Nanoscale blending of aliphatic and aromatic polyimides: A clue for forming semi-molecular composites and in-situ generation of copolyimide fractions

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Summary

Nanoscale blending of aromatic and aliphatic polyimides has been attempted by employing corresponding poly(amic acid) precursors in order to elucidate clues for achieving a semi-molecular composite film. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were used to make the precursor polymer of aromatic polyimide (PMDA-ODA PI) as a semi-rigid rod-like component, whilst bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) and 4,4'-methylenebis(cyclohexylamine) (MCA) were used to prepare the precursor of aliphatic polyimide (BOCA-MCA PI) as a flexible coil-like component. The weight ratio of aromatic to aliphatic polyimides was varied from 100:0: to 0:100 by 10 wt.% gap for monitoring the critical composition upon nanostructure changes. The micro/nanostructure of composite films was characterized by using small-angle x-ray scattering (SAXS) and x-ray diffraction (XRD), while the evolution and thermal property of semi-molecular composites were studied by using FT-IR spectroscopy and dynamic mechanical thermal analysis (DMTA). The result showed that the composite films exhibited a single glass transition behavior, which is ascribed to the molecular level mixing, in the presence of copolyimide fractions.

Introduction

Since the introduction of molecular composite concept, a variety of polymers has been employed to make molecular composites due to their promising synergistic effect on the physical properties of each component [1-3]. Most of them are prepared by mixing rigid rod-like polymers, as a reinforcing component, and flexible coil-like polymers as a binding matrix (see Fig. 1). The previous studies showed that the resulting molecular composites improved environmental resistance, thermal stability, toughness, and electronic and optical properties [4-8].

The concept of conventional molecular composites has been extended to the polyimides that have been considered emerging high performance polymers for microelectronics and aerospace applications [9-14]. Of these studies for polyimide
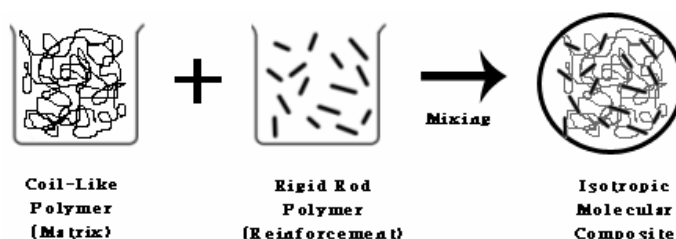
Figure 1. Schematic illustration of making conventional molecular composites using rigid rod-like and flexible coil-like polymers in a solvent.

molecular composites, the keen interest has been paid to the application of dielectric (insulating or packaging) layer for microelectronic devices such as very large scale integration (VLSI) and/or ultra large scale integration (ULSI) [15]. Because these applications required high thermal stability/low dielectric constant and good adhesion at the same time, the nanomorphology control of polyimide molecular composites was of crucial importance to adjust these properties.

Recently, aliphatic and/or alicyclic polyimides are being highlighted for their applications in optoelectronics (substrates for displays) and nanoelectronics (inter-insulating layers) thanks to their higher transparency and lower dielectric constant than aromatic polyimides [16-19]. However, the thermal stability of aliphatic polyimides needs to be improved to the level of aromatic polyimides in order to make sure the reliability of proven devices [20].

In this regard, this work has tried to improve the properties (thermal stability) of aliphatic polyimides through the nanoscale blending with aromatic polyimide. In particular, the aromatic polyimide chosen here features a semi-rigid-partially-rod-like chain conformation because fully rigid polymer could definitely reduce the adhesion characteristics as well as the anisotropic dielectric properties [15]. As a result, the present work creates semi-molecular composites which are composed of flexible coil-like aliphatic polyimides and semi-rigid-partially-rod-like aromatic polyimides.

Experimental part

Materials

Fig. 2 shows the chemical structures of monomers used in this study. The alicyclic monomers, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) and 4,4'-methylene bis (cyclohexylamine) (MCA), were used to synthesize the precursor poly(amic acid), BOCA-MCA PAA, whilst the aromatic monomers, pyromellitic dianhydride (PMDA, 97%) and 4,4'-oxydianiline (ODA), were used to make the
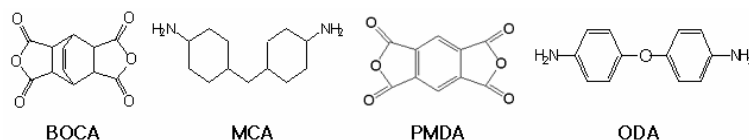

Figure 2. Monomers for synthesizing aliphatic poly(amic acid) (BOCA-MCA PAA) and aromatic poly(amic acid) (PMDA-ODA PAA).

precursor poly(amic acid), PMDA-ODA PAA. All these materials were purchased from Aldrich (St. Louis, MO) and used as received. *m*-Cresol was purified by drying over calcium dichloride and molecular sieves, distilled under reduced pressure, and then stored under nitrogen in the dark. N,N'-dimethyl acetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were distilled over calcium hydride under reduced pressure.

Synthesis of aliphatic poly(amic acid) (BOCA-MCA PAA)

Equimolar amounts of BOCA and MCA in m-cresol were placed in a three necked flask which is equipped with a mechanical agitator, nitrogen inlet tube, and thermocouple lead. The flask was then warmed in oil bath at 60°C for 1 h and then heated up to 80°C to make a homogeneous solution. This homogeneous solution was maintained at that temperature for 2 h. Next the solution was heated up to 100°C under a flow of nitrogen and maintained at these conditions until no further rise in viscosity was observed which indicates almost the completion of polymerization reaction. This viscous product solution was cooled down to room temperature under nitrogen flow and poured into an excess volume of methanol to make solid precipitates. The solid precipitates were filtered off using methanol and were subject to washing several times with methanol in order to get rid of any remaining solvent molecules (m-cresol). Finally the washed solid, BOCA-MCA PAA, was dried under vacuum at 60°C for 6 h [21].

Synthesis of aromatic poly(amic acid) (PMDA-ODA PAA)

PMDA-ODA PAA was prepared as usual by reacting equimolar quantities of PMDA and ODA in DMAc under nitrogen atmosphere at room temperature. The setup for reactions is the same as described for the BOCA-MCA PAA. The reaction was continued for 24 h to achieve a homogeneous mixture solution. After terminating the reaction, the solution was poured into an excess volume of toluene for precipitation. The precipitated solid, PMDA-ODA PAA, was filtered off and washed several times with toluene to remove any remaining solvent molecules (DMAc). The final solid was dried under vacuum at 60°C for 6 h.

Preparation of precursor blend films and polyimide/polyimide composite films

BOCA-MCA PAA and PMDA-ODA PAA were blended in NMP at various compositions (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 0/100 by weight ratio). The solid concentration of the solutions was kept 10 wt.% for all compositions. These blend solutions were stirred for 2 days at room temperature for well mixing and then were subject to the filtration using a Teflon membrane filter (pore size = 0.45μm) in order to remove impurities including dusts. Finally these solutions were poured into a Petri dish to make precursor films. After casting the precursor films were kept at 40°C for 12 h and then softbaked at 80°C for 6 h. These precursor films were thermally imidized at 250°C for 4 h for achieving polyimide/polyimide composite films. The average thickness of the composite films was varied from 100μm to 130μm. Table I summarizes the composition and thickness of precursor blend films and polyimide/polyimide composite films prepared in this work.

Table 1. Preparation of aromatic PI and aliphatic PI composite films.

Sample Name	Aliphatic / Aromatic PAA (wt. %)	Thickness (PI) (µm)
MC0	0/100	100
MC1	10/90	110
MC2	20/80	100
MC3	30/70	110
MC4	40/60	120
MC5	50/50	130
MC6	60/40	110
MC7	70/30	120
MC8	80/20	100
MC9	90/10	110
MC10	100/0	110

Synthesis of PI copolymer

For comparison, a PI copolymer was prepared as follows; Equimolar amounts of BOCA and PMDA in NMP were placed in a three necked flask which is equipped with a mechanical agitator under nitrogen atmosphere. Also diamine mixture was prepared by reacting equimolar quantities of ODA and MCA in NMP under nitrogen atmosphere at 60°C. Then BOCA-PMDA mixture and ODA-MCA mixture were blended by 50/50 weight ratio. The flask was then warmed in an oil bath at 60°C for 1 h and was heated to 80°C to prepare a homogeneous solution that was maintained at that temperature for 2 h. The solution is then heated to 100°C under a flow of nitrogen and maintained under these conditions until no further rise in viscosity was observed. On completion of the reaction, the viscous polymer solution was cooled under nitrogen and poured into a large quantity of methanol to precipitate the PAA, which were filtered off, was washed repeatedly with methanol to remove any remaining NMP, and was dried under vacuum at 60°C for 6 h. The PAA obtained in this way was thermally imidized under the same conditions as for the PI/PI composite films.

Measurements

The functional groups of composite films were examined using a FT-IR spectrometer (React IR^{TM} 1000, Applied System, ASi). The nanostructure of polyimide/polyimide composite films was studied with small angle x-ray scattering (SAXS) and wide angle x-ray diffraction (WAXD) techniques. The SAXS measurement was carried out using synchrotron x-ray source of Pohang Accelerator Laboratory (PAL, South Korea): Co-K$_\alpha$(λ=1.608Å) radiation with an energy range of 4~16 keV [energy resolution ($\Delta E/E$) = 5×10^{-4}, photon flux =10^{10}~10^{11} ph/s, beam size =1 mm^2]. The SAXS scan range was fixed 0.0012 nm^{-1}<q< 0.3316nm^{-1}. The WAXD measurement was performed using a conventional x-ray diffractometer [Model: Rigaku Miniflex, CuK$_\alpha$ (λ=1.5418Å)]. The thermal decomposition stability of composite films was measured using thermogravimetric analyser (TGA Q50 Q Series, TA Instrument) The heating rate was 10°C/min in the temperature range between 30 and 900°C. The thermal transition temperature of composite films was measured using dynamic mechanical thermal analyser (DMTA Q800, TA Instrument) by employing the sample (gauge) length of 2.5cm, the sample width of 0.5 cm, the heating rate of

5°C/min from room temperature to 400°C, and the head oscillation frequency of 3Hz). The mechanical (tensile) property of composite films were measured using a universal test machine (UTM, Korea Apparel Testing & Research Institute) by employing a strain rate of 10 mm/min at room temperature: Sample length and width were 2.5cm and 0.5 cm, respectively, and five specimens per each were averaged to take final values.

Results and Discussion

Synthesis and Thermal Property of a PI Copolymer

Before we prepare polyimide/polyimide composite films, we synthesized a polyimide random copolymer containing two different types of diamine monomers and dianhydride, respectively. Fig. 3 illustrates an IR spectrum of the PI copolymer. The spectrum shows the earmark absorption bands of the imide group around 1780, 1711, 1368, and 730 cm^{-1}. Among them, the peak at 1711 cm^{-1} of C=O asymmetric stretching, representing an imide group, as well as the peak at 1780 cm^{-1} of C=O symmetric stretching, indicates a cyclic five-member ring, confirming the imide formation. The bands at 1368 and 730 cm^{-1} are attributed to the C-N-C bond and the imide ring deformation, respectively. Also, the aromatic C=C stretching is observed at 1500 cm^{-1}. The alicyclic C-H stretching and the CH$_2$ bending are observed at 2923 cm^{-1} and 1465 cm^{-1}, respectively. It should be noted, however, that self-standing films were not obtained for the property measurements. Thus, we measured only TGA data of the PI copolymer. Fig. 4 shows the TGA curves of the PI copolymer and pristine aliphatic and aromatic PI's. In general, the thermal stability in terms of thermal degradation temperatures of the PI copolymer was not better than that of both aliphatic and aromatic PI.
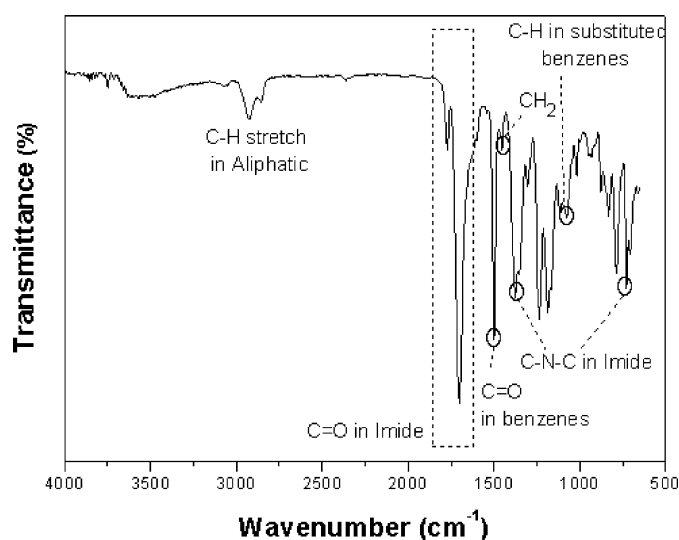

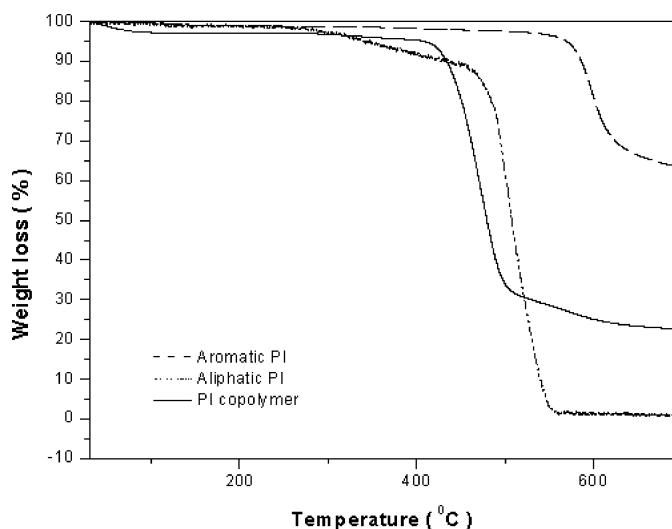**Figure 3.** FT-IR spectrum of a polyimide copolymer.

Figure 4. TGA curves of a PI copolymer and pristine polyimides.

Perspective into Molecular Structure of Polyimides

As shown in Fig. 5, PMDA-ODA PI is consisted of bended rigid rod segments that are expected to deliver physical rigidity on a given nanoscale, whereas BOCA-MCA PI shows very flexible chain geometry that can bestow adhesive property. Therefore an optimized characteristic adjusting rigidity and flexibility could be achieved by blending of these two polyimides. Here it is noteworthy that the blending of two polyimides is enabled using corresponding precursor PAA polymers which are well dissolved in organic solvents so that the scale of blending can be on a nano or molecular scale.

(a)   (b)

Figure 5. Energy minimized structure of two repeating units of polyimides: (a) PMDA-ODA PI and (b) BOCA-MCA PI.

Spectroscopic Analysis

The change of particular functional groups has been investigated to examine a variation of environment of each constituent molecular unit upon nanoscale blending of two precursor polymers. As shown in Fig. 6, both BOCA-MCA PAA and PMDA-ODA PAA films exhibit a split feature (double peak) of carbonyl groups at the wavenumber of 1500~1750cm^{-1} (see 'a' part in Fig. 6). However, the blend films

show only single peak with regardless of compositions and the peak position is in between the two peaks of pristine precursor polymers. In addition, the precursor blend films show two distinct peaks at 1117 and 988cm^{-1} (1,4 disubstituted benzene's aromatic C-H in plane deformation vibrations and cyclohexane alkane's C-C skeletal vibration, respectively) in which the intensity of the peak at 1117 cm^{-1} is higher than that of the peak at 988cm^{-1} (see 'c' part in Fig. 6). This trend is the reverse case of PMDA-ODA PAA (note that the main peak is at 1020cm^{-1}), whilst BOCA-MCA PAA shows the same intensity for both peaks. Finally, a peak splitting is observed at 1309 and 1266cm^{-1} (imide C=O) for the blend films, whereas a broad single peak is monitored for each pristine precursor film(see 'b' part in Fig. 6). Given the spectroscopic finger prints, the blending of the two precursor polymers is considered to change the environment of functional groups in each precursor. This indicates that the present blending did indeed result in the precursor blend films on a nano or molecular scale when it comes to the typical size of the functional groups in the precursor polymers.
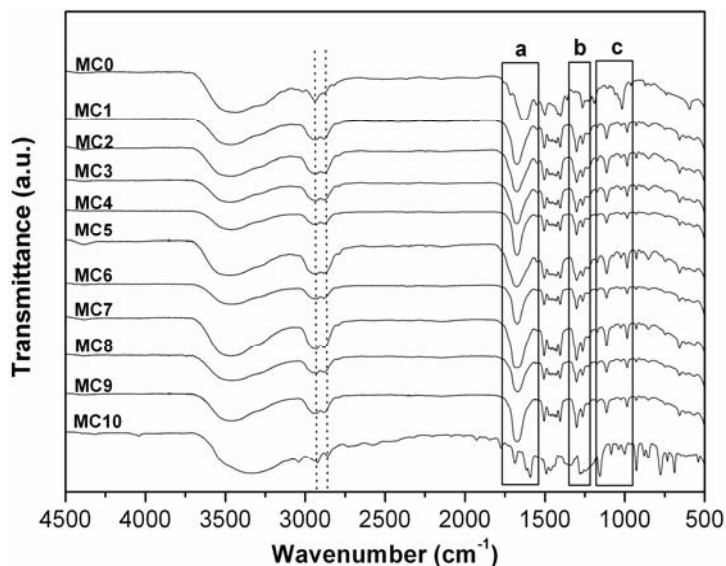

Figure 6. FT-IR spectra of precursor polymer blend films (see sample names in Table I).

After thermal imidization the FT-IR spectra were considerably changed as shown in Fig. 7. The characteristic peak of the carbonyl groups became broad after thermal imidiztion, which indicates the partial freezing of vibration mode by the ring close reaction (thermal imidization) (see 'a' part in Fig. 7). We note that the double peak feature of the pristine aliphatic polyimide (BOCA-MCA PI) is still maintained after thermal imization even though the shape became broader. In particular, the peak shift by blending at this position, which was observed for the precursor blend films in Fig. 6, was completely hidden by this broadening feature. The gradual decrease of the peak at 2923 cm^{-1} (aliphatic C-H stretching) does clearly reflect the change of the aliphatic PI composition. However, no clues could be found on the nano and/or molecular scale phase segregation between two components with this spectroscopic
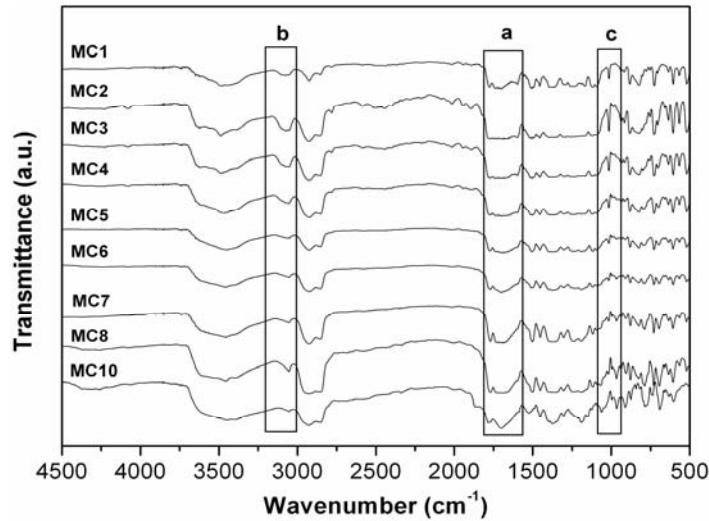
Figure 7. FT-IR spectra of polyimide/polyimide blend (composite) films (see sample names in Table I).

information, since only changes are the intensity reduction in 'b' and 'c' regions in Fig. 7. (b; aliphatic C-H stretch, c; 1,4 disubstituted benzene's aromatic C-H in plane deformation vibrations and cyclohexane alkane's C-C skeletal vibration)

Micro/Nanostructure Analysis by SAXS and WAXD

As shown in Fig. 8, the polyimide composite film that has 10 wt.% of aliphatic polyimide shows intense and broad peak from the Lorentz-corrected SAXS profile in which the calculated mean long period is ~80Å [11]. Based on the molecular structure
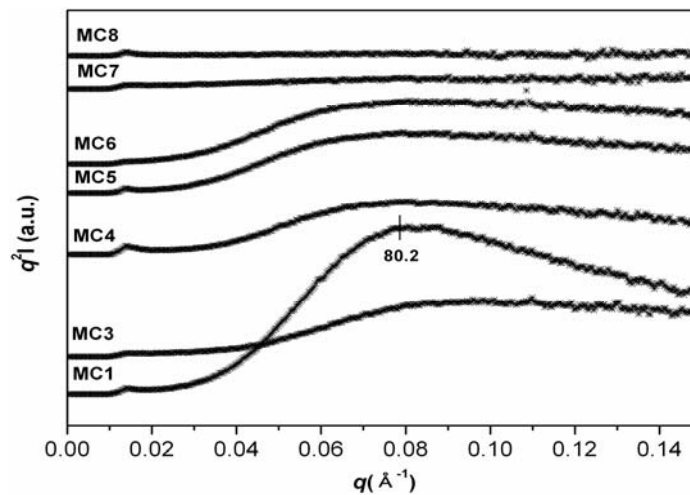
Figure 8. Lorentz-corrected SAXS profiles of polyimide/polyimide composite films (see sample names in Table I).

of PMDA-ODA PI in Fig. 3a, more than six PMDA-ODA units are assembled to make this long period domain which is consisted of ordered and disordered parts. Therefore this indicates that the 10 wt.% of flexible coil-like component is insufficient to disrupt the domain feature of semi-rigid rod-like PMDA-ODA PI. At 30 wt.% BOCA-MCA PI composition the peak intensity decreased and the peak position shifted toward higher scattering vector, indicative of making smaller crystalline domain. However, as the BOCA-MCA PI content increased up to 60 wt.%, the shift of peak position was toward lower scattering vector that means forming bigger size crystalline domains. At above 70 wt.%, this feature was completely gone off. Summarizing the SAXS results, it is expected that a significant change of the molecular structure on a nanoscale was initialized at 20~30 wt.% and then after these compositions the crystalline domain would be scattered out to make the peaks much broader.

The deeper nanostructural change of polyimide composite films has been investigated using WAXD. As shown in Fig. 9, the main peak of the pristine PMDA-ODA PI film was gradually shifted toward lower diffraction angles with increasing the BOCA-MCA PI content. This indicates that the interchain distance amongst PMDA-ODA PI chains becomes bigger by adding BOCA-MCA PI chains: from 4.8Å for the pristine PMDA-ODA PI to 5.6Å for the composite film with 60 wt.% BOCA-MCA PI. This is a critical evidence that the two polyimides are molecularly mixed because the fine nanostructure should be maintained if the blending is beyond nano or molecular scale. However, the shoulder peak of the pristine PMDA-ODA PI shifted toward higher diffraction angles. We assume that this might be attributed to the formation of smaller and well-packed PI chain domains as a result of broken main domains (featuring of 4.8Å interchain distance) by incorporating the flexible coil-like components (BOCA-MCA PI). Additionally, this particular feature seems to be a clue for the formation of copolyimide between the two polyimides when they were made from the corresponding precursors by transamidation reaction [11].
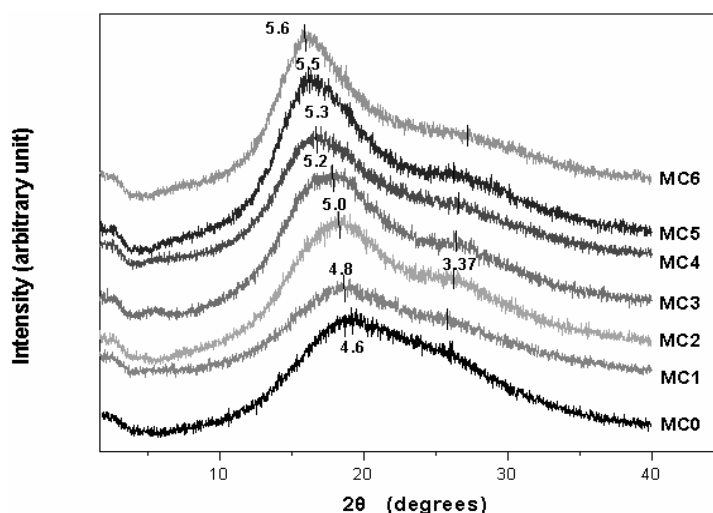

Figure 9. WAXD diffractograms of polyimide/polyimide composite films (see sample names in Table 1).

Thermal Stability

As shown in Fig. 10, the pristine polyimides show almost single step thermal decomposition behavior, whereas two step decomposition is observed for the polyimide composite films. In case of MC1, the weight residue at ~650°C is larger than that of the pristine polyimides. Based on this and the WAXD results, we would conclude the formation of copolyimide fractions between these two polyimides. Apart from this, it is obvious that compositing two polyimides does basically improve the thermal stablility of BOCA-MCA PI owing to the high thermal resistance of PMDA-ODA PI.

The glass transition temperature (Tg) of the polyimide composite films were measured using DMTA (see Fig. 11). As the aliphatic polyimide (BOCA-MCA PI) content increases, the glass transition temperature seems to be linearly increased in the presence of reducing the intensity. With mixing 40 wt.% of PMDA-ODA PI, the glass
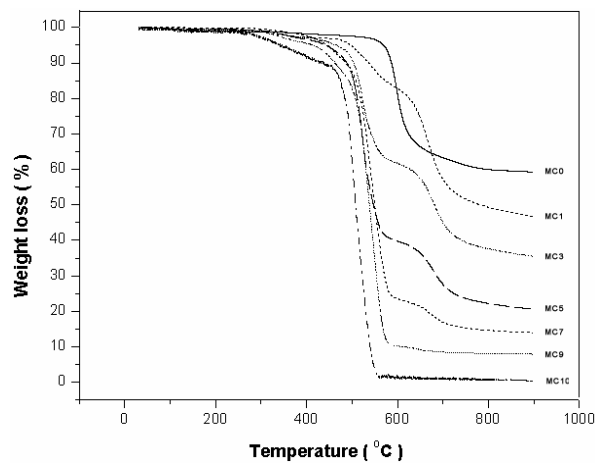

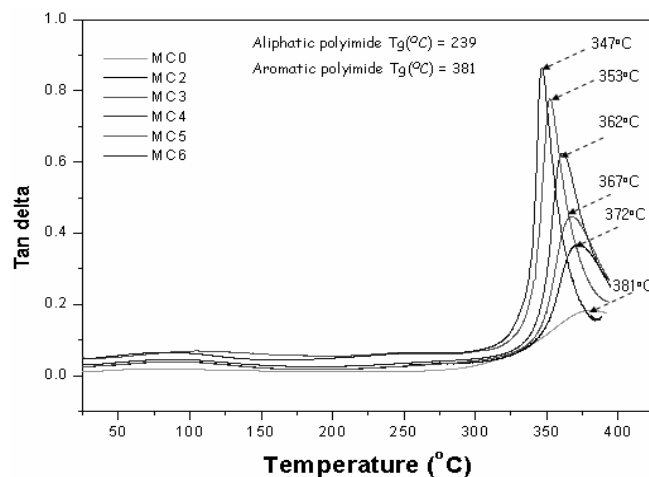**Figure 10.** TGA curves of polyimide/polyimide composite films.

Figure 11. Loss tangent of polyimide composite films as a function of temperature.

transition temperature of BOCA-MCA PI (Tg=239°C) was increased to 347°C, which is quite a remarkable increase.

In order to closely look at the trend of the glass transition change by making composites, the glass transition temperatures are replotted as a function of the composition. In addition, the well-known Fox equation ($1/Tg = w_1/Tg_1 + w_2/Tg_2$) has been employed to simply predict the glass transition temperature by mixing the two pristine polyimides [23]. As shown in Fig. 12, the measured Tg values are almost linearly dropped as the aliphatic polyimide content increases. However, the decreasing slope is slower for the measured values than for the values obtained by using the Fox equation. This result indicates that the present composite system has an additional effect on the Tg values. The first reason could be assigned to the molecular level mixing of the two constituent polyimides which adds a specific interaction between the two polyimide components, resulting in the increased Tg. Another reason might be on the formation of compolyimide fractions by the transamidation reaction, which is already evidenced from the WAXD and TGA results.
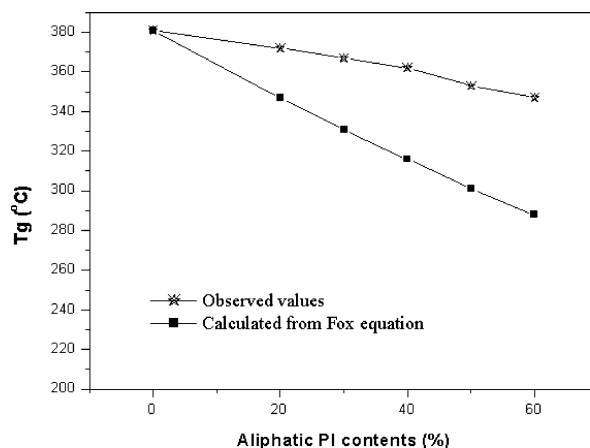

Figure 12. Glass transition temperature of polyimide composite films as a function of BOCA-MCA PI composition.

Mechanical Properties

The tensile mechanical properties of polyimide composite films were measured at room temperature. In general, for a particular polymer, the tensile properties are dependent on many factors such as viscosity (molecular weight), processing conditions, thermal history of polymer specimens, etc. As expected, the tensile strength of the semi-rigid rod type PMDA-ODA PI was higher than that of the flexible coil-like BOCA-MCA PI [17]. As shown in Fig. 13, the tensile strength of polyimide composite films are in between the values of the pristine polyimides. However, no special synergistic effect was found as in the TGA result.

Finally, we examined the thermomechanical properties of polyimide composite films. As shown in Fig. 14, the storage modulus of composite films was gradually decreased as the aliphatic polyimide content increased, which is in accordance with the tensile result. However, the shape as a function of temperature is almost similar each other, whereas the relaxation position at above 300°C is different.
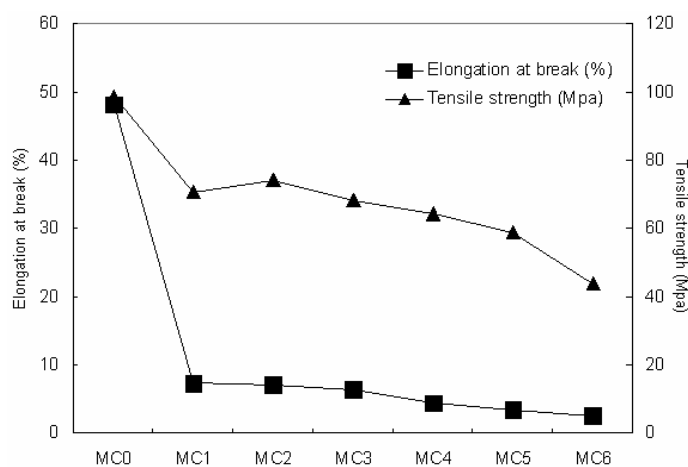
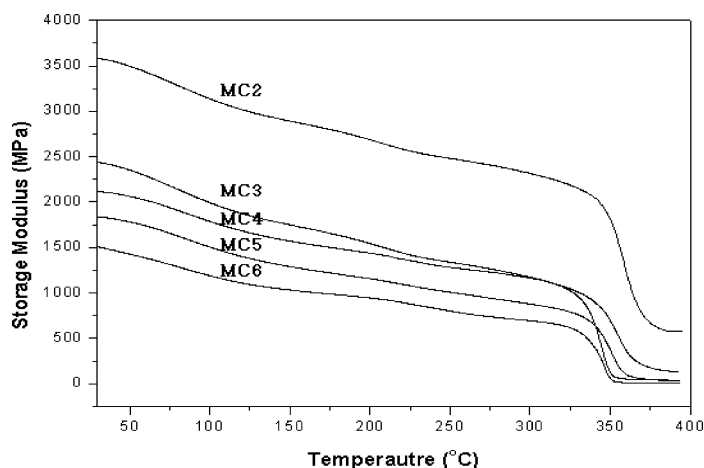**Figure 13.** Mechanical properties of polyimide composite films.

Figure 14. Storage modulus values of polyimide composite films.

Conclusions

We have prepared polyimide composite films by employing corresponding precursor polymers. The spectroscopic result showed that the precursor polymers are mixed almost on a nano or molecular scale. The SAXS measurement disclosed that the critical nanostructure change was occurred by including 20~30 w.% of flexible coil-like polyimide. The inclusion of flexible coil-like polyimide components made the interchain distance of semi-rigid rod-like polyimide wider. The WAXD and TGA results gave a clue for the formation of copolyimide fractions. In addition, the Tg trend of composite films also evidenced forming a semi-molecular composite and/or copolyimide fractions. However, no special characteristics were found from the tensile strength and modulus of composite films.

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