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Synthesis, miscibility, and properties of rodlike/flexible polymer composites via in-situ rod chain formation

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Summary

Flexible, soluble poly(amic diethyl ester) precursors of rodlike poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) and poly(4,4'-oxydiphenylene biphenyltetracarboximide) (BPDA-ODA), which are more stable than the respective poly(amic acid)s and are not in the equiliration with the constituent anhydride and amine monomers so that chemical exchange reactions are prevented in their solution blending, were synthesized. Homogeneous precursor/precursor solutions with various compositions were obtained in N-methyl-2-pyrrolidinone with appreciably high solid contents. The dried precursor blend films and resulting polyimide composite films thermally imidized were optically transparent, regardless of compositions and film process conditions. The composites showed single T_g behavior. Conclusively, rodlike BPDA-PDA/flexible BPDA-ODA molecular composites were achieved from the blend of the respective flexible poly(amic diethyl ester) precursors through conventional drying and imidization process. In addition, film properties of composites were characterized.

Introduction

Polyimides have become of important materials in the microelectronics and the aircraft industry owing to their excellent mechanical properties, high thermal stability, high chemical resistance, low dielectric constant, and easy processability.[1-3] The advanced technological applications require materials having high ductility, high modulus, high strength, low thermal expansion, high interfacial adhesion and so on.[1-4] A rodlike polyimide exhibits high thermomechanical stability, high modulus, and low thermal expansion, whereas a flexible polymer shows good adhesion and high elongation. The properties required to the advanced applications can be achievable through molecular composite formations of rodlike and flexible polymers. However, it is difficult to achieve rodlike/flexible polymer composites with a desired level of molecular mixing because of their

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inherent immiscibility usually leading large scale phase separation.[5-7]

One approach to overcome the problem is to utilize a flexible, soluble precursor polymer to be convertable to the rodlike polymer, instead of the inherently rodlike polymer, in order to improve its miscibility with a flexible polymer. Polyimide is one of best candidate materials for the approach since it is usually used as a flexible, soluble precursor polymer rather than the insoluble polyimide.[8,9] With this sense, rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA) composites with various flexible polyimides were previously demonstrated by the in-situ rod formation of its flexible poly(amic diethyl ester) precursor through thermal imidization.[8,9] However, the PMDA-PDA composites exhibited phase separations with a scale larger than submicrometers. That is, there were mostly obtained microcomposites rather than molecular composites. The phase separation took place in the concentrated precursor/precursor solution before reaching to the binary precursor blend during solvent evaporation. The phase-separated domain size, which was primarily set by solvent evapoartion in dry process, was very much preserved through subsequent thermal imidization.

In the present study, the approach was extended to the composite formation of rodlike poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) with flexible poly(4,4'-oxydiphenylene biphenyltetracarboximide). Yokota *et al.*[10] have previously reported to make BPDA-PDA/BPDA-ODA molecular composites by solution blending of the respective poly(amic acid)s and subsequent drying/thermal imidization. However, poly(amic acid) precursor is well known to be in the equilibration with its constituent anhydride and amine monomers.[11-15] Because of this equilibration nature, mixing of poly(amic acid)s in a mutual solvent can lead to the formation of segmented blocky or random copolymers via transamidation reactions rather than molecularly mixed precursor blends, depending on the mixing time and temperature.[11] Thus, the miscibility observed in the BPDA-PDA/BPDA-ODA composites has been claimed to result from the chemical exchange reaction occurred between the poly(amic acid)s during their solution blending.[9] Even

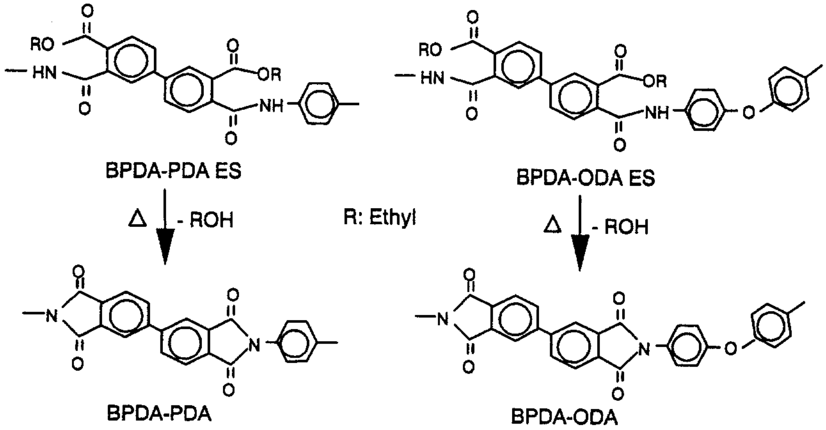

Figure 1. Chemical structures of poly(amic diethyl ester)s and resulting polyimides used in this study.

though the pair of poly(amic acid)s are thermodynamically miscible, their miscibility cannot be easily determined experimentally because of the involvement of chemical exchange reaction between the precursor components. Consequently, solution blending of poly(amic acid)s is not adequate to make polyimide/polyimide blends or composites.

Unlike poly(amic acid), poly(amic dialkyl ester) in a solvent is not in the equilibration with their constituent monomers.[9,16] The lack of the polymer-monomer equilibrium and accompanying propensity for monomer randomization reactions can allow the preparation of polyimide blends or composites by solution blending of poly(amic dialkyl ester)s. Furthermore, poly(amic dialkyl ester) is known to be hydrolytically stable and highly soluble in N-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc) and so on.[9,16] For the advantageous property characteristics, in this study BPDA-PDA and BPDA-ODA poly(amic diethyl ester) precursors were synthesized (see Figure 1) and used to investigate their molecular mixing behavior in the precursor mixtures and resulting composites. In addition, film properties of composites were measured.

Experimental

A flexible precursor of rodlike poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA), poly(p-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA ES) was synthesized by the low temperature polymerization of *p*-phenylene diamine (PDA) and BPDA diethyl ester diacyl chloride in NMP,[9,17] washed with deionized water and methanol to remove HCl produced as byproduct, and dried for 1 day at 50°C in a vacuum of 1 x 10^{-3} torr. The poly(4,4'-oxydiphenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA ES) precursor of flexible poly(4,4'-oxydiphenylene biphenyltetra-carboximide) (BPDA-ODA) was synthesized from 4,4'-oxydiphenylene diamine (ODA) and BPDA diethyl ester diacyl chloride in the same way as the BPDA-PDA ES was prepared. Intrinsic viscosities of BPDA-PDA ES and BPDA-ODA ES were 0.85 *dl/g* and 0.45 *dl/g* in NMP at 25°C, respectively. These precursor polymers were blended at various

Table I. Apparent miscibility behavior of BPDA-PDA/BPDA-ODA mixtures by optical microscopy

BPDA-PDA/BPDA-OD-A (w / w)	Precursor solution (20 wt.% in NMP)	Precursor film dried at 90°C/3-5 h	Composite film imidized at 380°C/1.5 h
100 / 0	clear	clear	clear
85 / 15	clear	clear	clear
70 / 30	clear	clear	clear
50 / 50	clear	clear	clear
30 / 70	clear	clear	clear
15 / 85	clear	clear	clear
0 / 100	clear	clear	clear

compositions (100/0, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100 in w/w) in NMP for 2 days and filtered with silver membranes of 5.0 μm pore size. The ternary solutions obtained were optically clear and their solid content was 10 - 20 wt%.

The precursor/precursor solutions were spin-coated at 700 - 1500 rpm for 20 - 25 sec on glass slides and dried on a hot-plate at 20 - 90°C under air ambient conditions. The dried precursor mixtures were thermally imidized at 380°C for 1.5 hrs in an oven with a nitrogen flow. Here, a ramping rate of 2.0 K/min was employed. The thickness of films imidized was in the range of 16.0 - 19.0 μm.

The transparency of both dried and imidized films was determined using an optical microscope (Carl Zeiss, Model Axioplan) under crossed polarization. The glass transition behavior in films imidized was examined at a heating rate of 5.0 K/min and a frequency of 10 Hz over 70 - 500°C using a dynamic mechanical thermal analyzer (DMTA) (Polymer Laboratories, Model Mark-II) equipped with a tensile head and controlled with a Hewlett-Packard computer. In DMTA measurements, the gauge length was 10 mm. Mechanical properties were measured in air ambient conditions using an Instron mechanical tester (Model 4206) controlled by a computer. The gauge length and crosshead speed were 50 mm and

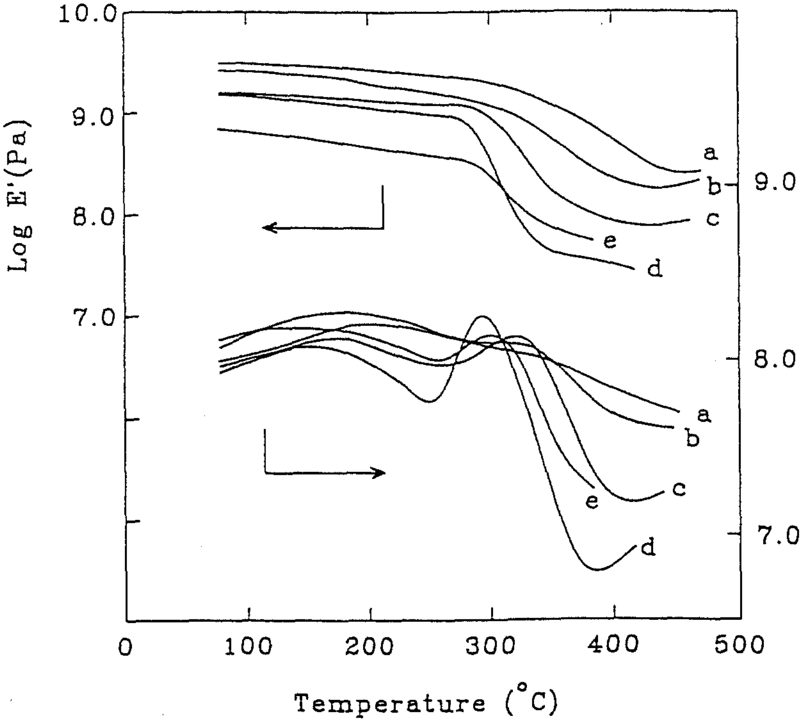

Figure 2. Dynamic mechanical relaxation behaviors (storage and loss modulus, E' and E'') of polyimide composite films thermally imidized at 380°C for 1.5 hrs measured at 5.0 K/min heating rate and 10 Hz frequency: a, BPDA-PDA; b, 70/30 composite; c, 50/50; d, 30/70; e, BPDA-ODA.

2 mm/min, respectively. The width of all film strips used was 6.35 mm.

Results and Discussion

BPDA-PDA ES/BPDA-ODA ES solutions with various compositions were made in NMP with a solid content of 20 wt%. The ternary solutions were optically clear, indicative of the formation of miscible solutions. The solid content of 20 wt% is appreciably high so that the ternary precursor solutions are practically quite useful in the fabrication of microelectronic devices because the concentration of poly(4,4'-oxydiphenylene pyromellitamic acid) solutions commonly used is ca. 16 wt%. The homogeneous solution of BPDA-PDA ES/BPDA-ODA ES (50/50, w/w) mixture was spin-coated onto glass slides and followed by drying at either room temperature for 2 weeks under a dried air flow, 50°C for 1 week in air ambient or 90°C for 3 - 5 hrs in air ambient. The dried films showed complete transparency on an optical microscope under cross polarization, regardless of the drying conditions, fast and slow drying. Similar results were obtained for the other compositions (see Table I). Here, the dried films contained residual NMP solvent of 5 - 30 wt%, depending upon the drying temperatures. The optical microscopic observations suggest that BPDA-PDA ES precursor polymer is miscible with BPDA-ODA ES under the presence of NMP in a small amount.

The dried films were thermally imidized at 380°C so that the flexible BPDA-PDA ES precursor was converted to the rodlike polyimide whereas the flexible BPDA-ODA ES precursor was changed to the flexible polyimide. The resulting BPDA-PDA/BPDA-ODA polyimide composites also exhibited optical transparency, regardless of the compositions (see Table I). The composite films were further investigated by means of dynamic mechanical and thermal analysis.

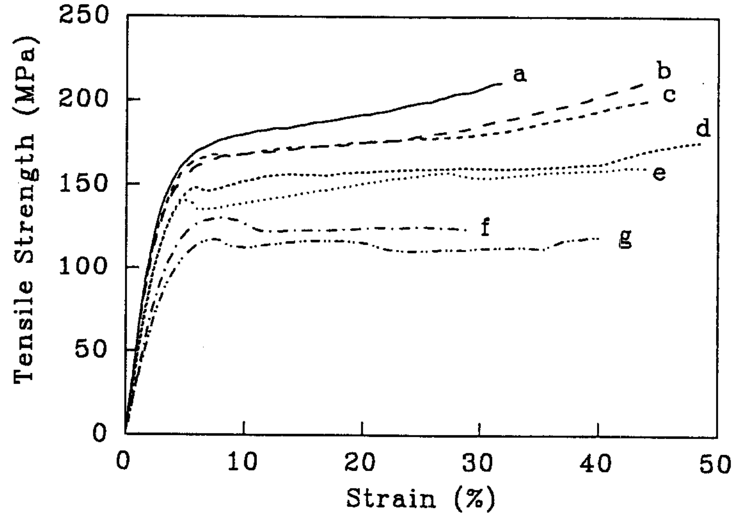

Figure 3. Stress-strain curves of BPDA-PDA/BPDA-ODA composite films thermally imidized at 380°C for 1.5 hrs: a, BPDA-PDA; b, 85/15 composite; c, 70/30; d, 50/50; e, 30/70; f, 15/85; g, BPDA-ODA. Measurements were performed with a crosshead speed of 2.0 mm/min.

The results are presented in Figure 2. On heating runs the storage modulus *E'* decreases very slowly upto a temperature at which glass transition begins, and thereafter drops rapidly through the glass transition. BPDA-PDA component exhibited a broad glass transition over the range of 320 - 470°C, whereas BPDA-ODA component showed a relatively sharp glass transition over the range of 265 - 370°C. The composite films exhibited intermediate glass transition behavior between those of the components. For all composite films, the variation of loss modulus *E"* versus temperature shows two peaks, one broad peak at 70 - 265°C and the other peak at > 265°C. The first broad, weak peak is due to the motion of aromatic moieties on the backbone coupled with water absorbed in the film.[18,19] This peak is typically observed in all aromatic polyimides and is assigned by β relaxation. The broad relaxation around 100°C, which results from water absorbed, is assigned by β' relaxation. The other peak at the higher temperature region is the relaxation due to the glass transition and is always assigned by α relaxation. Here, glass transition temperature (T_g) is chosen by temperature at the peak maximum of α relaxation. T_g was 352°C for BPDA-PDA component, 335°C for the 70/30 composite, 323°C for the 50/50 composite, 292°C for the 30/70 composite, and 302°C for BPDA-ODA component. In the composite films, T_g decreased as the content of BPDA-ODA increased. In particular, the 30/70 composite exhibited a T_g (292°C) lower than that (302°C) of BPDA-ODA. This abnormally low T_g behavior is not fully understood at this moment. Overall, all the composite films exhibited a single T_g which varied between those of the components except the 30/70 composite. Based on the optical microscopic transparency and the single T_g behavior, BPDA-PDA seems to be molecularly well mixed with BPDA-ODA in the composite films. In other words, the molecular mixing obtained in the precusor mixtures is well retained by thermal imidization, resulting molecular composites. This result might result from the favorable molecular interaction of the polymer components which have similar chemical structures. However, it is noted here that the optical transparency and single T_g measurements are not enough to distinguish clearly the molecular level of mixing in the composites because of the resolution

Table II. Mechanical properties of BPDA-PDA/BPDA-ODA composite films

BPDA-PDA/BPDA-ODA (w / w)	Modulus (GPa)	Yield Stress (MPa)	Yield Strain (%)	Tensile Strength (MPa)	Strain at break (%)
100 / 0	5.9	170	4	210	32
85 / 15	5.9	165	4	212	44
70 / 30	5.9	160	5	201	45
50 / 50	4.9	148	6	177	49
30 / 70	4.9	141	5	161	45
15 / 85	3.8	131	8	122	29
0 / 100	3.4	117	7	119	41

limit of conventional optical microscopes as well as the relatively broad nature of glass transition of the polyimide components. Thus, in order to get more information on the degree of molecular mixing in the precursor blends and resulting polyimide composites there are needed dynamic turbidity measurements with the aid of a light scattering apparatus during drying of cast precursor blend films and subsequent imidization.

In addition, the mechanical properties of composite films were measured at room temperature. The stress-strain curves are illustrated in Figure 3 and the results analyzed are summarized in Table II. BPDA-PDA showed 5.9 GPa modulus, 170 MPa yield stress, 4 % yield strain, 210 MPa tensile strength, and 32 % strain at break. BPDA-ODA exhibited 3.4 GPa modulus, 117 MPa yield stress, 7 % yield strain, 119 MPa tensile strength, and 41 % strain at break. For the composite films, the mechanical stresses, such as modulus, yield stress and tensile stress increased as the content of BPDA-PDA increased. The strain properties (i.e., yield strain and strain at break) improved as the content of BPDA-ODA increased. The relatively low strain at break for the 15/85 composite might be due to defects in the film. Conclusively, by the composite formation, the strain properties of BPDA-PDA were improved whereby the stress properties (modulus, yield stress, and tensile stress) of BPDA-ODA were enhanced.

Conclusions

In the present study, the formation of polyimide/polyimide blends or composites, that is not possible from blending of conventional poly(amic acid) precursors because of their blocky or random copolymer formation via monomer randomization due to the nature of monomer-polymer equilibrium, has been successfully demonstrated by utilizing poly(amic diethyl ester) precursors, such as BPDA-PDA ES and BPDA-ODA ES, which are free from the problems associated with the monomer-polymer equilibrium and furthermore, hydrolytically stable. Highly soluble BPDA-PDA ES and BPDA-ODA ES were well mixed in NMP, leading to the homogeneous solution for all compositions. Precursor blend films prepared were optically clear, regardless of compositions and drying conditions. The optical transparency observed in the precursor blend films was retained in the resultant composite films prepared by thermal imidization. Conclusively, rodlike BPDA-PDA/flexible BPDA-ODA molecular composites were successfully achieved from solution blending of the respective flexible poly(amic diethyl ester) precursors and followed by conventional drying and thermal imidization. This high degree of molecular mixing might result from the chemical structural similarity of the polymer components. In addition, the T_g behavior and mechanical properties of the polyimide composite films were investigated.

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