier, the films from the blends are still not fully imidised at 350 °C. Thus, complete imidisation occurs in the following order with respect to imidisation temperature: PAA < MAP < blends. The higher temperature of imidisation for MAP may be due to the lower reactivity of ester groups compared to that of the acid groups

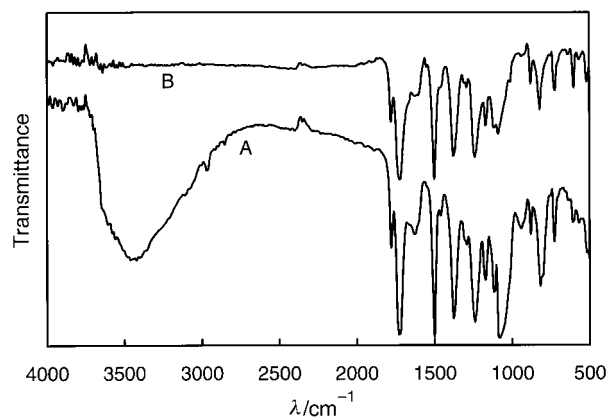


Fig. 3 FTIR spectra of composites; (A) partially imidised, (B) completely imidised.

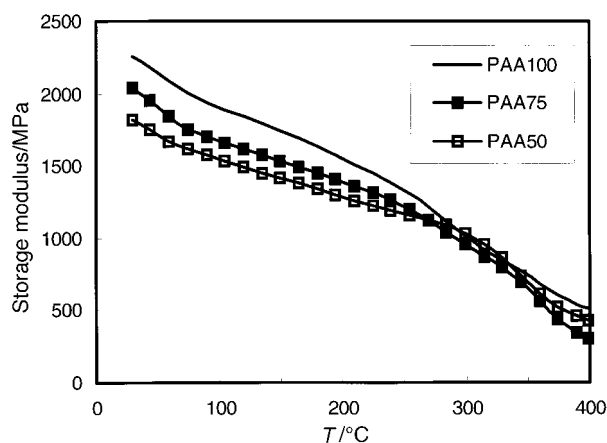
in PAA. The even higher temperature required for the imidisation in the case of the blends could be due to staggered imidisation that hinders ring closure. This situation appears to resemble the solvent effect encountered during thermal imidisation of PAA. It is known that the solvent exerts a plasticising influence and provides mobility for the chains to undergo imidisation.<sup>14,15</sup> Thus, samples which retain a higher proportion of solvent during imidisation (for example, thick films) undergo a greater degree of imidisation. In the case of the blends, imidisation proceeds first for the PAA moieties and subsequently for the MAP. However, due to the rigidity imposed on the material by the imidised PAA, imidisation of MAP proceeds at a slower rate, or alternatively, requires higher temperatures.

### Thermo-mechanical analysis

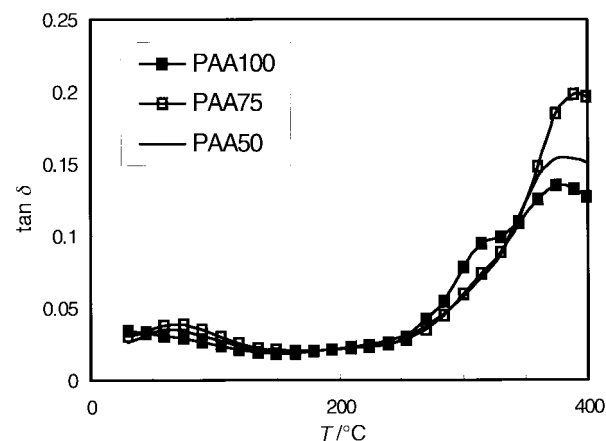
Even though imidisation is not complete for the blends after heat treatment at 250 °C or even at 350 °C, thermo-mechanical analyses of samples subsequent to heat treatment at these temperatures are illustrative in terms of corroborating the inferences from infrared spectra; also, a comparison of the data at these temperatures shows a shift of the dominating influence over the mechanical strength of the composite from PAA at the lower temperature to MAP at the higher temperature. This is also commensurate with the increase in the extent of imidisation for MAP as the temperature of imidisation is increased.

**Samples imidised at 250 °C.** Fig. 4 shows that the storage modulus decreases with increasing temperature from about 2000 MPa at room temperature to about 300 MPa at 400 °C. The pure PAA polyimide (PAA100) has the highest storage modulus followed successively by blends with increasing MAP content. Fig. 5 shows the tan delta change (calculated as the ratio of loss modulus to storage modulus) with increasing temperature. All curves exhibit two peaks, one at 75 °C, and the other at 350 °C which corresponds to the secondary glass transition temperature.

The higher value of the modulus for PAA at all temperatures is evidently due to the completion of the imidisation reaction in this sample in contrast to the partial imidisation of the blends. This is also confirmed by the greater degree of crystallinity indicated in Fig. 5 for PAA in the form of a smaller peak at the secondary transition. While the blends would have undergone imidisation even as the thermo-mechanical analysis proceeds, they are still less robust than the pure PAA. Since only a portion of the MAP would be imidised at the lower temperature of 250 °C, the mechanical strength and glass transition temperature of the film would be mostly dependent



**Fig. 4** Storage modulus as a function of temperature for samples imidised at 250 °C; PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content.



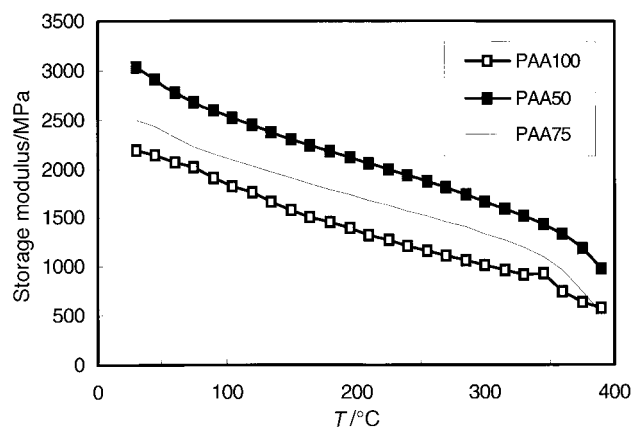
**Fig. 5** Tan delta as a function of temperature for samples imidised at 250 °C. PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content.

on the characteristics of the linear polyimide. The unimidized MAP would act as an impurity and thus contribute to a reduction in the modulus. Higher amounts of MAP in the film may lead to microphase separation,<sup>4</sup> and thus the mechanical strength of the film is expected to be further reduced.

**Samples imidised at 350 °C.** Fig. 6 shows that the films obtained from blends possessed higher storage moduli than those obtained from pure PAA; also, the values increased with MAP content. The pure PAA film had the same initial storage modulus and the same trend with temperature whether imidised at 250 or 350 °C. However, the films from blends displayed higher values when cured at 350 °C than when cured at 250 °C. This reinforces the earlier observation that both the pure MAP and the blends required higher temperatures for completion of imidisation and also indicates that presence of MAP improved the storage modulus of the material.

Fig. 7 shows the variation of tan delta with temperature for the various compositions. It can be seen from Fig. 5 and 7 that the different films have the same first glass transition temperature at about 75 °C. The PAA films display similar secondary glass transition irrespective of the temperature of imidisation. However, the films from blends showed an increase in the secondary glass transition temperature from about 350–400 °C or above when the films were heated to 350 °C.

Besides the possibility that the network component provides reinforcement to the composite film, cross-linking between PAA and MAP may account for these results.<sup>7</sup> At high temperatures, some ester and amide groups in MAP can react



**Fig. 6** Storage modulus as a function of temperature for samples imidised at 350 °C; PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content.

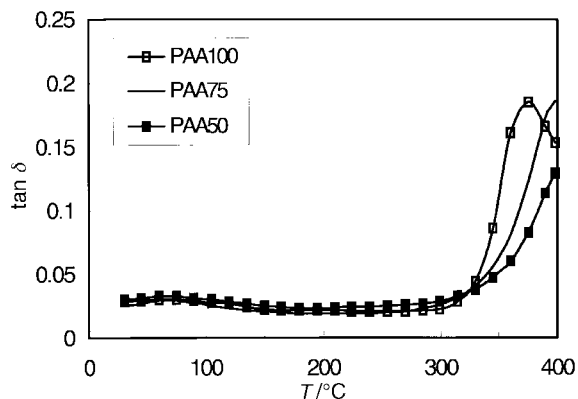


Fig. 7 Tan delta as a function of temperature for samples imidised at 350 °C. PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content.

with amide and acid groups, respectively, in PAA. Therefore the inter-species linkage in addition to the network structure formed by MAP would improve the strength and glass transition temperature of the blends. Furthermore, a higher content of network component results in a flatter and broader peak in Fig. 7 which would be an indication of a higher degree of crosslinking.

#### Differential thermal analysis (DTA)

Though close to each other, the decomposition points of pure PAA and MAP (PAA0) polyimides are seen to be different (Fig. 8). Both the PAA75 (75% PAA) and PAA50 (50% PAA) samples show smooth peaks, indicating single transitions. If the nature of the reinforcement was purely physical, additional peaks or shoulders would be expected in their scans. The absence of separate peaks for the blends, together with the relative reduction in the strength of the peaks with increasing MAP content, suggests cross-linking between PAA and MAP segments. In order to check whether broadening resulted in loss of peaks due to overlap, PAA and MAP were separately imidised at 350 °C and mixed in proportions corresponding to PAA75 and PAA50. When these samples were subjected to differential thermal analysis, shoulders appeared in the scans, clearly showing two decomposition points in each of the compositions (Fig. 9). This is a strong indication that some covalent linkage has taken place in the blends. The decomposition temperatures are observed to be in the following order: PAA > PAA75 > PAA50 > MAP. This order could also be seen from the following TG results.

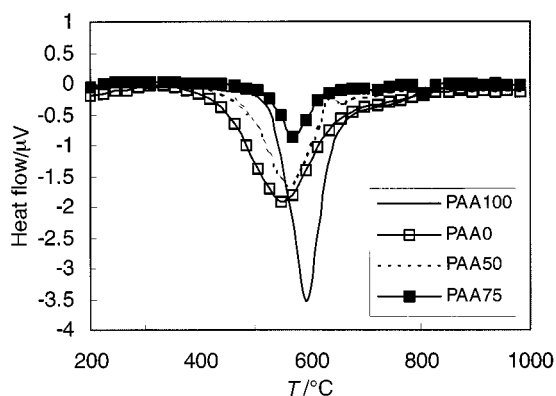


Fig. 8 DTA curves for samples imidised at 350 °C; PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content; PAA0: pure MAP.

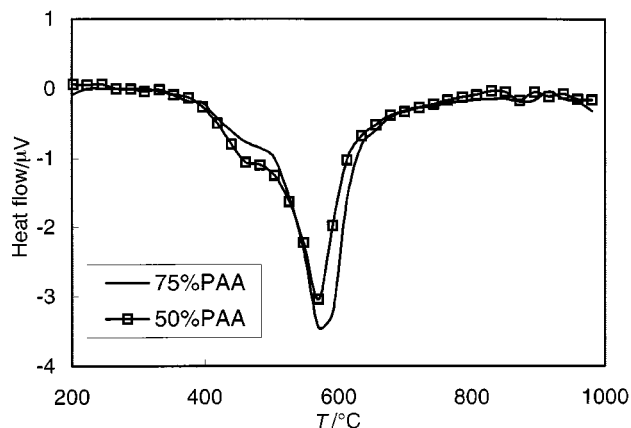


Fig. 9 DTA curves for mixtures of pure PAA and MAP separately imidised at 350 °C.

#### Thermogravimetric analyses (TG)

Fig. 10 shows TG curves of the blended films imidised at 350 °C. The decomposition temperatures of the composite films are lower than for pure PAA film but higher than for the pure MAP, and conform to the observation from DTA; however, the residues for all the blended films at the end of the analysis were higher than for pure PAA and MAP. These results are similar to those shown by Nagata *et al.*,<sup>11</sup> where they considered the formation of a carbonised structure as one promoted by the network structure of MAP.

#### Scanning electron microscopy

Fig. 11 shows the SEM micrographs of the cross section of the films. Fig. 11(a) and (b) represent the morphology of pure PAA and MAP samples, respectively, both imidised at 350 °C for 1 h. The pure PAA film is featureless except for the traces of incision. Discrete particles dominate in Fig. 11(b), revealing a brittle morphology and thus presumably, poor mechanical properties. Fig. 11(c), representing the 50% blend imidised at 400 °C for 1 h, shows undulating features together with discrete particles—presumably MAP—embedded in the background. However, the proportion of the discrete particles appears to be less than that commensurate with a 50% composition. This suggests that, while MAP may be a physically reinforcing constituent, it also contributes to the strength by means of cross-linking with the linear component.

#### Conclusions

Pre-polymer solutions derived from mellitic acid hexamethyl ester could be prepared with different stoichiometric concen-

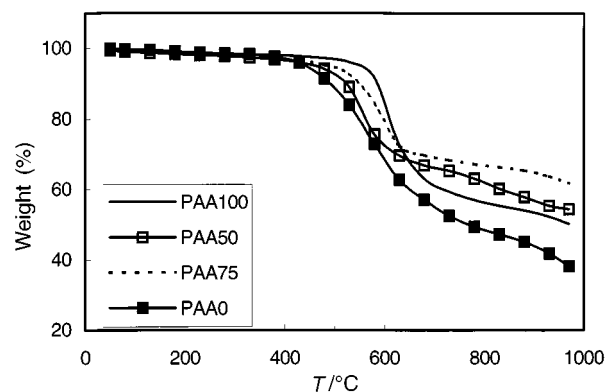
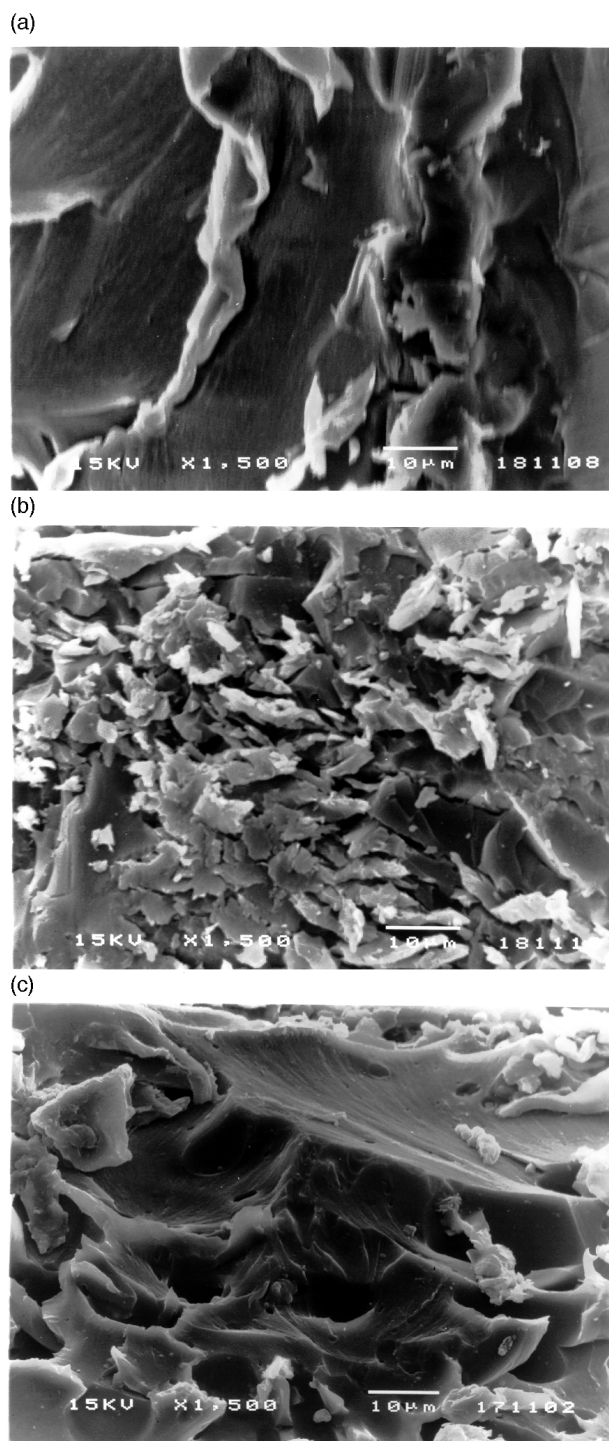


Fig. 10 TGA curves for samples imidised at 350 °C; PAA100: pure PAA; PAA75: blend with 75% PAA content; PAA50: blend with 50% PAA content; PAA0: pure MAP.



**Fig. 11** Scanning electron micrographs of the cross section of the films imidised at 350 °C for 1 h: (a) pure PAA film, (b) pure MAP and (c) composite film containing 50% PAA.

trations of reactants; when heated, the solutions formed gel-like structures at temperatures inversely dependent on the concentrations.

Blends of PAA and MAP were prepared and the mechanical and thermal properties of cast films were investigated as functions of composition, and temperature of imidisation. The temperature for complete imidisation was found to be in the

following order: blends > MAP > PAA. The high temperature required for the blends may be due to staggered imidisation of the linear and cross-linked segments. The blends displayed higher storage modulus and secondary glass transition temperatures than pure PAA films, indicating that the properties improved with increasing MAP content. However, films with MAP content greater than 50% by weight were too brittle to measure the mechanical properties.

Differential thermal analysis suggested that there was covalent linkage between PAA and MAP segments. The decomposition temperatures of the pure and composite films were found to be in the following order: pure PAA > PAA75 > PAA50 > pure MAP. Thermogravimetry showed that the composites had lower decomposition temperatures but higher contents of residue compared to pure PAA.

Scanning electron micrographs showed the blends to possess an intermediate morphology between the featureless, undulating topography of the PAA polyimide and the brittle, particulate cross section of the MAP polyimide. However, the relatively small amount of discrete particles further reinforces the indication from DTA that the two constituents were substantially cross-linked.

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