

High-temperature polyimide composites prepared from soluble polymeric and crosslinkable oligomeric precursors: phase demixing and properties

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Rigid/crosslinked flexible polyimide composites were prepared from soluble polymeric and oligomeric precursors: poly(4,4'-oxydiphenylene pyromellitic acid) [PMDA-ODA(PAA)], poly(4,4'-oxydiphenylene pyromellitic diethyl ester) [PMDA-ODA(ES)], acetylene-terminated isoimide oligomer of 3,3',4,4'-benzophenonetetracarboxylic dianhydride/1,3-bis(3-aminophenoxy)benzene (BTDA-APB) and acetylene-terminated imide oligomer of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/1,3-bis(3-aminophenoxy)benzene (6FDA-APB). PMDA-ODA(PAA) precursor was found to react with BTDA-APB isoimide oligomer in *N*-methyl-2-pyrrolidone (NMP), resulting in gels. Furthermore, PMDA-ODA(PAA) exhibited a limited miscibility in making its homogeneous solution with 6FDA-APB imide oligomer in NMP, consequently leading to large domains in the softbaked blend films as well as in the resultant composite films. In contrast, for PMDA-ODA(ES) blends with 6FDA-APB and BTDA-APB, homogeneous ternary solutions with a relatively high solids content of ≤ 30 wt% were easily achieved in NMP over the entire composition range. Dried blend films were optically clear except a few compositions. For some compositions, the optical transparency in the dried films was retained through the thermal curing process, providing optically transparent semi-interpenetrating network (semi-IPN) composites. However, for the other compositions, phase separation took place through thermal curing, forming domains of submicrometre scales in the resultant composites. Properties of the polyimide composites were investigated by dynamic mechanical thermal analysis (d.m.t.a.), stress-strain analysis and self-adhesion measurement. In particular, the self-adhesion property of PMDA-ODA was significantly improved by the composite formation with 6FDA-APB, but not improved by the composite formation with BTDA-APB. The good self-adhesion in the PMDA-ODA/6FDA-APB composite was characterized by X-ray photoelectron spectroscopy and attributed mainly to the favourable molecular interdiffusion through the 6FDA-APB component segregated on the surface. In addition, the residual stress and relaxation behaviour were measured. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

High-temperature aromatic polyimides are widely used as high-performance speciality polymers, because of their excellent thermal stability and mechanical properties^{1–4}. In particular, their applications in advanced microelectronic devices require excellent chemical and physical properties, such as high chemical resistance, high glass transition temperature, high thermal stability, good toughness, low dielectric constant, low thermal expansivity, high chemical resistance and good adhesion⁵. Some of the required properties can be achieved from a rigid polymer, whereas some other properties are characteristic of a flexible chain polymer. However, all the property requirements cannot easily be met by a single homopolymer.

One approach to meet the property requirements is to blend a rigid polymer with a flexible polymer in order to combine their beneficial properties. However, it is difficult to achieve a rigid/flexible polymer blend with the desired level of molecular mixing through direct mixing in a mutual

solvent, because they are inherently immiscible and usually lead to phase separation on a large scale. Another difficulty is finding a mutual solvent that is sufficient to make a homogeneous solution with an appreciable concentration of the polymer mixture. In the case of polyimides, these difficult problems can be avoided since they are usually mixed and processed in their random, coil-like polymeric or oligomeric precursors instead of the insoluble rigid and flexible polyimides, and finally converted to the polyimides.

Recently, Ree *et al.*^{6–9} reported several rod-like/flexible polyimide composites via *in situ* rod-like chain formation by thermal imidization. In the studies, a poly(amic dialkyl ester) precursor of one component was mixed with a poly(amic acid) or poly(amic dialkyl ester) precursor of another component in *N*-methyl-2-pyrrolidone (NMP). This mixture prevents the formation of a segmented blocky copolymer of both components due to transamidation reactions in a mixture of poly(amic acid) precursors, as reported previously by Ree *et al.*^{10,11} and Feger¹². The polyimide precursors used always phase-separated from each other during drying after film casting from the homogeneous solution in NMP, because of their immiscibility.

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The dried precursor blend films were subjected to thermal imidization in order to convert the rod-like/flexible polyimide composites. Once phase separation took place in the precursor mixtures through the drying process, the size of the phase-separated domains was not changed further by the subsequent thermal imidization. However, rod-like/flexible polyimide composites on a submicrometre scale were easily achieved through the conventional polyimide fabrication process.

In the present study, the concept of rod-like/flexible composites via *in situ* rod formation was extended to a semi-interpenetrating polymer network (semi-IPN) system for making semi-IPN based polyimide composites. They may be achievable from soluble polyimide precursor blends with crosslinkable oligomers. Here, a big question that arises is how much molecular demixing can be achieved in the blends. The degree of phase demixing in the resultant composites may depend primarily upon the history of molecular demixing in the polymeric precursor/crosslinkable oligomer mixtures during solvent drying and subsequent curing. As illustrated schematically in *Figure 1*, when the polymeric and oligomeric precursors are well mixed at the molecular level, it is possible to obtain a semi-IPN type of molecular composite by minimizing further phase separation via thermal curing. Otherwise, phase separation is involved in the precursor mixtures, consequently leading to demixed linear rigid/crosslinked polyimide composites. Sometimes, submicrometre-scale polyimide composites may be obtained if the phase separation is controlled on a submicrometre scale through the drying and curing process.

Potential candidate materials for the crosslinkable flexible component are acetylene-terminated oligomeric imide and isoimide, which are known to exhibit excellent solubility and good interfacial adhesion to themselves, ceramic substrates and metals^{13,14}. The representative oligomers are acetylene-terminated imide oligomer of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/1,3-bis(3-aminophenoxy)benzene (6FDA-APB) and isoimide oligomer of 3,3',4,4'-benzophenonetetracarboxylic dianhydride/1,3-bis(3-aminophenoxy)benzene (BTDA-APB)

(see the chemical structures in *Figure 2*)^{15,16}. The crosslinking reactions of acetylene-terminated oligomers have been investigated in detail by several research groups¹⁶⁻¹⁹. On heating runs with a rate of 2.5–10.0°C min⁻¹, the thermal crosslinking reaction of the acetylene groups was detected calorimetrically and spectroscopically (infra-red) to occur over the range 190–310°C even though they were not assisted by any catalyst¹⁶⁻¹⁸. In the case of isoimide oligomers, the thermal isomerization of isoimide to imide was also detected to take place over the range 150–350°C¹⁶⁻¹⁸. Thus, for the BTDA-APB isoimide oligomer, on heating runs both the crosslinking reaction and the isomerization occur simultaneously over 150–350°C. On the other hand, good candidate materials for the linear rigid polymer component are soluble poly(amic acid) and poly(amic diethyl ester) precursors of rigid poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA): poly(4,4'-oxydiphenylene pyromellitic acid) [PMDA-ODA(PAA)] and poly(4,4'-oxydiphenylene pyromellitic diethyl ester) [PMDA-ODA(ES)]. The precursor polymers are well known to be easily converted to the linear rigid PMDA-ODA polyimide by thermal imidization^{1-4,6-11,20,21}. On heating runs with a rate of 2.0–5.0°C min⁻¹, the PMDA-ODA(PAA) precursor was thermally imidized over the range 130–250°C, whereas the PMDA-ODA(ES) precursor was imidized over the range 190–350°C²⁰⁻²³.

In this study, the crosslinkable oligomers were blended with soluble poly(amic acid) and poly(amic diethyl ester) precursors of rigid PMDA-ODA polyimide in a mutual solvent, NMP. The miscibility of the polymeric and oligomeric precursors was investigated in NMP solution, in the condensed state, and in the thermally cured solid state by optical microscopy, light scattering and dynamic mechanical thermal analysis. Rigid/crosslinked polyimide composites in films were prepared from homogeneous ternary solutions of the polymeric and oligomeric precursors in NMP through a conventional film-formation process (i.e. solution casting, drying and curing process) that is widely used in the microelectronics industry: PMDA-ODA/6FDA-APB and PMDA-ODA/BTDA-APB composites. Properties of the polyimide composite films were

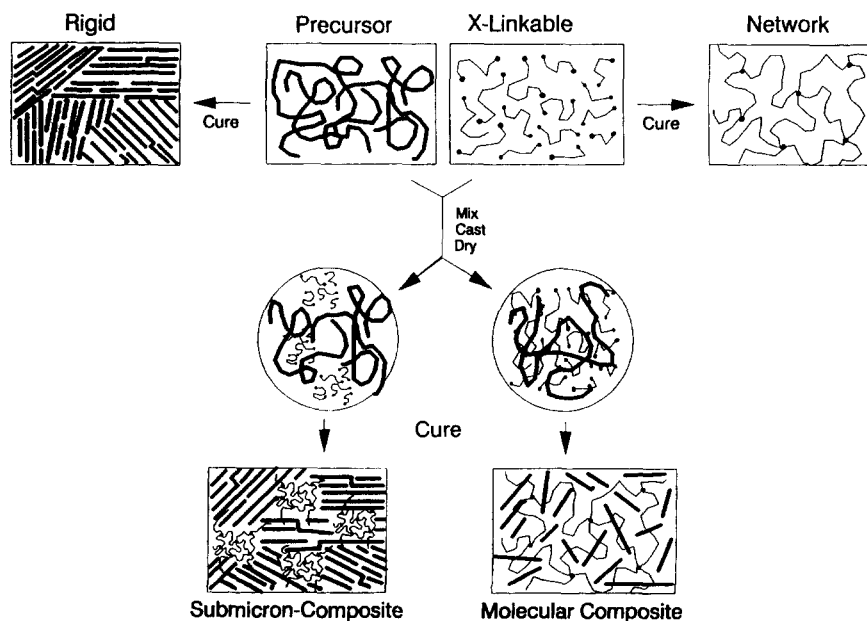


Figure 1 Schematic representation of types of rigid/flexible polyimide composites via *in situ* rigid and crosslinked chain formation

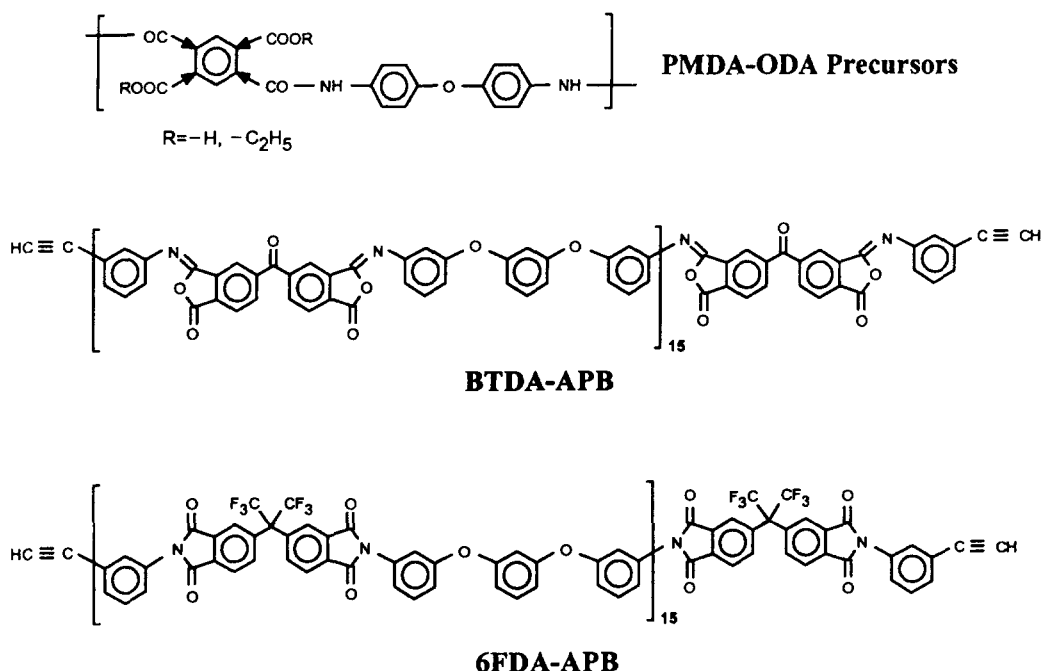


Figure 2 Chemical structures of flexible precursors [poly(amic acid) and poly(amic diethyl ester)] of rigid poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA) and acetylene-terminated oligomers (BTDA-APB isoimide and 6FDA-APB imide)

investigated by d.m.t.a., stress-strain analysis, residual stress analysis and self-adhesion measurement. In addition, the surface composition characteristic was examined, in particular for the PMDA-ODA/6FDA-APB composite.

EXPERIMENTAL

Poly(4,4'-oxydiphenylene pyromellitic acid) [PMDA-ODA(PAA)] ($M_w = ca. 30\,000$; 16.0 wt% solids content) and poly(4,4'-oxydiphenylene pyromellitic diethyl ester) [PMDA-ODA(ES)] ($M_w = ca. 35\,000$; 16.7 wt% solids content) solutions in NMP were supplied from Du Pont Chemical Company and used as the flexible precursors of linear rigid PMDA-ODA polyimide. Crosslinkable oligomers, acetylene-terminated imide oligomer of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/1,3-bis(3-aminophenoxy)benzene (6FDA-APB; degree of polymerization, \overline{DP} , of 15) and isoimide oligomer of 3,3',4,4'-benzophenonetetracarboxylic dianhydride/1,3-bis(3-aminophenoxy)benzene (BTDA-APB; $\overline{DP} = 15$) were supplied from National Starch and Chemical Company as powders. These oligomers were dissolved in NMP and filtered with 1.0 μm Fluoropore filter membranes, to produce 34.5 wt% 6FDA-APB and 35.0 wt% BTDA-APB solutions, respectively.

From these precursors, four binary blend systems were made: PMDA-ODA(PAA)/BTDA-APB, PMDA-ODA(PAA)/6FDA-APB, PMDA-ODA(ES)/6FDA-APB and PMDA-ODA(ES)/BTDA-APB. For each blend system, ternary solutions in NMP were prepared with various compositions by mixing for 1 day on a roller mixer. The ternary solutions were spin-cast on glass slides or silicon wafers, followed by softbaking on a hot-plate at 80°C for 60 min. Then, the softbaked blend films were thermally cured in an oven with nitrogen flow by means of the following cure protocol: 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h with a heating rate of 2.0°C min⁻¹. For residual stress measurements, film samples were prepared on A1100 (0.1% γ -aminopropyltriethoxysilane in 90 vol% ethanol/10 vol%

deionized water) primed Si(100) wafers of 82.5 mm diameter. The thickness of composite films was 10 μm . For self-adhesion tests, another film layer was overcoated on the top of some film samples prepared on glass slides. The thickness of the second layer films was 20 μm .

Both softbaked and cured blend films were examined with the aid of an optical microscope (Jena or Polyvar-Met) under crossed polarization and a photographic light-scattering apparatus with a He-Ne laser source under parallel polarization. Dynamic mechanical thermal properties were measured at a heating rate of 10.0°C min⁻¹ and a frequency of 10 Hz in nitrogen atmosphere over the range 25°C to 500°C with a dynamic mechanical thermal analyser (model Mark II, Polymer Laboratories) with a tensile head. Mechanical properties were measured at room temperature, on a tensile tester (model 1122, Instron). In the mechanical testing, the grip gauge length was ca. 50 mm and the strain rate was 1.6 $\times 10^{-2}$ s⁻¹. The width of film strips was 3.175 mm. For each sample, more than 10 film strips were tested, and their mechanical data were averaged out. Peel tests for self-adhesion were performed in 90° peeling mode with the aid of the Instron tester equipped with a 90° peel test fixture. The crosshead speed was 0.2–2.0 mm min⁻¹ and the width of peel strips was 2.0–5.0 mm. All the film strips were prepared with the aid of a dicer equipped with a circular blade and controlled by a computer. Residual stress measurements were performed dynamically in nitrogen atmosphere during thermal curing of the softbaked films on Si(100) wafers through the same cure process as described above and subsequent cooling at 1.0°C min⁻¹ rate; such measurements were performed with a Flexus stress analyser (model 2-300) or a similar stress analyser made in our laboratory, which was equipped with a He-Ne laser, a hot-stage and controlled by a personal computer. For the composite films, the relaxation of residual stress was monitored at 25°C in 50% relative humidity (RH) as a function of time. In addition, the surface composition was analysed for the PMDA-ODA/6FDA-APB composites, by using an X-ray

photoelectron spectrometer (SSX-100 model 05, Surface Science Instruments).

RESULTS AND DISCUSSION

Miscibility behaviour

Attempts were made to produce ternary solutions of PMDA-ODA(PAA)/BTDA-APB in NMP. However, when PMDA-ODA(PAA) precursor was mixed with BTDA-APB isoimide oligomer, they reacted each other through the reactive amic acids and isoimide groups and finally came out as gels. On the other hand, for the PMDA-ODA(PAA)/6FDA-APB blend system, its ternary solution in NMP was found to be homogeneous up to 20 wt% solids content for various compositions; however, it became turbid at >20 wt% solids content. Both softbaked and cured films, which were prepared from the homogeneous solutions with only 10 wt% solids content, exhibited large-scale phase separation. The size of the phase-separated domains was of the order of tens of micrometres. For these reasons, the PMDA-ODA(PAA) blend systems were not investigated further.

In contrast, for the PMDA-ODA(ES)/6FDA-APB system, ternary homogeneous solutions in NMP were obtained over the entire composition range for a solids content of ≤ 30 wt%. The homogeneous solutions with a solids content of 10 wt% were cast on glass slides and subsequently softbaked at 80°C for 1 h. Then, optical clear films were obtained for the entire range of composition. Furthermore, the optical transparency of these blend films, except for the 30/70 [= PMDA-ODA(ES)/6FDA-APB in weight ratio] and 50/50 compositions, was retained even after thermal curing at 400°C (see Table 1). Both the 50/50 and the 30/70 blends revealed phase-separated domains on the submicrometre scale. Here, it is noted that the optical clarity observed for some compositions does not mean that the two components are miscible with each other at a molecular level. The optically clear films are perhaps composed with domains phase-separated on a scale of less than a submicrometre. This evidence was detected in the d.m.t.a. results. This will be discussed in detail later.

For the PMDA-ODA(ES)/BTDA-APB blend system,

homogeneous ternary solutions in NMP were obtained over ≤ 30 wt% solids content, as observed in the PMDA-ODA(ES)/6FDA-APB blend system. The blend films, which were cast from the homogeneous solutions of 10 wt% solids content, were optically clear for various compositions, except for the 30/70 composition. The 30/70 composition exhibited phase separation on the scale of several micrometres (see Table 2). After curing, only the 10/90 composition still retained optical clarity. However, the other compositions exhibited phase-separated domains on a submicrometre scale. In comparison, the miscibility behaviour of PMDA-ODA(ES)/BTDA-APB blends was similar to that of PMDA-ODA(ES)/6FDA-APB blends, but their phase-separated domain size was relatively larger than that of PMDA-ODA(ES)/6FDA-APB blends.

Overall, for the polyimide precursor blends considered here, miscible ternary solutions in NMP have been easily achieved up to 20–30 wt% solids content. In the case of commercial polyimide precursor solutions for microelectronic applications, solids content is generally less than 20 wt%. In the practical sense, the high concentration of 20–30 wt% is very useful for the fabrication of microelectronic devices.

For both the 30/70 composition of the PMDA-ODA(ES)/BTDA-APB blend and all the compositions in the PMDA-ODA(PAA) blend with 6FDA-APB, phase separation took place primarily during solvent drying from the homogeneous ternary solutions in NMP. In the phase separation, the level of demixing is controlled by the compositional quenching process that results from the removal of NMP solvent. During evaporation of NMP solvent, the ternary solution may be instantaneously plunged into the spinodal decomposition region. Then, the spinodal decomposition, which leads phase separation, competes with the compositional quenching process driven by solvent evaporation. Of course, when the evaporation of solvent is slow, the nucleation and growth mechanism may be involved and, consequently, the ternary solution reaches into the binodal region. However, this process is slow in comparison to the spinodal decomposition process. In fact, the solvent evaporation is a continuous process, so that the nucleation and growth process should not have enough time to occur. Therefore, for the precursor blend films obtained from their homogeneous ternary solutions through the conventional solution casting and drying process, the level of demixing is believed to be controlled predominantly by the competition between the spinodal decomposition and the compositional quenching driven by continuous solvent evaporation.

In contrast, for the PMDA-ODA(ES) blends with 6FDA-APB and BTDA-APB, optically clear blend films were obtained by the conventional solvent drying process as illustrated in Tables 1 and 2. Phase separation was observed to occur for the blend films with a few compositions on the submicrometre scale during subsequent thermal curing at 400°C. This is different from the rod-like poly(*p*-phenylene pyromellitimide) (PMDA-PDA) composites with flexible linear polyimides in which phase separation took place primarily during solvent drying and the domains developed were very much preserved in size without further significant phase separation during thermal imidization^{5,7,8}. The difference in the phase-separation behaviours might result from a difference between molecular chain mobilities in the two different blend systems. Both BTDA-APB and 6FDA-APB were known to have glass transition temperatures (T_g s) of ca. 160°C and 175°C, respectively^{16–18}, which are relatively lower than those of the precursor polymers employed

Table 1 Apparent miscibility behaviour of PMDA-ODA(ES) blends with 6FDA-APB observed by optical microscopy and light scattering

PMDA-ODA(ES)/ 6FDA-APB (w/w)	Solution (10 wt% in NMP)	Softbaked film (80°C/1 h)	Cured film (400°C/1 h)
90/10	clear ^a	clear	clear
70/30	clear	clear	clear
50/50	clear	clear	$\leq 1 \mu\text{m}^b$
30/70	clear	clear	$< 1 \mu\text{m}$
10/90	clear	clear	clear

^aOptically clear

^bDomain size

Table 2 Apparent miscibility behaviour of PMDA-ODA(ES) blends with BTDA-APB observed by optical microscopy and light scattering

PMDA-ODA(ES)/ 6FDA-APB (w/w)	Solution (10 wt% in NMP)	Softbaked film (80°C/1 h)	Cured film (400°C/1 h)
90/10	clear ^a	clear	$< 1 \mu\text{m}^b$
70/30	clear	clear	$< 1 \mu\text{m}$
50/50	clear	clear	$< 1 \mu\text{m}$
30/70	clear	$> 1 \mu\text{m}$	$> 1 \mu\text{m}$
10/90	clear	clear	clear

^aOptically clear

^bDomain size

in the formation of the rod-like PMDA-PDA polyimide composites. The relatively low T_g s of the crosslinkable oligomeric components may provide relatively high molecular mobility in their blends with PMDA-ODA(ES) having undergone thermal curing, consequently allowing a limited level of phase separation.

Properties

The properties of composite films cured at 400°C were measured by means of dynamic mechanical thermal analysis, stress-strain analysis, and residual stress analysis. The glass transition behaviour and dynamic mechanical properties (storage and loss moduli, E' and E'') were investigated over the temperature range 25–500°C. The d.m.t.a. results of PMDA-ODA/6FDA-APB composite films are shown in Figure 3. For the PMDA-ODA polyimide the storage modulus E' showed a gradual decrease up to ca. 380°C and a relatively large drop above 380°C. The T_g of the PMDA-ODA was estimated to be ca. 410°C. The thermally crosslinked 6FDA-APB exhibited E' versus temperature behaviour up to ca. 240°C similar to the behaviour observed for the PMDA-ODA. However, the 6FDA-APB polyimide showed a very sharp glass transition at ca. 245°C, which is much lower than for the PMDA-ODA. The composite films of 6FDA-APB and PMDA-ODA revealed two transitions: one at ca. 245°C and the other in the range 330–410°C. The softening point at 245°C, which corresponds to the T_g of the 6FDA-APB component, changed little with composition, indicating that the PMDA-ODA and 6FDA-APB components demixed in the composites. The other softening

behaviour in the higher temperature region is due to the glass transition of the PMDA-ODA component. This softening temperature decreased as the content of PMDA-ODA in the composite decreased. This decrease might be due to the characteristic tensile mode near the glass transition of the higher T_g component (PMDA-ODA) in the d.m.t.a. measurement, rather than its miscibility with 6FDA-APB. That is, above the T_g of the 6FDA-APB component, the dimensional stability of the composite film decreases with decreasing the content of PMDA-ODA. The variation of this dimensional stability in the composite film might be directly reflected in the E' versus temperature behaviour measured in the tensile mode. A similar d.m.t.a. behaviour was observed for the BTDA-APB composite system.

The mechanical properties of composite films were investigated at room temperature. The results are summarized in Table 3. The Young's modulus (E) was 2.9 GPa for PMDA-ODA, and 3.7 GPa for 6FDA-APB and BTDA-APB polyimides. The strain at break (ϵ_b) was 106% for PMDA-ODA, and 5% for 6FDA-APB and BTDA-APB. Composite films of these components exhibited mechanical properties intermediate between those of the components.

For the PMDA-ODA/6FDA-APB composite, the ϵ_b was 33% for the 25/75 composition and 107–109% for both the 50/50 and 75/25 compositions. In particular, the 25/75 composite exhibited highly improved strain behaviour, even though the matrix component was 6FDA-APB. Both 25/75 and 50/50 composite films showed a yielding behaviour on the stress-strain curves typically observed for most flexible

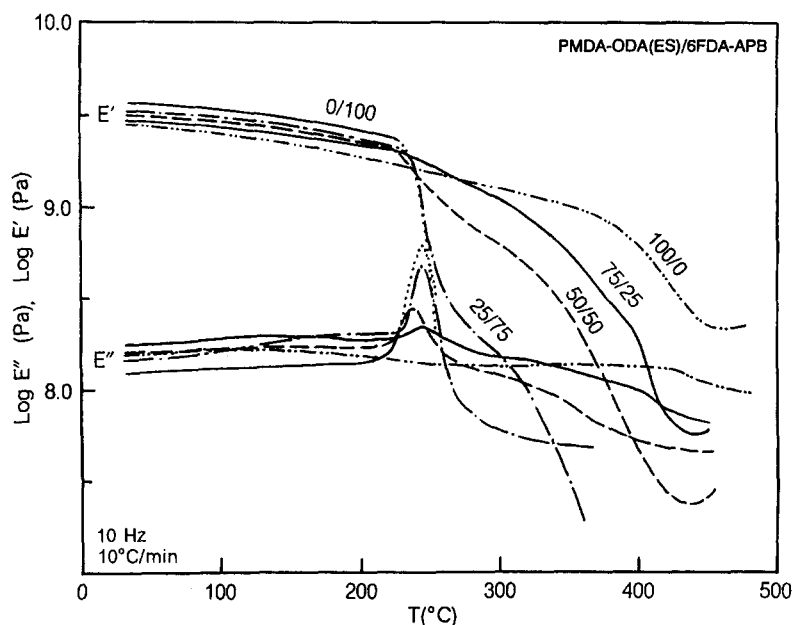


Figure 3 Dynamic mechanical relaxation behaviour (storage and loss moduli, E' and E'') of PMDA-ODA/6FDA-APB composite films cured at 400°C

Table 3 Mechanical properties of PMDA-ODA/6FDA-APB composite films thermally cured at 400°C

Mechanical properties	PMDA-ODA/6FDA-APB (w/w)				
	100/0	75/25	50/50	25/75	0/100
Modulus (GPa)	2.9 (0.1) ^a	3.2 (0.1)	3.3 (0.1)	3.5 (0.1)	3.7 (0.1)
Stress at break (MPa)	221 (17)	216 (21)	187 (23)	139 (10)	134 (8)
Strain at break (%)	106 (12)	107 (15)	109 (18)	33 (9)	5 (2)
Stress at yield (MPa)	—	—	127 (3)	145 (3)	—
Strain at yield (%)	—	—	6 (0.2)	6 (0.2)	—

^aThe numbers in parentheses indicate one standard deviation

polymers. The yield stress and strain (σ_y and ϵ_y) were 145.4 MPa and 6% for the 25/75 composite and 126.9 MPa and 6% for the 50/50 composite, respectively. This yielding behaviour might result from the 6FDA-APB component in the composites. Thus, this indicates that the yield strain of 6FDA-APB is 6%, which could not be measured for the 6FDA-APB polyimide because its strain at break was lower than the yield strain. In addition to the yielding behaviour, these composite films showed a multiple necking behaviour. However, the yielding and multiple necking behaviour was not observed for the 75/25 composite and the PMDA-ODA polyimide film. Overall, the mechanical properties of 6FDA-APB polyimide were significantly improved by the composite formation with PMDA-ODA.

The residual stress behaviours of precursor blends and

their resulting polyimide composites were investigated on Si(1 0 0) wafers with the aid of a stress analyser equipped with a hot-stage. Here, the residual stress (σ_F) was calculated from radii of wafer curvatures measured before and after polyimide film deposition²⁴. During thermal curing and subsequent cooling, the stress of precursor blend films on Si wafers was monitored *in situ* as a function of temperature over the range 25–400°C. As a representative example, the stress *versus* temperature behaviour of a PMDA-ODA(ES) precursor film is illustrated in Figure 4. During thermal curing, the stress level of the PMDA-ODA(ES) precursor film softbaked at 80°C was less than 5 MPa over the range 25–400°C, reflecting the variation of intrinsic stress of the softbaked precursor film owing to its continuous curing and volume change through the removal

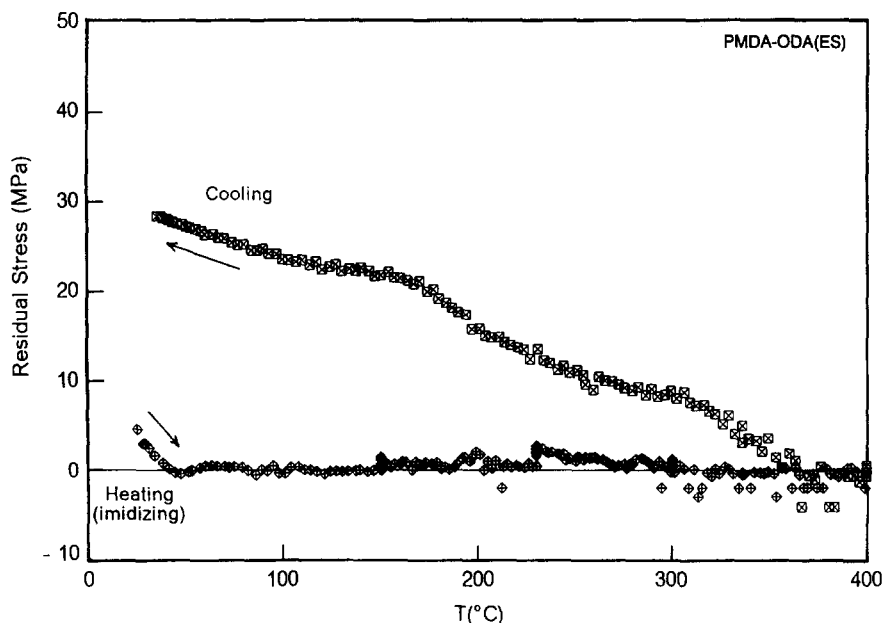


Figure 4 Residual stress *versus* temperature of the softbaked PMDA-ODA(ES) film on a silicon substrate monitored *in situ* during thermal curing and subsequent cooling. The curing protocol employed was 150°C/30 min, 230°C/30 min, 300°C/30 min and 400°C/1 h with a heating rate of 2.0°C min⁻¹. A cooling rate of 1.0°C min⁻¹ was used

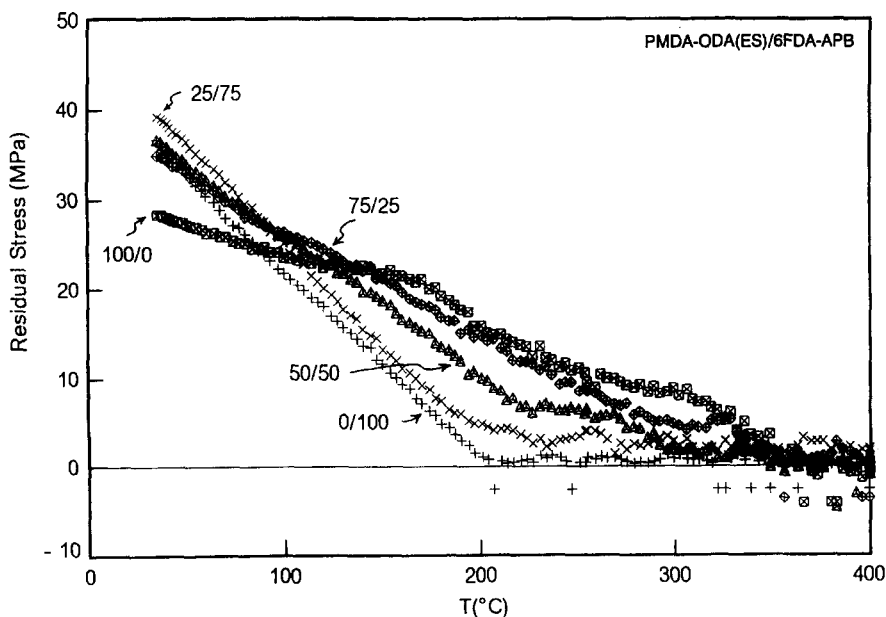


Figure 5 Residual stresses *versus* temperature of the PMDA-ODA/6FDA-APB composite films on silicon substrates measured *in situ* during subsequent cooling with 1.0°C min⁻¹ rate after curing at 400°C

of residual NMP and ethyl alcohol byproduct. After the completion of curing at 400°C, the stress built up with decreasing temperature on cooling and finally reached 29 MPa at room temperature.

A similar stress *versus* temperature behaviour was observed for the other polyimides studied here but the stress level was dependent upon backbone chemistry. For the films dried at 80°C for 30 min, the residual stress at room temperature was 12 MPa for both BTDA-APB and 6FDA-APB. The stress of a dried precursor film depends strongly on the degree of drying in addition to the chemical backbone. The high residual solvent in the film gives the lower stress. After thermal curing at 400°C, the stress at room temperature was 29 MPa for PMDA-ODA, 35 MPa for BTDA-APB, and 38 MPa for 6FDA-APB.

Composite films of these materials exhibited stress behaviour intermediate between those of the components. However, the stress in the composite films was significantly influenced by the high-stress component, BTDA-APB or 6FDA-APB. As an example, the stress behaviour of the PMDA-ODA/6FDA-APB composite films cured at 400°C is illustrated in Figure 5. On cooling from 400°C, for 6FDA-APB polyimide with a relatively low T_g of 245°C, the stress started to rapidly increase at *ca.* 210°C, whereas for PMDA-ODA polyimide with a high T_g of 410°C the stress increased gradually from 400°C. In the stress–temperature curve, the slope for 6FDA-APB is relatively steeper than for the PMDA-ODA polyimide. The slope is primarily proportional to the degree of mismatch between the thermal expansion coefficients (TECs) of the polyimide film and silicon substrate²⁵. The TEC of Si(1 0 0) substrates is *ca.* $3.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ over the range 25–400°C. Therefore, the TEC of 6FDA-APB is much higher than the TEC ($30 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) of PMDA-ODA polyimide²⁶.

The stress *versus* temperature plots in Figure 5 can be divided into two temperature regions: (1) room temperature to 90°C and (2) 90°C to 400°C. First, in the 90–400°C range, the stress level of PMDA-ODA polyimide exhibiting a higher T_g is higher than the stress level of 6FDA-APB, despite its relatively less steep slope in the stress–temperature curve.

For this temperature range, the composite films show stress behaviour intermediate between those of both components. However, below *ca.* 90°C, the stress level of PMDA-ODA polyimide is lower than that of the 6FDA-APB. In addition, the composite films no longer exhibit intermediate stress behaviour, but rather show the same or slightly higher stress level than 6FDA-APB polyimide. The stress results indicate that the TEC of PMDA-ODA/6FDA-APB composite film, which is primarily responsible for generating thermal stress^{24,26}, is highly influenced by the flexible, high-stress 6FDA-APB component.

The stress relaxation of PMDA-ODA/6FDA-APB composite films was also studied in ambient air with 50% relative humidity (RH) at room temperature. In general, the residual stress in a polymer film is known to relax in two different modes: creep- and moisture-induced modes²⁷. For high T_g polymers, such as PMDA-ODA and 6FDA-APB polyimides, the creep-induced stress relaxation may be small at room temperature, because of their very restricted molecular chain mobility in the highly supercooled state²⁸. For this reason, the stress relaxation of the composite films measured in 50% RH at room temperature is believed to be mainly due to moisture-induced relaxation. The stress relaxation results of the composite films are illustrated in Figure 6. When a composite film on Si substrates was exposed to ambient air with 50% RH, the stress rapidly relaxed with time at the initial stage, thereafter gradually decreased, and finally levelled off. The stress difference between the initial and relaxed states, $\Delta\sigma [= \sigma(t = \infty) - \sigma(t = 0)]$, reflects a degree of moisture uptake in the composite film. The stress difference $\Delta\sigma$ was 1.8 MPa for the 6FDA-APB, 2.1 MPa for the 25/75 composite, 2.3 MPa for the 50/50, 3.7 MPa for the 75/25, and 3.9 MPa for the PMDA-ODA polyimide. The initial slope in the $\Delta\sigma$ *versus* time plot is dependent on the diffusion coefficient of moisture in the composite film. The steeper slope results from the higher diffusion coefficient of moisture. The stress relaxation plots in Figure 6 indicate that the PMDA-ODA polyimide quickly absorbs more water in comparison with the 6FDA-APB polyimide. The composite films showed

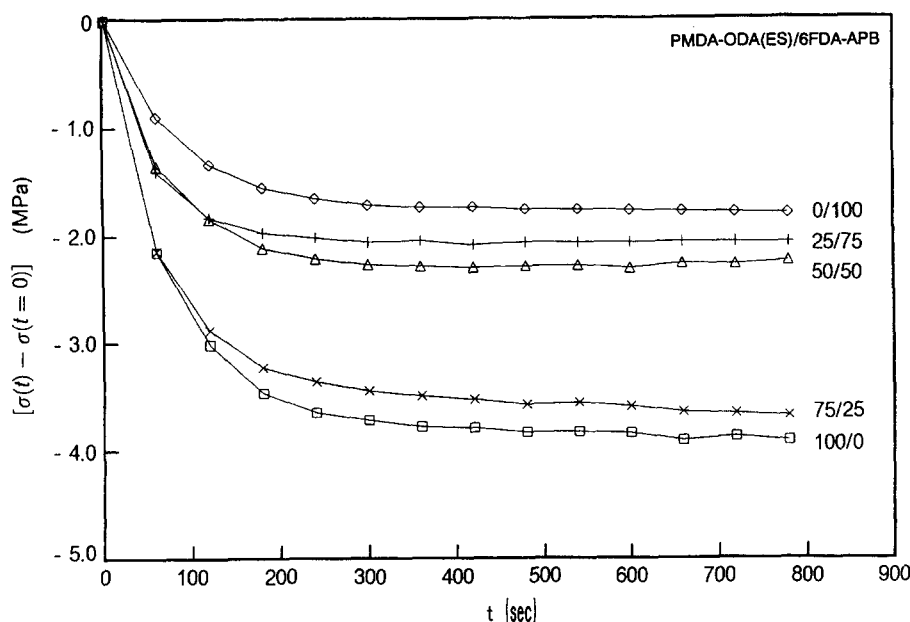


Figure 6 Moisture-induced residual stress relaxations of the PMDA-ODA/6FDA-APB composite films on silicon substrates measured at 25°C and 50% RH as a function of time

water uptake behaviour intermediate between those of the components.

Adhesion properties and surface composition

Several bilayered samples were prepared to investigate the self-adhesion characteristic of polyimides and their composites. In this study, each layer was thermally cured at 400°C as described in the Experimental section. The thicknesses of the top and the bottom layers were 20 μm and 10 μm , respectively. Peel tests were performed at room temperature in 90° peel mode. For PMDA-ODA, peel strength was only *ca.* 1 g mm^{-1} at a peeling rate of 2 mm min^{-1} , regardless of the precursor origins: PMDA-ODA(PAA) and PMDA-ODA(ES). That is, the self-adhesion of PMDA-ODA polyimide was very poor. On the other hand, both 6FDA-APB and BTDA-APB samples could not be peeled apart, which indicates that enough molecular interdiffusion occurred between the film layers to result in good adhesion.

For the PMDA-ODA/6FDA-APB and PMDA-ODA/BTDA-APB composite systems, the 30/70 composition showed excellent self-adhesion ('cannot peel') as expected on the basis of the matrix component, 6FDA-APB or BTDA-APB. However, for the 70/30 composition, peel strength depended strongly on the crosslinkable oligomer component, 6FDA-APB or BTDA-APB. That is, the 6FDA-APB composite showed a high peel strength of *ca.* 80 g mm^{-1} , whereas the BTDA-APB composite exhibited a very poor peel strength of *ca.* 1 g mm^{-1} (see Table 4). These results suggest that the self-adhesion of the composites with the PMDA-ODA matrix depends strongly on the crosslinked, flexible polyimide dispersant, BTDA-APB or 6FDA-APB. Furthermore, the surface composition of the 6FDA-APB composites is quite different from the surface composition of the BTDA-APB composites.

For the 6FDA-APB composites that exhibited excellent self-adhesion, the surface composition was analysed by X-ray photoelectron spectroscopy (XPS). In XPS measurements, the penetration depth into the film surface was 50 Å. The content of 6FDA-APB at the surface region was estimated from the surface atomic concentration of fluorine.

Table 4 Self-adhesion properties of PMDA-PDA polyimide and its composites

Polyimide or composite (w/w)	Peel strength ^a (g mm^{-1})
PMDA-ODA	<i>ca.</i> 1
PMDA-ODA/6FDA-APB (70/30)	80
PMDA-ODA/BTDA-APB (70/30)	<i>ca.</i> 1
6FDA-APB	cannot peel
BTDA-APB	cannot peel

^a $T_1 = T_2 = 400^\circ\text{C}$

Table 5 Surface composition and self-adhesion strength of PMDA-ODA/6FDA-APB composites

PMDA-ODA/ 6FDA-APB (w/w)	6FDA-APB content		Peel strength ^b (g mm^{-1})
	Bulk (wt%)	Surface (at%) ^a [top 50 Å]	
100/0	0	0	<i>ca.</i> 1
75/25	25	90.2	80
50/50	50	98.4	> 80
25/75	75	97.5	cannot peel
0/100	100	100	cannot peel

^aXPS data

^b $T_1 = T_2 = 400^\circ\text{C}$

The results are shown in Table 5. The film surface of the PMDA-ODA/6FDA-APB (= 75/25) composite at a depth of 50 Å was composed of 90.2% 6FDA-APB. This high concentration of 6FDA-APB component at the film surface increased slightly with increasing concentration in the bulk: 98.4% 6FDA-APB for the 50/50 and 97.6% for the 25/75 composite. The results indicate that the 6FDA-APB component has been highly segregated on the surface of its composite films even with the PMDA-ODA matrix. This surface segregation might be taking place during solvent drying and subsequent thermal curing, owing to the relatively lower surface energy accompanied by phase separation because of its immiscibility with PMDA-ODA. Therefore, when the second layer film is cast on the 6FDA-APB rich surface of the first film layer, enough molecular interdiffusion takes place between the layers, resulting in high adhesion strength. This molecular interdiffusion of the 6FDA-APB component is due to its flexible chain conformation characteristic with lower T_g as well as high swelling in NMP.

Such surface segregation may not be favourable in the BTDA-APB composites because of the surface energy is similar to that of PMDA-ODA, even under the circumstance of phase separation, as a consequence of their immiscibility. In this case, there is still a question about the surface composition of the BTDA-APB composites. There are two possibilities: (1) the surface is composed of the open type of phase-separated domains of the BTDA-APB component and its composition is equivalent to the bulk composition and (2) the surface composition is dominated by the matrix component. If the BTDA-APB composites are like the first case, their self-adhesion is dependent upon the amount of BTDA-APB component added into the PMDA-ODA matrix, as well on as the degree of phase separation. Consequently, in the first case, the self-adhesion of PMDA-ODA composites can be improved by adding the BTDA-APB component, which exhibits excellent adhesion. However, if the second type of surface composition occurs in the BTDA-APB composites, the adhesion of the BTDA-APB composites with PMDA-ODA matrix may be as poor as the adhesion of the PMDA-ODA alone. In the peel test, PMDA-ODA composites with the BTDA-APB dispersant did not show any improvement in self-adhesion. This result suggests that the adhesion of PMDA-ODA/BTDA-APB composites is dominated by the matrix component. In conclusion, the adhesion of the polyimide composites studied here is dependent on the nature of the flexible component and surface composition characteristics, which include phase separation and surface segregation.

CONCLUSIONS

We attempted to prepare semi-IPN type of rigid polyimide/flexible polyimide composites from soluble precursors of rigid PMDA-ODA polyimide and acetylene-terminated 6FDA-APB and BTDA-APB oligomers through solution blending and conventional solution casting/thermal curing process. A homogeneous ternary solution with a relatively high concentration of ≤ 30 wt% was easily obtained in NMP for various compositions of the blend systems studied here. The PMDA-ODA(ES) precursor exhibited better miscibility with 6FDA-APB in NMP than the PMDA-ODA(PAA) precursor. The 6FDA-APB imide oligomer was more miscible with the PMDA-ODA(ES) in NMP than the BTDA-APB isoimide oligomer. In particular, for the PMDA-ODA(ES) blends, dried films were optically

transparent for various compositions with a few exceptions. For some compositions the optical transparency was retained through thermal curing, whereas for the other compositions, phase separation occurred through thermal curing, resulting in domains of submicrometre size in the composites. However, on the d.m.t.a. spectra, two T_g s were detected even for the optically transparent films, indicating that the composite components were demixed.

The mechanical properties of crosslinked 6FDA-APB and BTDA-APB polyimides were significantly improved by the composite formation with PMDA-ODA polyimide, owing to its good mechanical properties. However, the residual stress of the crosslinked 6FDA-APB was not improved by composite formation: that is, the stress of the composite film was influenced significantly by the 6FDA-APB component. This suggests that the TEC of the PMDA-ODA composites is significantly increased by the added 6FDA-APB component. A similar stress behaviour is expected for the other polyimide composite systems considered here. The stress relaxation results due to moisture uptake indicate that the PMDA-ODA polyimide quickly absorbs more water than 6FDA-APB and their composites show water absorption intermediate between those of both components.

The self-adhesion of the polyimide composites has been found to be strongly dependent on the surface composition characteristics, which are generally controlled by bulk composition as well as surface segregation and phase separation due to the surface energy difference and degree of molecular demixing. The 6FDA-APB composites with PMDA-ODA matrix exhibited excellent self-adhesion strength that was attributed to the formation of a 6FDA-APB rich surface, owing to its favourable surface segregation. In contrast, the BTDA-APB composites with PMDA-ODA matrix showed no improved self-adhesion, indicating that their surfaces are dominated by the matrix component.

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