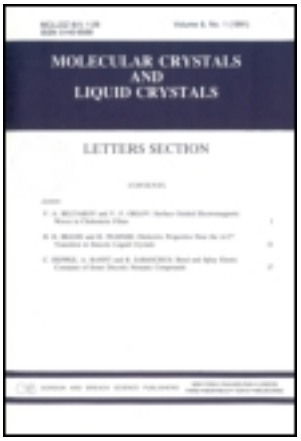

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Preparation and Characterization of Transparent Polyimide/Silica Composite Films by a Sol-Gel Reaction

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A series of transparent, 100 μm thick, polyimide (PI) composite films were prepared by a sol-gel reaction using a thermal imidization process between poly(amic acid) (PAA) and various amounts of tetraethyl orthosilicate (TEOS) in N,N*-dimethylacetamide. The PAA were prepared using 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2'-bis(trifluoromethyl)benzidine (TFMB) and 3,5-diaminobenzoic acid (DABA). The chemical structure and thermal stability of the PI/silica composite films were examined in detail by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The PI/silica composite films showed high thermal stability, and the degradation behavior was found to be dependent on the amount used. In addition, the optical and thermo-mechanical properties of the films were investigated, including the haze values, yellow indices and in-plane coefficients of thermal expansion (CTE). The CTE values of the PI/silica composite films were 52.0 - 43.5 ppm/°C, and were dependent on the amount of TEOS used. The haze values and yellow indices increased with increasing TEOS concentration. Optically transparent PI/silica composite films were obtained with a TEOS content of up to 20 wt%.*

Keywords Coefficients of thermal expansion; haze; sol-gel reaction; transparent polyimide/silica composite; thermal imidization process; yellow index

Introduction

Flexible organic electronic devices, such as flexible solar cells, liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs), fabricated on polymer substrates are the next generation of electronic display products [1–6]. A suitable polymer substrate for

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electronic device manufacture would combine the gas barrier, thermal and chemical properties of glass with the flexibility, toughness and processability of polymers. Of the many polymeric materials available, polyimides (PIs) have been used widely in the electronic device industry owing to their high glass transition temperature, dimensional stability and heat resistance, as well as their excellent mechanical, adhesion and dielectric properties.

Recently, transparent colorless PI films have attracted considerable attention because of their optical properties [7–11]. Transparent PIs have been prepared using dianhydride and diamine monomers substituted with fluorine moieties in their side groups. On the other hand, transparent PIs have many technical problems, such as those related to the optical and thermo-mechanical properties, e.g. haze, yellow index and coefficient of thermal expansion (CTE).

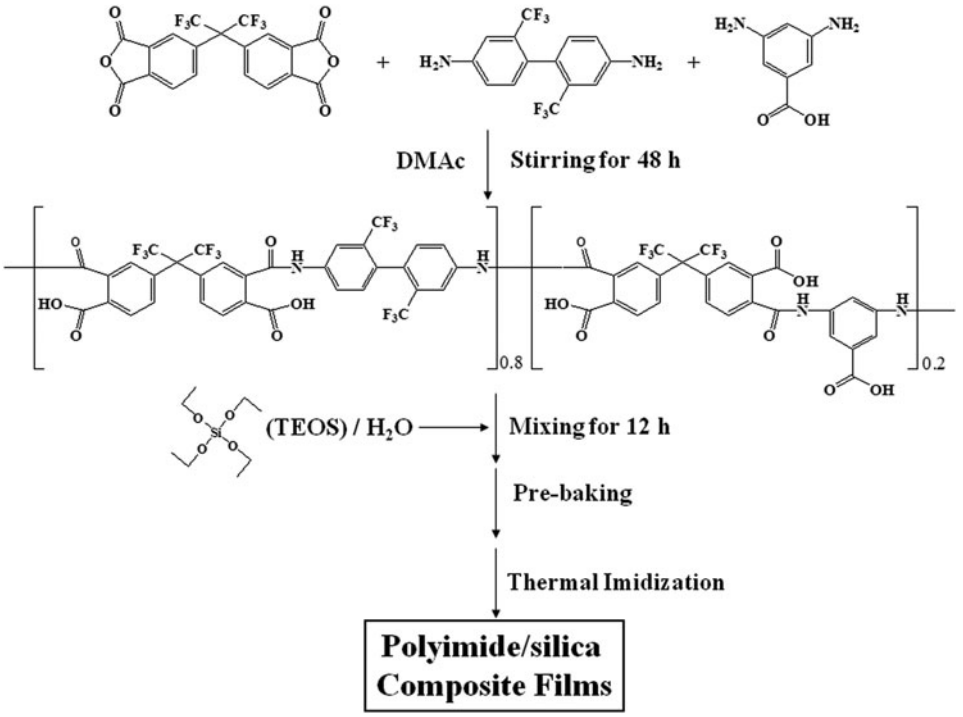
To improve the mechanical, thermal, magnetic, optical, electronic and optoelectronic properties of PIs, many studies have examined ways of producing PI-inorganic composite films that combine PI and inorganic materials. In addition, a range of fabrication techniques have improved the thermal, optical and mechanical properties of PI-inorganic composite films than individual PI components [11–17]. Nevertheless, phase separation was reported at higher inorganic material contents and that the physical properties, such as optical, thermal and mechanical properties, of the composite films are lower than that of the pure PIs [18–20]. Accordingly, the preparation of homogeneous PI-inorganic films without inorganic material aggregation in the PI matrix by controlling the interfacial interactions between the PIs and inorganic materials is an important issue for the sol-gel hybridization approach.

This paper reports the preparation of transparent PI/silica composite films using transparent poly(amic acid) (PAA) with carboxylic acid groups and different amounts of tetraethyl orthosilicate (TEOS) as a inorganic material on the interfacial interactions between PI and TEOS. Transparent PI/silica composite films were prepared by the thermal imidization of PAA/silica composite solutions based on the reaction between TEOS and PAA solutions composed of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2'-bis(trifluoromethyl)benzidine (TFMB) and 3,5-diaminobenzoic acid (DABA). The chemical structures and inherent viscosity of the synthesized PAAs were determined. In addition, the chemical structures, and optical and thermal properties of the transparent PI and PI/silica composite films were investigated with respect to the effect of the TEOS composition.

Experimental

Materials. 2,2'-Bis-(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) was supplied by Chriskev Company and purified by recrystallization from acetic anhydride. 3,5-Diaminobenzoic acid (DABA) and 2,2'-bis(trifluoromethyl)benzidine (TFMB) were purchased from Aldrich and Chriskev, respectively, and purified by vacuum drying at 100 ^{o}C. *N,N*-Dimethylacetamide (DMAc) was obtained from Aldrich and distilled over calcium hydride under reduced pressure. Tetraethyl orthosilicate (TEOS) and hydrochloric acid (HCl) were purchased from Aldrich and used as received.

Synthesis of Poly(amic acid). Poly(amic acid) (PAA) was prepared by adding 1 equivalent of 6FDA in a DMAc solution into 0.8 equivalents of TFMB and 0.2 equivalents of DABA, which were pre-dissolved in DMAc to form a 15.0 wt% solution, under nitrogen with vigorous stirring (see Scheme 1). Once the addition was complete, the reaction flask was



Scheme 1. Chemical structure of poly(amic acid) and the preparation procedure of the polyimide/silica composite films.

sealed tightly and stirred continuously for 48 h to produce a homogeneous and viscous polymerization mixture. The PAA solution obtained was filtered through a syringe with a 1.0 μm filter and stored in a refrigerator until needed.

Preparation of PI/Silica composite films. A series of PI/silica composite films was prepared via the sol-gel route. Various quantities of TEOS with deionized water and a catalytic amount of HCl in DMAc were added to a PAA solution to form 10 wt% PAA/silica composite solutions. The applied amounts of TEOS in PAA were 5, 10, 15 and 20 wt%. The PAA/silica composite solutions were stirred for 12 h at room temperature until they were homogeneous (see Scheme 1). A series of PI/silica composite films was prepared by further imidization using a thermal process. The PAA solution was coated onto Cr-coated steel plate substrates, and dried on a hot plate at 80°C for 1 h. The dried films were imidized thermally in an oven under a dry nitrogen gas flow using a three-step imidization protocol (150°C/60 min, 200°C/60 min and 250°C/120 min), and a ramping rate of 2.0°C/min. The samples were cooled to room temperature at a rate of 10°C/min, resulting in the production of good quality free standing films, 104 – 107 μm in thickness.

Measurements. The ^{1}H nuclear magnetic resonance (NMR, Bruker AM 300) spectra were obtained at room temperature. For the synthesized PAA precursor, the inherent viscosity was measured in DMAc at 25°C using an Ubbelohde suspended level capillary viscometer using a method described in the literature [21]. The UV-visible absorption spectra were obtained using a Shimadzu UV-1800 UV-visible spectrophotometer. The yellow indices

and haze values of the free standing composite films were determined using a CM-3700d (Minolta, Osaka, Japan) colorimeter and a Haze 4725 (Gardner Company, Reston, VA), respectively. The Fourier transform infrared (FTIR, BOMEM DA8 FTIR) spectra were obtained on a spectrometer equipped with a Diamond ATR system (Harrick Scientific). The FTIR spectra were recorded at a resolution of 4 cm^{-1} using a liquid nitrogen-cooled mercury cadmium telluride detector under vacuum. The glass transition temperatures were measured over the temperature range, 25–300°C, using a differential scanning calorimeter (model DSC-60C, Shimadzu, Japan). For these measurements, a ramping rate of 10.0°C/min was used, and the system was purged with dry nitrogen gas at a flow rate of 80 cc/min. The degradation temperatures were measured over the temperature range, 50–800°C, by thermogravimetric analysis (model TGA7, Perkin-Elmer). During the measurements, the system was purged with dry nitrogen gas at a flow rate of 100 cc/min and a temperature ramping rate of 10.0°C/min was used. The in-plane coefficients of thermal expansion (CTE) of the samples were measured by thermomechanical analysis (TMA, TA Q400, TA Instrument) with a 0.05 N expansion force applied to the film and heating rate of 5°C /min in the temperature range, 50–250°C. The CTE values were determined within the temperature range, 200–250°C.

Results and Discussion

The PAA with residual DMAc was characterized by ^{1}H NMR spectroscopy. The two proton peaks at 10.8 and 10.3 ppm were assigned to the amide linkages from TFMB and DABA to 6FDA in the backbone of PAA, respectively. PAA revealed aromatic proton peaks at 7.5–8.4 ppm (See Fig. 1). The estimated peak integration corresponded well with the expected chemical structure. For PAA, the measured inherent viscosity was 0.67 dL/g. The ^{1}H NMR spectrum and inherent viscosity suggests that PAA had been synthesized with a reasonably high molecular weight.

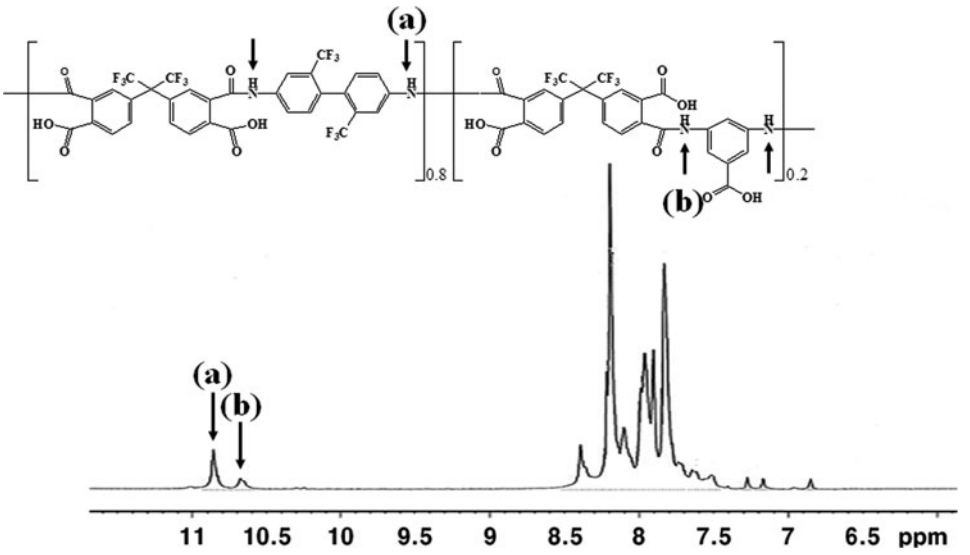


Figure 1. ^{1}H NMR spectra of poly(amic acid) including DMAc dissolved in dimethyl-d_6 sulfoxide (DMSO-d_6).

Table 1. Compositions, glass transition temperatures (T_g), decomposition temperatures (T_d), and residual weight percentage of polyimide and polyimide/silica composite films.

Sample designation	Feed ratio of TEOS[a]	T_g (°C)[b]	T_d (°C)[c]	RW (%)[d]	Remarks[e]
PI	—	—[f]	364	46.2	T
PI/Si-5	5	—	492	48.6	T
PI/Si-10	10	—	515	51.7	T
PI/Si-20	20	—	530	58.8	T

[a]Molar ratio of tetraethyl orthosilicate (TEOS) fed during the preparation of composite solutions.
[b]Measured by DSC with a heating rate of 10.0°C/min.
[c]Determined by TGA at a heating rate of 10.0°C/min under a nitrogen atmosphere: T_d = temperature of 5.0% weight loss.
[d]Determined by TGA at a heating rate of 10.0°C/min under a nitrogen atmosphere: RW = Residual weight percentage at 750°C.
[e]Abbreviation: T, Transparent
[f]Not detected in the range 25–300°C from DSC

A series of PI/silica composite films were prepared by the thermal imidization of homogeneous PAA/silica composite solutions with different TEOS contents. Table 1 summarizes the preparation and appearance of PI/silica composite films. Transparent PI/silica composite films were obtained as free standing films after thermal imidization.

The thermal stability of the PI film and PI/silica composite films was investigated by TGA (Fig. 2 and Table 1). The pure PI films exhibited a two-step thermal degradation pattern. The first weight loss at temperatures of up to 300°C was attributed to the loss of a carboxylic acid (-CO_2H) group of DABA in the main chain and the second weight loss

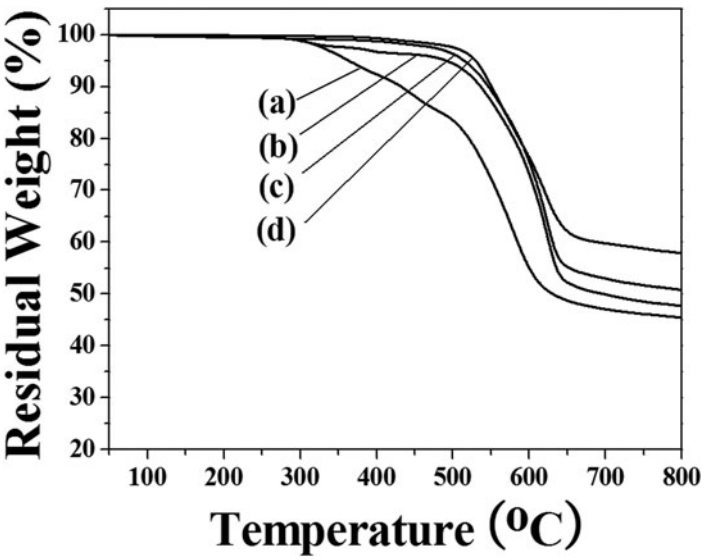


Figure 2. TGA thermograms of polyimide and polyimide/silica composite films with various compositions of TEOS, which were measured at a heating rate of 10°C/min: (a) PI, (b) PI/Si-5, (c) PI/Si-10, and (d) PI/Si-20.

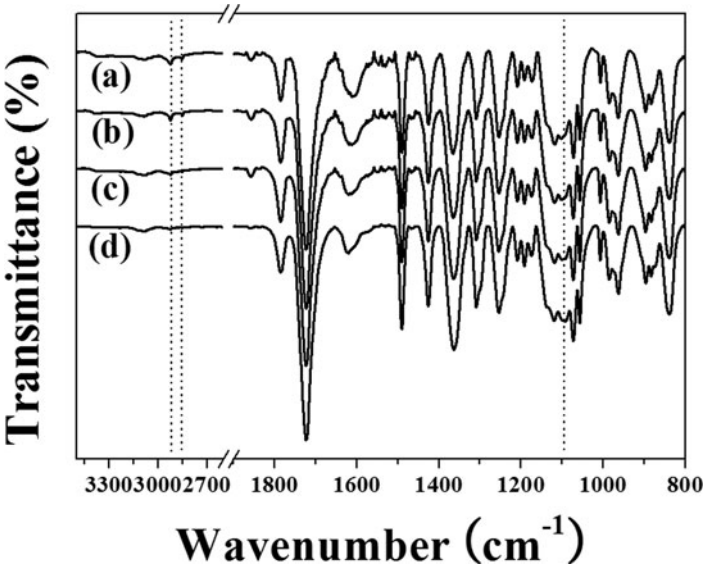


Figure 3. ATR-FTIR spectra of polyimide and polyimide/silica composite films with various compositions of TEOS: (a) PI, (b) PI/Si-5, (c) PI/Si-10, and (d) PI/Si-20.

at $\sim 470^{\circ}$C was assigned to the decomposition of the aromatic component in the PI main chain [22]. In contrast, the PI/silica composite films exhibited mainly a one-step thermal degradation pattern, which was dependent on the TEOS composition. The decomposition temperatures (T_d) of the composite films increased with increasing TEOS content, the PI/Si-20 film had the highest T_d. These results might be due to two factors. First, the thermally stable silica networks produced by the sol-gel reaction of TEOS in the PI/silica composite matrix improved the thermal stability of the PI/silica composite films. Second, the disappearance of the free carboxylic acid unit of DABA in the PI main chain, due to a reaction with TEOS, increased the T_d of the PI/silica composite films. Moreover, the residues of the composite films at 750°C were 46.2–58.8 wt% of the original weight and the measured residue of the PI and composite films increased in the order, PI < PI/Si-5 < PI/Si-10 < PI/Si-20. The glass transitions temperature of the PI and PI/silica composite films were examined by DSC. The PI and PI/silica composite films did not show any phase transition over the temperature range, 25–300°C, even after the thermal treatment and repeated scanning. These results show that the prepared PI/silica composite films have good thermal stability.

Figure 3 shows the FTIR spectra of the PI film and PI/silica composite films. The FTIR peaks of the PI and composite films were assigned according to the previously reported data [23,24]. The pure PI film exhibited vibrational absorption bands at 2923, 2850, 1785, 1723, 1490 and 1363 cm^{-1}. The two bands at 2923 and 2850 cm^{-1} were assigned to the O-H stretching vibration of carboxylic acid groups [25]. The two bands at 1785 and 1723 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of the carbonyl group of the imide ring, respectively, which are typical of PIs. The band at 1363 cm^{-1} and 1490 cm^{-1} corresponds to the C-N stretching vibration and the aromatic ring in the PI main chain, respectively. All these vibrational modes are associated with the polymer main chains. The PI/silica composite films showed similar characteristic bands independent of

Table 2. Film thicknesses, Yellow indices, Haze, and CTE values of polyimide and polyimide/silica composite films.

Sample designation	Film Thickness (μm)	Yellow Index[a]	Haze (%)	CTE[b]
PI	105.7	21.3	0.83	52.0
PI/Si-5	107.3	30.8	1.16	48.4
PI/Si-10	104.3	33.2	1.21	45.2
PI/Si-20	106.3	40.0	1.34	43.5

[a]Measured by ASTM D 1925, E 308.
[b]Measured by TMA at a heating rate of 5.0°C/min. The CTE values were determined within the temperature range, 200 – 250°C.

the TEOS content. On the other hand, the characteristic absorbance bands at 1080 cm^{-1}, which were assigned to the Si-O-Si bond stretching vibration, increased with increasing TEOS content in the series of composite films [26,27]. The observation of a characteristic band of the Si-O-Si vibration revealed silica networks in the PI matrix film, showing that PI/silica composite films with different TEOS compositions had been prepared. In addition, the intensities of the bands at approximately 2923 and 2850 cm^{-1} increased with increasing TEOS content. Therefore, these observations suggest that the changes in intensity of the bands at 1785 and 1695 cm^{-1} could be attributed to the formation of products associated with TEOS and carboxylic acid, even though the C=O stretching vibrational bands originating from ester derivatives of the reaction products could not be resolved [25]. These results are consistent with those of the TGA thermograms. Furthermore, the characteristic absorption bands of PAA at 1665 cm^{-1} and 1540 cm^{-1}, corresponding to amide-I and amide-II, [28] respectively, were not detected in the pure PI film and PI/silica composite films, indicating that the thermal imidization reaction was complete.

The CTE values of a series of composite films were measured by TMA. The optical properties including transmittance, yellow indices and haze values of a series of composite films were measured by transmitted UV-visible spectroscopy and colorimetry. Table 2 summarizes the optical properties and CTE values. The in-plane CTE of the PI/silica composite films decreased gradually with increasing TEOS content. The measured CTE values of the PI and composite films decreased in the order, PI < PI/Si-5 < PI/Si-10 < PI/Si-20. The silica networks formed by the sol-gel reaction in the PI matrix are believed to inhibit the mobility of the PI main chains in the composite films. The CTE values of the PI hybrids decreased from 52.0 to 43.5 ppm/°C when the TEOS content was increased from 0 to 20 wt%. Composite films containing 20 wt% TEOS had a CTE of 43.5 ppm/°C, which was 16% lower than that of the pure PI film. On the other hand, the haze values and yellow indices of the PI/silica composite films increased with increasing TEOS composition. The measured haze values and yellow indices of the pure PI and PI/silica composite films increased in the order of PI < PI/Si-5 < PI/Si-10 < PI/Si-20. Figure 4(A) shows that the PI film and all PI/silica composite films were obviously transparent. On the other hand, the transmittance of the composite films decreased slightly with increasing TEOS content. The PI/silica composite films were prepared using the thermal imidization process. All PI/silica composite films were only slightly colored, suggesting good transparency, even up to a TEOS content of 20 wt%.

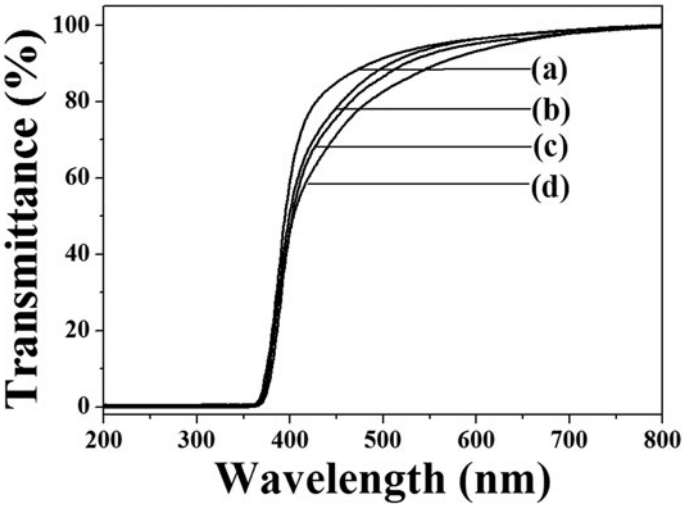


Figure 4. UV transmittance spectra of the polyimide and polyimide/silica composite films with various compositions of TEOS: (a) PI, (b) PI/Si-5, (c) PI/Si-10, and (d) PI/Si-20.

Conclusions

A series of PI/silica composite films, ca. 100 μm in thickness, were synthesized using a thermal imidization process with poly(amic acid) (PAA) solutions prepared using 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2'-bis(trifluoromethyl)benzidine (TFMB) and 3,5-diaminobenzoic acid (DABA), as an interaction moiety, with silica and various amounts of tetraethyl orthosilicate (TEOS) in *N*,*N*-dimethylacetamide (DMAc). PAA was synthesized at reasonably high molecular weight, and homogeneous PAA/silica composite solutions were prepared. Good quality, free standing, transparent PI/silica composite films were obtained by the thermal imidization of mixtures of PAA and different amounts of TEOS. The transparent PI/silica composite films showed no glass transition over the temperature range 25–300°C and had a high decomposition temperature, suggesting high thermal stability. The relationship between the amount of TEOS in the composite films, and the haze values, yellow indices and in-plane coefficients of thermal expansion (CTE) were examined. The haze values and yellow indices increased in the order, PI < PI/Si-5 < PI/Si-10 < PI/Si-20. On the other hand, the CTE decreased with increasing TEOS amount in the composite films, suggesting that silica contributes to the optical and thermo-mechanical properties of the PI/silica composite films. Optically transparent PI/silica composite films were obtained up to a TEOS content of 20 wt%. These findings suggest that these PI/silica composite films are good candidate materials for applications to flexible electronic substrates.

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