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Surface Segregation-typed Polyimide Blends between Silicon-containing Polyimide and Polyimides of Varied Chain Flexibility

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Surface segregation behaviors of blending systems between polysiloxane-block-polyimide (SPI) and three polyimides with different chain flexibility (PMDA/ODA, s-BPDA/ODA, and ODPA/ODA) have been investigated. All film samples with 50 μm thickness were characterized by surface profilometer, attenuated total reflection infrared (ATR-IR), and ATR microscope. In this study, the films with various PSI contents were processed on a glass substrate. At low concentration of PSI (less than 10 phr), three types of the polyimides trended to migrate to the glass-side surface, while PSI component trended to migrate to the air-side surface. For high concentration of PSI (i.e., 10 phr and 30 phr), the glass-side surface was covered with the polyimides, whereas the air-side surface showed two different colors. ATR microscope revealed PMDA/ODA blending system exhibited the highest segregation level.

Keywords blends, phase-segregation, polyimide, silicon-containing polyimide

INTRODUCTION

Since the first commercialization of polyimides in the late 1960s by Du Pont, the advancement in the science and technology of the polymers, particularly in the field of aromatic polyimides, has led to a wide range of their utilization among in which the most relevant are in the microelectronic industries (as optical components or dielectric and passivation layers),[1–3] in the membrane industries,[4] as well as in the space application field.[5–11] Nowadays, s-BPDA/ODA (Upilex-R trademark from Ube Industries), and PMDA/ODA (Kapton trademark from DuPont), and ODPA/ODA are widely used in many applications such as microelectronic, and filtration fields. These three kinds of polyimide has been a dramatic increase in demand of polyimides. Therefore, PMDA/ODA, s-BPDA/ODA, and ODPA/ODA were chosen as a major component of polyimide blends in this study.

Si-containing polymers such as poly(dimethyl siloxane), copolymer of poly(dimethyl siloxane) and polyimide, or polysilsesquioxane have been reported to possess high UV stability, enhanced solubility, high impact resistance, modified surface properties, etc.[12–15] It has been well known that polyimide and Si-containing block copolyimide polymers are immiscible. Rimdusit et al.[16] studied the segregation behavior of the blends between s-BPDA/ODA and silicon-containing block copolyimide, and reported that the behavior of the blend confirms the surface segregation of gradient structure.

As mentioned before, three types of polyimide, i.e., PMDA/ODA, s-BPDA/ODA, and ODPA/ODA, have been used in this study because of their different chain structures. PMDA/ODA includes only one benzene ring in each repeating unit; the structure of s-BPDA/ODA includes two benzene rings, and that of ODPA/ODA include ether group linked between two benzene rings. The conformation of ODPA/ODA is the most, while that of PMDA/ODA is the least. The differences of internal structures of these polyimides in the blends possibly lead to interesting different behavior of segregation. Due to the differences of the chain flexibilities among three polyimides (major component), the segregation degrees of the blends are expected to be different.

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The aim of this research is to study the surface-segregation of polyimide blend between BSF30 and the three types of polyimides. In this study, the degree of segregation of the polyimide blends was determined via surface profilometry, ATR, and ATR microscope.

EXPERIMENTAL SECTION

Materials

4,4′-diaminodiphenyl ether (4,4′-ODA) was purchased from Tokyo Kasei Kogyo Co., Ltd. 3,3′,4,4′-biphyltetracarboxylic dianhydride (s-BPDA) was obtained from Ube Chemical Co., Ltd. Benzene-1,2,4,5-tetracarboxylic anhydride (PMDA) was bought from Tokyo Kasei Kogyo Co., Ltd. 3,3′,4,4′-oxydiphthalic anhydride (ODPA) was supplied by Shanghai Research Institute of Synthetic Resins. N-methyl-2-pyrrolidinone (NMP), the solvent for poly(amic acid) synthesis, was purchased from Fluka. Tetrahydrofuran (THF), the cosolvent for polyimide blend, was purchased from Merck Company. All chemicals were used as received without any further purification. As shown in Figure 1, polysiloxane-block-polyimide (SPI) under the trademark of "BSF30" with molecular weight of 167,720 was obtained from Nippon Steel Chemical Co., Ltd. The ratio of the block components (polysiloxane/polyimide) is 36.8 mol%. Glass petri dishes were used as substrate for polymer blend processing.

Sample Preparations

Poly(amic acid) Preparation for Three Polyimides

The three polyimides of ODPA/ODA ($Tg = 270^{\circ}C$), s-BPDA/ODA ($Tg = 285^{\circ}C$), and PMDA/ODA ($Tg = 385^{\circ}C$) were synthesized by the condensation polymerization via conventional two-step method, consisting of polymerization of a soluble poly(amic acid) intermediate. This approach was based on the reaction of diamine and tetracarboxylic acid in a polar aprotic solvent such as N-methylpyrolidone (NMP) at room temperature. The rendered poly(amic acid) was then thermally imidized in a further step to produce the desired polyimides.

Polyimide Blend Preparation and Imidization Condition

Three kinds of poly(amic acid) (PAA) were prepared via two-step method, while polysiloxane-block-polyimide solution was made by dissolving calculated amounts of the dried copolymer film in THF solution to yield desired concentrations. Solution mixture of PAA solution and the copolymer solution were thoroughly mixed using a vortex mixer. The resulting clear solution mixtures were poured onto a petri dish, and dried in an air-circulated chamber at room temperature for 1 hour and at 60°C for 8 hours. The imidization was performed stepwise in vacuum oven using the heating program at 150°C for 1 hour, 200°C for 1 hour, and 300°C for 1 hour. Then the films were cooled to room temperature and removed from the glass plates. The thickness of rendered films was controlled to 50 microns.

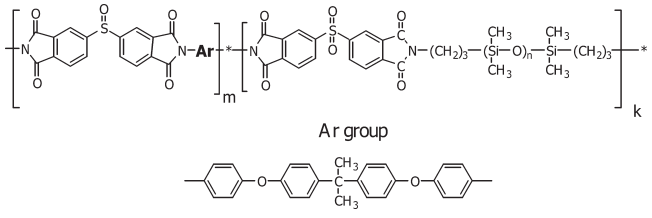

FIG. 1. Polysiloxane-block-polyimide (SPI) obtained from Nippon Steel Chemical.

Characterization of Blend Films

Contact angle measurement was performed at room temperature using a contact angle meter model CAM-PLUS MICCRO equipped with an optical microscope from TANTEC INC. The measured liquid was deionized water and ethylene glycol droplets with a radius of 10 μm. The Sample's contact angle was averaged from 10 measured values.

The surface profile was assessed with the Sloan DEKTAK III stylus profilometer. In comparison on the effect of polyimide type, the scan track was 10 mm. To depict the contour on the surface for hill and valley areas, the scan tract was 800 μm for determining the effect of SPI contents.

Infrared spectra of the air side and the glass side surfaces of polyimide blend films were measured using a PerkinElmer Spectrum GX FTIR spectrophotometer.

Attenuated total reflectance fourier Transform Infrared (ATR-FTIR) spectra were acquired using ZnSe as a prism at an incidence angle of 45°. The scan number and the spectral resolution were 64 and 8 cm^{-1}, respectively.

For higher depth profile, ATR microscope with Germanium tip was used to detect the functional groups on the hill and valley surface of the 30 phr blends in comparison with those on the surface of pure polyimides and pure SPI. The scan number and the spectral resolution were 64 and 8 cm^{-1}, respectively.

Dynamic mechanical properties of the polyimide blend systems were tested using the NETZSCH Model DMA 242. The experiment is done in a tension mode using the dimension of the specimen of approximately $23.7 \times 5 \times 0.05\ mm^3$ ($L \times W \times T$). The applied strain amplitude was 0.3% at the deformation frequency of 1 Hz. The specimen was heated using a temperature ramp rate of 3°C/min from room temperature to 300°C for ODPA/ODA blends, 320°C for s-BPDA/ODA blends, and 420°C for PMDA/ODA blends.

The decomposition temperature (T_d) and char yield of the blends were studied using TGA Instruments (model TGA/SDTA 851[e]). The experiments were performed using a heating rate of 20°C/min from 40 to 1000°C under nitrogen atmosphere. The flow of purging nitrogen was kept at 80 ml/min. The sample mass was approximately 20 mg.

Tensile modulus and tensile strength of polyimide blend films were determined utilizing a universal testing machine (model 5567) from Instron Instrument. The test method used was a tension mode with a specimen dimension of 8.0 cm in length, 0.50 cm in width, and 0.050 mm in thickness. The specimen gauge length was 4.0 cm and the crosshead speed for film testing was 0.50 cm/min. The tensile properties were obtained following the general procedure in ASTM D882 using five specimens per test condition.

RESULTS AND DISCUSSION

Figure 2 presents the water contact angle of three polyimide blends at various SPI compositions for both air-side surface and glass-side surface. It can be observed that the water contact angle on glass-side surface had no significant change for all SPI compositions. The contact angle of the blends on the air-exposed side tended to be the same as that of pure SPI. The average water contact angles on glass side surface were 75°C, 73°C, and 71°C for ODPA/ODA blends, s-BPDA/ODA blends, and PMDA/ODA blends, respectively, whereas that for all three types of the blends on the air side surface was about 102 °C in every blend ratio. That means the SPI component (more hydrophobic component) migrated to the air-exposed side, while the polyimide component was abundant on the glass-side. This is because the air is hydrophobic in nature.[17] These results are consistent with the previous study,[16] which reported that contact angle measurement evidently indicated an enrichment of the hydrophobic siloxane fraction on the air-exposed surface in the blends system of s-BPDA/ODA and SPI.

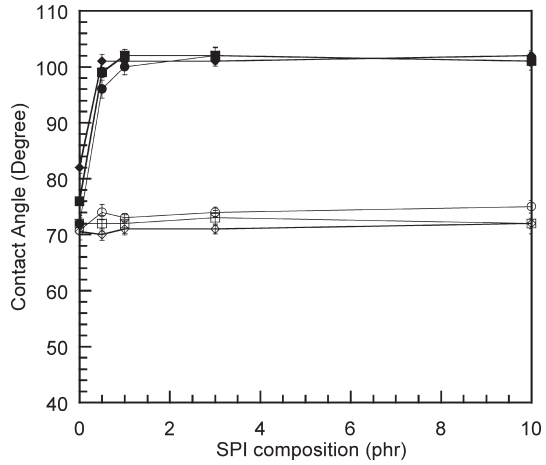

FIG. 2. Water contact angle measured on the glass-side surface: (○) ODPA/ODA(□) s-BPDA/ODA, (◇) PMDA/ODA; on the air-exposed surface: (●) ODPA/ODA, (■) s-BPDA/ODA, (◆) PMDA/ODA. [Contact angle on air side of ODPA/ODA blends (30 phr) = 102°, s-BPDA/ODA blends (30 phr) = 102°, PMDA/ODA blend (30 phr) = 102°, SPI = 105°; Contact angle on glass side of ODPA/ODA blends (30 phr) = 75°, s-BPDA/ODA blends (30 phr) = 73°, PMDA/ODA blends (30 phr) = 71°, SPI = 97°.]

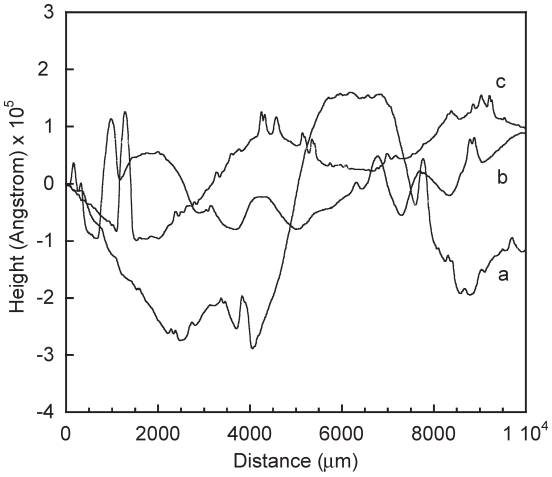

FIG. 3. Surface profile of three polyimide blends at 30 phr SPI: (a) PMDA/ODA blend, (b) ODPA ODA blend, (c) s-BPDA/ODA blend.

Figure 3 exhibits the profiles of three blending systems at 30 phr. The different patterns of contours were observed. The roughness of PMDA/ODA blend renders the greatest value, while that of the ODPA/ODA blend is slightly less than s-BPDA/ODA blend. It reveals that PMDA/ODA blend has the highest degree of segregation.

Figures 4a–c show the profiles of three polyimide blends in comparison between 10 phr and 30 phr (glass side surface). The results reveal that the increase of SPI content has the effect on the increase of roughness. This behavior was obviously observed in the blend of PMDA/ODA.

The results of ATR-FTIR spectra for glass-side surface of polyimide blend for three types of polyimides are presented in Figure 5a. It can be observed that the spectra of the polyimide blend on the glass side surface does not present the peaks of 1060 cm^{-1}, and 1015 cm^{-1}, which represented the Si-O-Si stretching vibration and 795 cm^{-1} of Si-C stretching were detected. These are important vibrational signatures of siloxane group in SPI. Furthermore, the spectra of glass side surface of the blends presented the same appearance as those of pure polyimide. That means the SPI component did not appear on the glass side, and the glass-side surface is covered with polyimide. Figure 5b shows the spectra for air-exposed surface of three types of polyimide blends. The spectra of the blends at 30 phr exhibit the Si-O-Si stretching vibration and 795 cm^{-1} of Si-C stretching of SPI, which indicated that the air-side surface is covered with SPI. This phenomenon does not occur in case of the blends of the lower SPI content, i.e., 3 phr or less, at highly diluted blend compositions (i.e., 0.5–5 phr), which yield a submicron layer of the SPI domain, the ATR technique is not sensitive enough to acquire the siloxane vibration on the surface. This is due to the fact that ATR-FTIR technique is sensitive to the chemical species with sufficient depth depending on the type of the crystal used. In this case, a ZnSe crystal used provide a depth profile

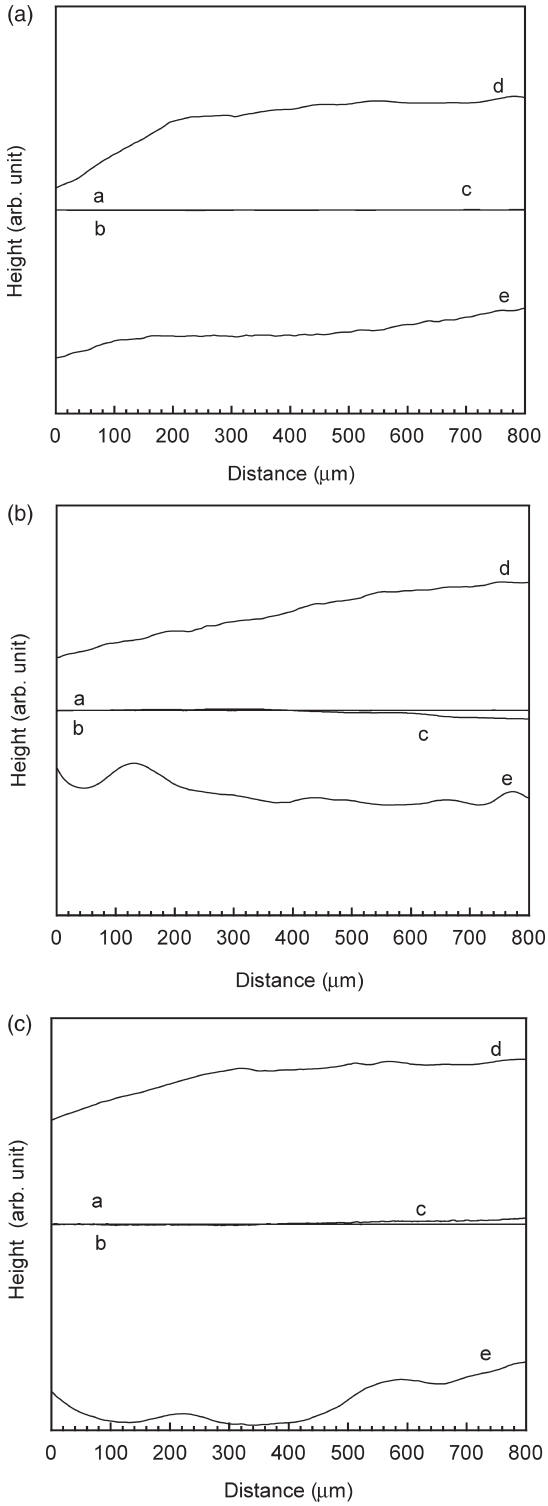

FIG. 4. (4a) Surface profile of ODPA/ODA blends at different SPI contents (air side surface): (a) ODPA/ODA, (b) SPI, (c) 10 phr, (d) 30 phr at hill, (e) 30 phr at valley. (4b) Surface profile of s-BPDA/ODA blends at different SPI contents (air side surface): (a) s-BPDA/ODA, (b) SPI, (c) 10 phr, (d) 30 phr at hill, (e) 30 phr at valley. (4c) Surface profile of PMDA/ODA blends at different SPI contents (air side surface): (a) PMDA/ODA, (b) SPI, (c) 10 phr, (d) 30 phr at hill, (e) 30 phr at valley.

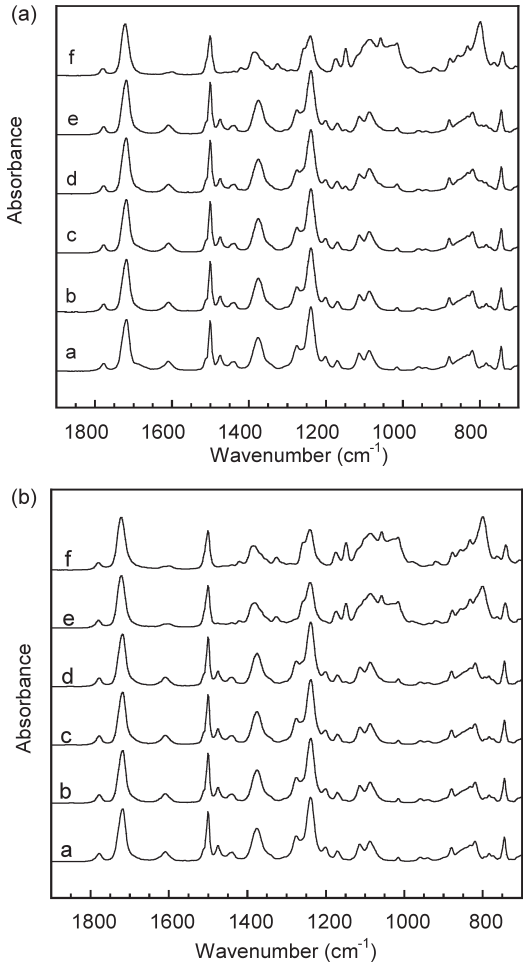

FIG. 5. (5a) ATR spectra of ODPA/ODA blends at various SPI contents (glass side surface). (a) ODPA/ODA, (b) 1 phr, (c) 3 phr, (d) 10 phr, (e) 30 phr, (f) SPI. (5b) ATR spectra of ODPA/ODA blends at various SPI contents (air side surface). (a) ODPA/ODA, (b) 1 phr, (c) 3 phr, (d) 10 phr, (e) 30 phr, (f) SPI.

in the range of 2–4 microns. This phenomenon corresponds to Rimdusit et al.[16] They reported that the segregation behavior of the blend between s-BPDA and SPI exhibited the polyimide moiety on the glass side surface, while SPI moiety on the air side surface.

As mentioned before, at high SPI content (i.e., 30 phr), the surface of the blends comprise of hill area and valley area. To determine the component of each area, ATR microscope was applied. For OPDA/ODA and s-BPDA/ODA blend, the hill area on the film could exhibit SPI spectra, while the valley one could show the combination spectra of SPI and polyimide (Figures 6a–6b). For PMDA/ODA blends, the hill area shows SPI spectra, but the valley one exhibits only polyimide spectra (Figure 6c).

The calculation of intensity at wavenumber 795 cm^{-1} is summarized in Figure 7 and Table 1. This result confirms the results of DEKTAK profiler that polysiloxane-block-polyimide

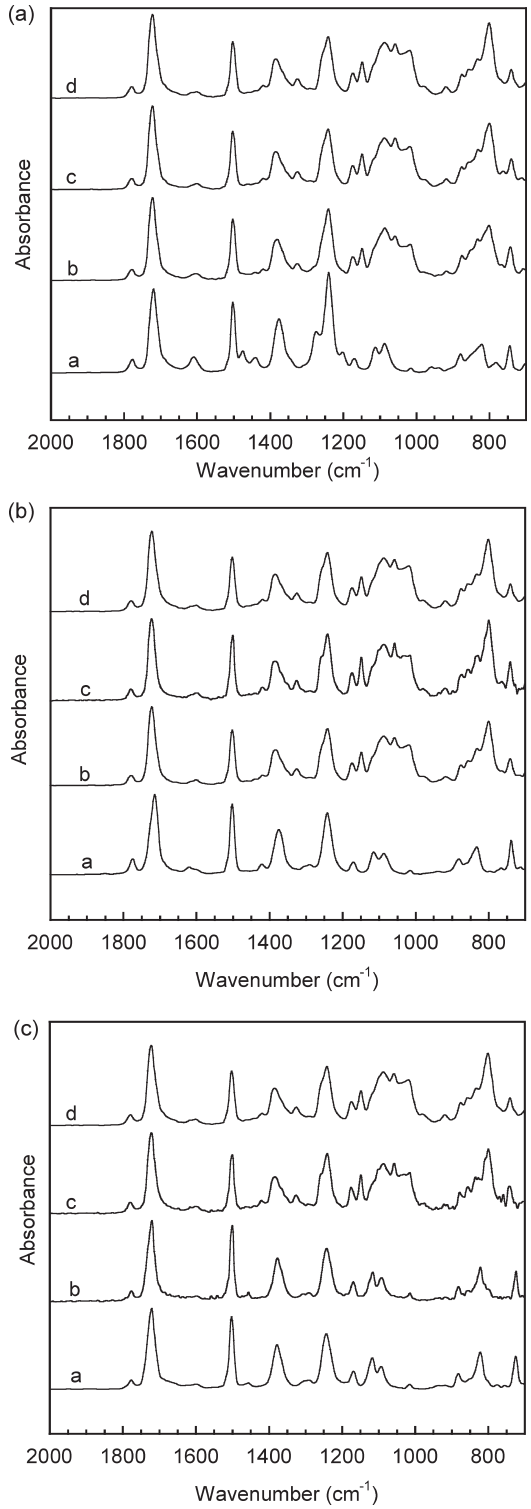

FIG. 6. (6a) Spectra from ATR microscope of ODPA/ODA blends at various SPI contents. (air side surface): (a) pure ODPA/ODA, (b) valley area of 30 phr, (c) hill area of 30 phr, (d) SPI. (6b) Spectra from ATR microscope of s-BPDA/ODA blends at various SPI contents. (air side surface): (a) pure s-BPDA/ODA, (b) valley area of 30 phr, (c) hill area of 30 phr, (d) SPI. (6c) Spectra from ATR microscope of PMDA/ODA blends at various SPI contents. (air side surface): (a) pure PMDA/ODA, (b) valley area of 30 phr, (c) hill area of 30 phr, (d) SPI.

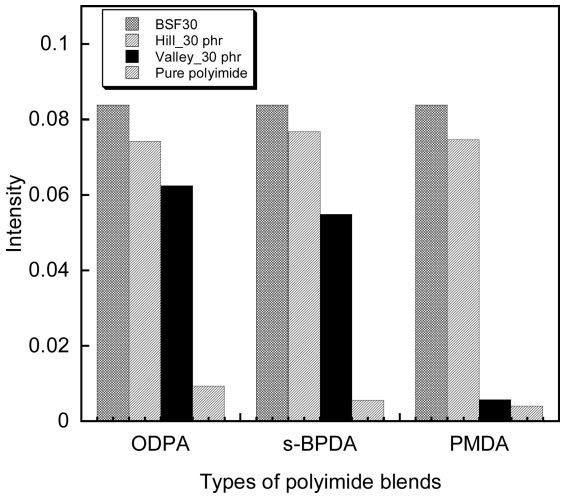

FIG. 7. Comparison of intensity at wavenumber 795 cm^{-1} (Si-C stretching).

(SPI). Furthermore, it shows that the segregation behavior of s-BPDA/ODA blend tends to be slightly higher than that of the ODPA/ODA blend.

Figures 8a–8c illustrate storage modulus of the ODPA/ODA blends, s-BPDA/ODA blends and PMDA/ODA blends at various SPI compositions. As reported at 40°C, the thermograms revealed the glassy state moduli of the ODPA/ODA film to be 3.06 GPa (Figure 8a), s-BPDA/ODA film to be 2.99 GPa (Figure 8b), PMDA/ODA film to be 2.70 GPa (Figure 8c), and that of SPI to be 1.21 GPa. The SPI is, therefore, much less stiff than all three pure polyimide films due to the presence of the soft silicone segments in its molecular structure as seen in Figure 1. Thermal stability of polymers can also be obtained from the slope of the glassy state modulus in the DMA thermograms. The lower the slope of the glassy state modulus, the greater the thermal stability of the polymer. As a result, the DMA thermograms in Figures 8a–8c clearly suggested that all three polyimide films were significantly more stable than the SPI polyimide. The large decrease in the storage modulus in the thermograms at elevated temperature indicated the corresponding glass transition region of each specimen. The storage modulus of the blend film at a large SPI content of 30 phr clearly showed the mixed characteristics of the two parent polyimides. The blend film displayed two successive drops in its storage modulus. However, when the amount of

TABLE 1
Estimated Si-C content (%) in the valley area of each polyimide blend

Type of polyimide blends	Estimated Si-C content (%)
ODPA/ODA	71
s-BPDA/ODA	63
PMDA/ODA	2

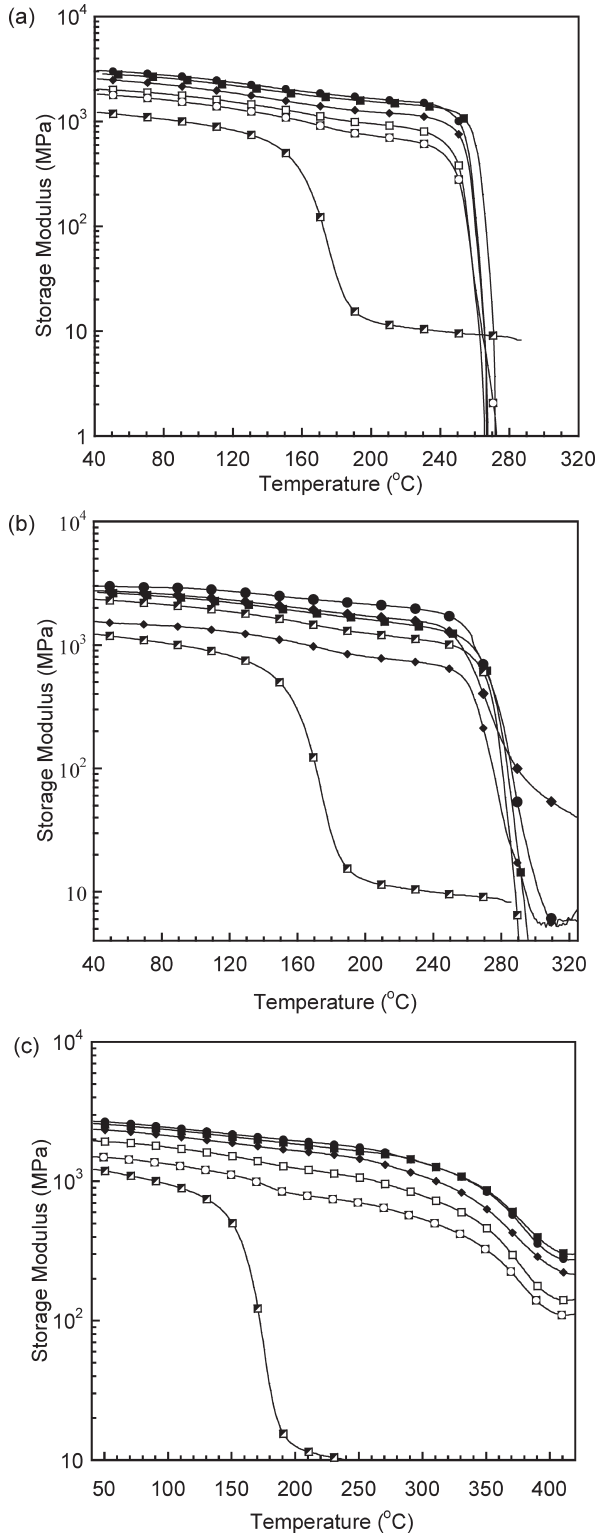

FIG. 8. (a) Storage modulus of the ODPA/ODA blends at various SPI contents: (●) ODPA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI. (b) Storage modulus of the s-BPDA/ODA blends at various SPI contents: (●) s-BPDA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI. (c) Storage modulus of the PMDA/ODA blends at various SPI contents: (●) PMDA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI.

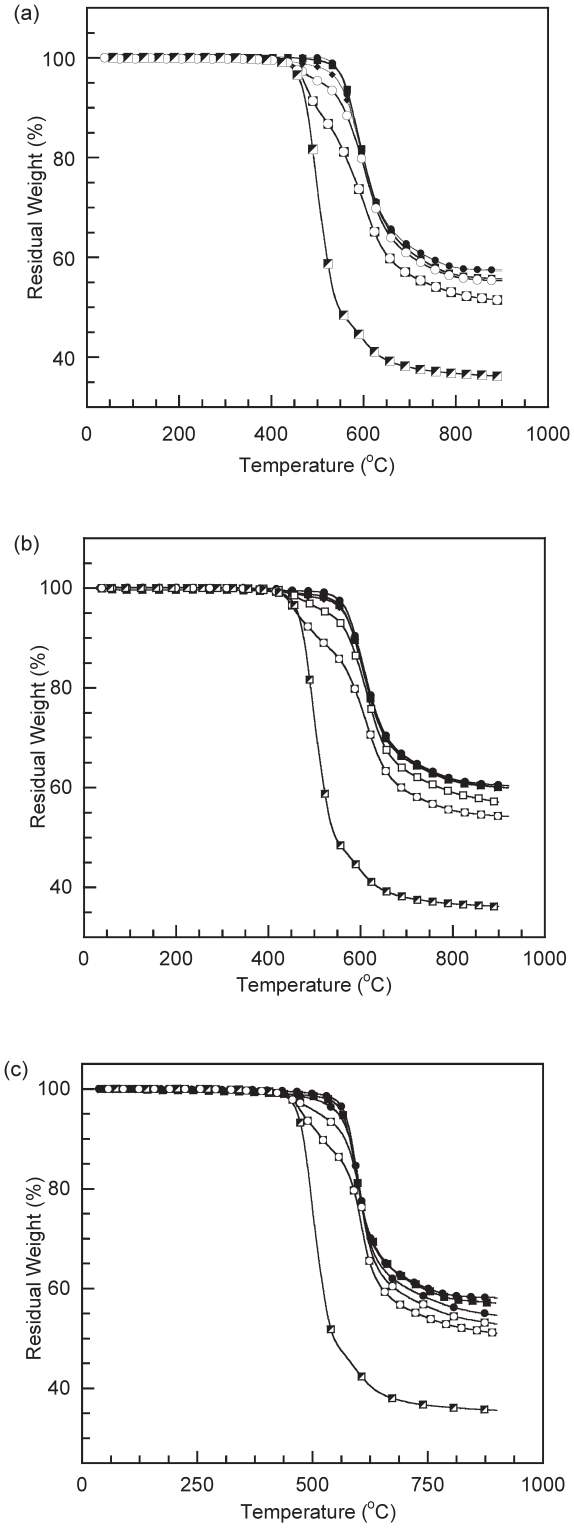

FIG. 9. (a) TGA thermograms of the ODPA/ODA blends at various SPI contents: (●) ODPA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI. (b) TGA thermograms of the s-BPDA/ODA blends at various SPI contents: (●) s-BPDA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI. (c) TGA thermograms of the PMDA//ODA blends at various SPI contnets: (●) PMDA/ODA, (■) 1 phr, (◆) 3 phr, (□) 10 phr, (◘) 30 phr, (◩) SPI.

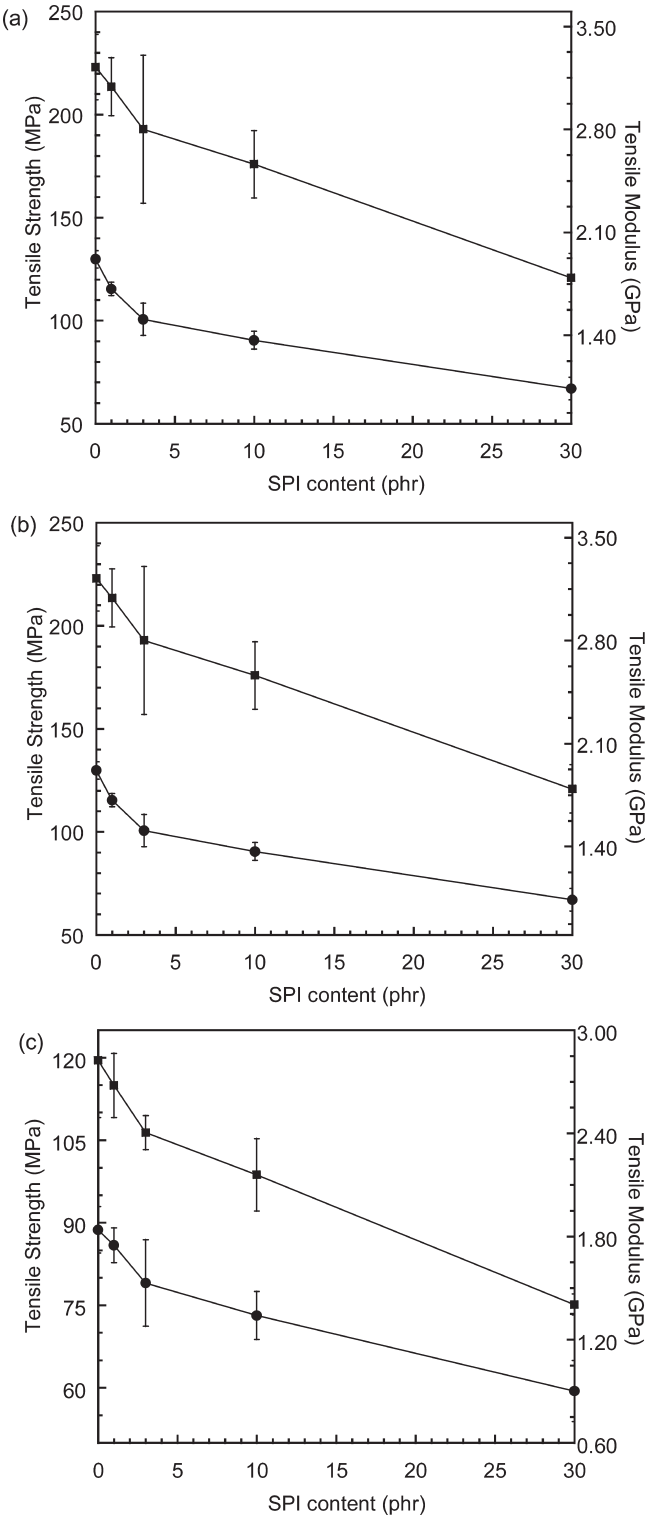

FIG. 10. (a) Tensile properties of the ODPA/ODA blends: (■) Tensile modulus, (●)Tensile strength; pure SPI modulus = 1.30 GPa, pure SPI strength = 52 MPa. (b) Tensile properties of the s-BPDA/ODA blends: (■) Tensile modulus, (●) Tensile strength; pure SPI modulus = 1.30 GPa, pure SPI strength = 52 MPa. (c) Tensile properties of the PMDA/ODA blends: (■) Tensile modulus, (●) Tensile strength; Pure SPI modulus = 1.30 GPa, pure SPI strength = 52 MPa.

the SPI in the blend films was kept to be in low SPI concentration, the decrease of their storage moduli, at about 160°C, due to the presence of SPI, was suppressed and hardly detected. The resulting thermograms emphasized the requirement to use a relatively small amount of the SPI in the blend systems in order to maintain the overall thermal and mechanical integrity of the resulting films.

From the above results, three types of polyimides and SPI blends particularly at 30 phr composition seemed to show two phase morphology with two distinct Tg's. The lower Tg corresponds to the glass transition temperature of the SPI phase. The higher Tg corresponds to the glass transition temperature of polyimide phase. Both Tg values of SPI and s-BPDA/ODA were also similar to those reported elsewhere.[16,18,19]

Thermal stability of the polyimide blends for ODPA/ODA blends, s-BPDA/ODA blends, and PMDA/ODA blends with various compositions of SPI was examined and presented in Figures 9a–9c, respectively. It was clearly seen that when relatively large amounts of the SPI, i.e., 10 phr and 30 phr, were shown in the blend film, the degradation temperature of the film was substantially sacrificed due to the inherently lower degradation temperature of the SPI portion in the blend films. All polyimide blends exhibit a two-step change, which corresponds to those of pure SPI and pure polyimides.

On the other hand, no significant change in degradation temperature of the blend films was observed within the composition range of 1 and 3 phr of the blends, obviously due to the small quantity of the SPI presented. For all three types of polyimide blends, it can be observed that the char yield of the blends tended to decrease with increasing the SPI content. In this study, the char yield of SPI (at 900 °C, 10 °C/min) was 36%, which was similar to our previous TGA study of SPI at 20 °C/min.[20]

Tensile properties of three polyimide blends are presented in Figures 10a–10c. In Figure 10a, the pure ODPA/ODA film rendered the tensile strength of 93 MPa and the tensile modulus of 2.52 GPa. In Figure 10b, the tensile strength and tensile modulus of the pure s-BPDA/ODA film were 130 MPa and 3.22 GPa, respectively. In Figure 10c, the ones of the pure PMDA/ODA film were 89 MPa and 2.82 GPa, respectively. It can be observed that the values of tensile strength and tensile modulus were decreased with increasing SPI content. That is due to the low tensile strength of SPI (52 MPa) and the low tensile modulus of SPI (1.30 GPa). These results are in agreement with the results from DMA thermograms.

CONCLUSIONS

Phase separation behavior of the surface segregation type of the blends between three kinds of polyimides and polysiloxane-block-polyimide (SPI) was investigated and confirmed using ATR-FTIR spectroscopy. Furthermore, the segregation phenomena evaluated by a surface profiler are in agreement with those investigated by ATR-microscope. It can be

concluded that the siloxane moieties in the SPI tended to migrate to the air-polymer interface and formed a siloxane-rich-surface. In addition, the degrees of segregation among these three polyimide blends are different. PMDA/ODA blending system exhibited the highest surface segregation level while the segregation behavior of the s-BPDA/ODA blend exhibited slightly higher level than that of the ODPA/ODA blend. This phenomenon is attributed to the lower degree of conformational entropy of the PMDA/ODA polyimide, which resulted in the greater surface segregation level.

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