

Synthesis and Properties of Low-Color Polyimide/Silica Hybrid Films

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Received 11 August 2006; accepted 16 October 2006

DOI 10.1002/app.25651

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of polyimide precursors, poly(amic acid)s, containing propyltrimethoxysilane at two chain ends were prepared from 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (I) with six commercially available dianhydrides, followed by end-capping with 3-aminopropyltrimethoxysilane (APrTMOS). A new class of fluorine-containing polyimide/silica composite films (III) with chemical bonds between the fluorinated polyimide backbone and the silica network has been synthesized from the APrTMOS-terminated precursors with tetramethoxysilane via the sol-gel process and thermal cyclodehydration. The resultant hybrid films were light-colored, flexible, and tough. They had high levels of thermal stability associated with high glass-transition temperatures ($>251^{\circ}\text{C}$), 10% weight-loss temperatures in

excess of 527°C , and char yields at 800°C in nitrogen higher than 60%. For a comparative study, the analogous nonfluorinated polyimide/silica hybrid films (III'), based on 4,4'-bis(4-aminophenoxy)biphenyl (I'), and the neat fluorinated polyimide films (IV), based on diamine I, were also synthesized and characterized. The hybrid films of the fluorinated series III showed a higher transparency and less color intensity when compared with the nonfluorinated III' analogs. They also revealed a lower refraction index and birefringence than pure polyimides (IV). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4046–4052, 2007

Key words: polyimide/silica hybrid; nanocomposites; organic/inorganic hybrid films

INTRODUCTION

Aromatic polyimides have been widely used as packaging material and dielectric layers for the electronics and microelectronics applications as a result of their excellent thermal and mechanical properties, good chemical resistance, high dimensional stability, and good dielectric properties.^{1,2} Among these features, the low dielectric constant is a critical factor in minimizing power dissipation and delay of signal transmission in interlayer dielectrics,³ thus allowing smaller and higher electronic devices. Therefore, a considerable amount of research has been carried out to lower the dielectric constant of polyimides through various methods such as fluorination,^{4–8} incorporation of adamantane or diamantane groups,^{9–11} polyimide nanofoam,^{12,13} and organic-inorganic hybrid nanocomposites.^{14–20}

Fluorinated aromatic polyimides, especially trifluoromethyl (CF_3)-containing polyimides,^{5–8} have been identified as one of the polyimide materials having attractive characteristics of excellent solubility, low dielectric constants, and high optical transparency. The lowered dielectric constants might be partly attributable to less-efficient chain packing and increased free volume caused by the CF_3 group. In addition, the low polarizability of C–F bond and the hydrophobic nature of the CF_3 group also contribute to lowering dielectric constant. However, fluorinated polyimides also have some drawbacks such as a lowered glass-transition temperature (T_g) and mechanical property, an increased coefficient of thermal expansion, and a poor adhesive property. To overcome such drawbacks, a new type of fluorine-containing polyimide/silica hybrid material was prepared via a well-established sol-gel process.

In the present study, we aim to prepare fluorinated polyimide/silica hybrid films with a low dielectric constant, light or no color, and good adhesive property. The fluorinated polyimides are composed of a CF_3 -substituted diamine, 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (I), with various commercially available dianhydrides. Our strategy for obtaining the hybrid films is to mix an 3-aminopropyltrimethoxysilane (APrTMOS)-terminated poly(amic acid) precursor and tetramethoxysilane (TMOS), followed

This article is dedicated to the memory of Professor Chin-Ping Yang, who cherished research and publications as his lifetime joys.

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*The first author died on August 17, 2005, at the age of 75.

Contract grant sponsor: National Science Council, Republic of China; contract grant number: NSC 94-2216-E-036-014.

Journal of Applied Polymer Science, Vol. 104, 4046–4052 (2007)
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by a sol-gel reaction involving the hydrolysis and polycondensation reaction of alkoxy silane, sol-casting, and multistep curing. The APrTMOS was used as a coupling agent to provide bonding between the silica network and polyimide phase, and the introduction of chemical bonds between the polyimide and silica was expected to improve their compatibility and further improve their mechanical properties. The thermal, mechanical, and optical properties of the prepared fluorinated polyimide/silica hybrid films were investigated and compared with those of the analogous nonfluorinated polyimide/silica hybrid films and the neat fluorinated polyimide films.

EXPERIMENTAL

Materials

4,4'-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**I**) was prepared from 4,4'-biphenol and 2-chloro-5-nitrobenzotrifluoride synthesized through the aromatic nucleophilic substitution in the presence of potassium carbonate and reduction of the intermediate dinitro compound using hydrazine as the reducing agent and palladium as catalyst. The synthetic details and characterization data have been described in a previous publication.⁷ Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA) (Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (Aldrich) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) (Oxychem), 4,4'-oxydiphthalic dianhydride (ODPA) (Oxychem), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA) (New Japan Chemical), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (Hoechst Celanese) were heated at 250°C *in vacuum* for 3 h before use. *N,N*-Dimethylacetamide (DMAc) was distilled under reduced pressure over calcium hydride. Other reagents including APrTMOS (Aldrich), TMOS (Fluka), and 4,4'-bis(4-aminophenoxy)biphenyl (**I'**; Chriskev) were used as received.

Preparation of the polyimide/silica hybrid films

The synthesis of polyimide/silica hybrid film **IIIa** was described as a typical procedure. A mixture of 0.504 g (1.00 μmol) of diamine **I** and 0.229 g (1.05 μmol) of PMDA was dissolved in 5.7 mL of dried DMAc and was stirred at room temperature for 4 h to obtain a poly(amic acid) (PAA) solution. Then 0.10 μmol of APrTMOS was added to the PAA solution and the stirring of the mixture was continued for 1 h. After which, a calculated quantity of TMOS solution (2.81 μmol of TMOS and 5.62 μmol of H₂O in 0.5 mL of DMAc) was added into the PAA-APrTMOS mixture, and stirring continued at room temperature for 24 h

to carry out the sol-gel reaction. The film was prepared by casting the solution onto flat aluminum foils, or spin coating on glass plates or wafers. After drying at 80°C for 1 h and at 120°C for 30 min, the film was further heated at the rate of 2°C/min to 270°C and held at that temperature for 30 min. The aluminum foil could be removed by soaking in an HCl aqueous solution (1M) to obtain the polyimide/silica hybrid film. The flow-sheet diagram for the preparation of polyimide/silica hybrid films is shown in Figure 1. Other hybrid films were prepared in a similar process.

IR (film) of **IIIa**: 1778 (asymmetric C=O stretch), 1726 (symmetric imide C=O stretch), 1620–1488 (aromatic skeletal vibration), 1375 (C–N stretch), 1255 (C–O stretch), 1095 and 725 (imide ring deformation), 1054 and 456 cm⁻¹ (Si–O–Si stretching and bending).

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Thermogravimetry analysis (TGA) was conducted with a TA Instruments TGA 2050. Experiments were carried out

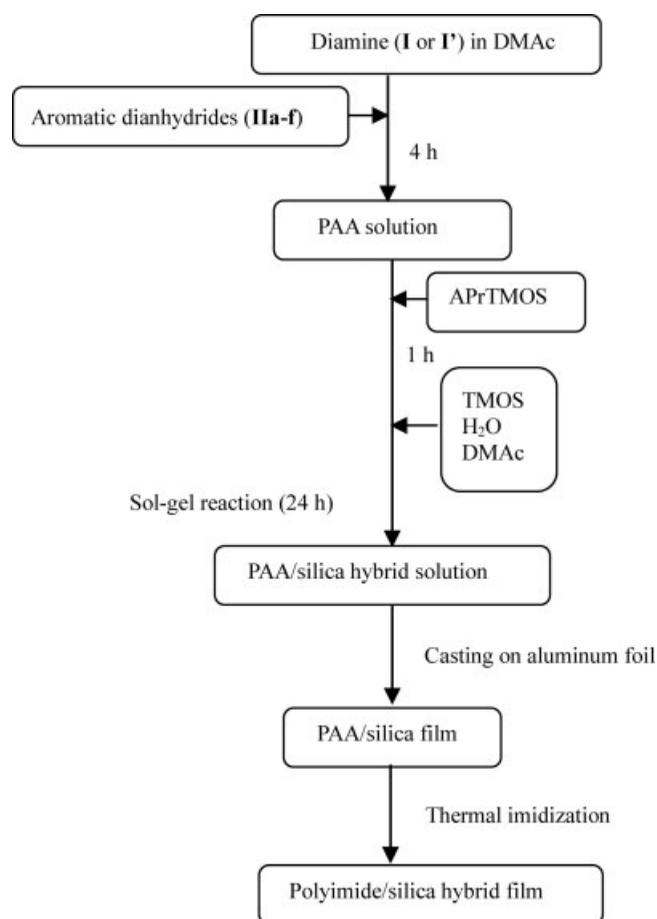


Figure 1 The flow-sheet diagram for the preparation of the polyimide/silica hybrid films.

on 13–15 mg film samples heated in flowing nitrogen or air (90 cm³/min) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) traces were measured on a TA Instruments DSC 2010 at the scan rate of 15°C/min in flowing nitrogen (40 cm³/min). T_g s were read as the midpoint temperature of the heat capacity jump and were taken from the second heating scan after a quick cooling down from 400°C to room temperature. Tensile properties of the films were measured with an Instron model 4400R tensile tester with a 5-kg load cell at a crosshead speed of 5 mm/min on strips ~ 40–60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least three replicates was used. A Metricon model 2100 prism coupler was used to measure the film thickness and refractive indices of the prepared thin films at the wavelength of 633 nm. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The color intensity of the polymers was evaluated by a

GretagMacbeth Color-Eye 3100 colorimeter. Measurements were performed with films, using an observational angle of 10° and a CIE (Commission International de l'Éclairage)-D illuminant. A CIE LAB color difference equation was used.

RESULTS AND DISCUSSION

Preparation of polyimide/silica hybrid films

Because polyimide/silica hybrids were insoluble in organic solvents, the sol-gel reaction was carried out in the DMAc solution of PAA. The polyimides chosen for our studies have structures depicted in Scheme 1. PAA chain and silica network were connected through covalent bonds via the introduction of APrTMOS as the coupling agent. This approach greatly reduced the phase separation between organic and inorganic phases. The polyimide/silica hybrid film was prepared as follows: first, TMOS

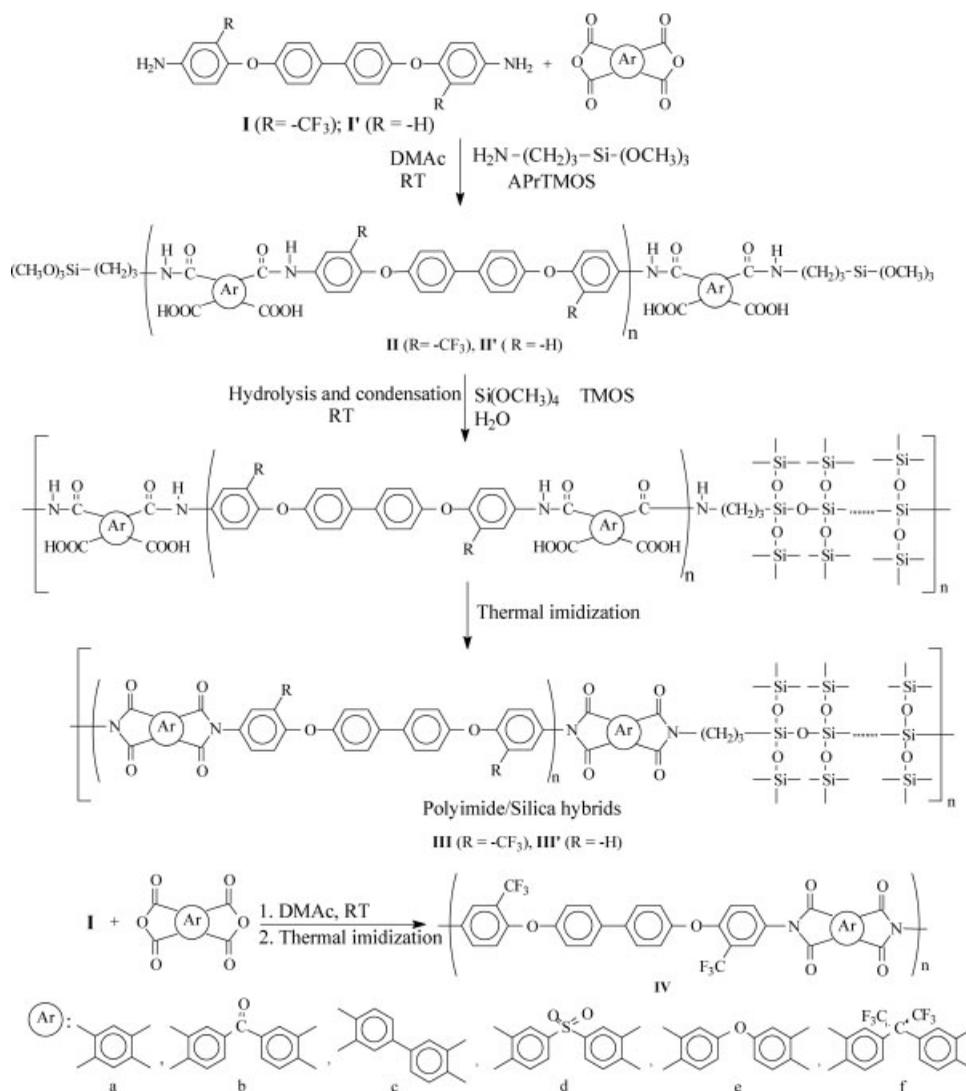


TABLE I
Preparation Recipe for the Polyimide/Silica Materials

Polymer	TMOS ^a (g/mmol)	H ₂ O (mmol)	Silica ^b (wt %)	Ash ^c (wt %)
IIIa	0.46/3.00	6.01	20	17
IIIb	0.52/3.44	6.88	20	11
IIIc	0.51/3.32	6.64	20	13
III'd	0.55/3.59	7.18	20	14
IIIe	0.52/3.39	6.78	20	13
III'f	0.60/3.95	7.89	20	13
III'a	0.37/2.44	4.88	20	20
III'b	0.44/2.87	5.75	20	17
III'c	0.42/2.76	5.51	20	19
III'd	0.46/3.02	6.05	20	20
III'e	0.43/2.82	5.65	20	20
III'f	0.51/3.38	6.76	20	17

^a The quantity of TMOS was based on a calculated 20 wt % silica content in the hybrid materials.

^b Calculated silica content in the hybrid film.

^c Residual ash when heated to 800°C at a heating rate of 20°C/min in air by TGA.

was hydrolyzed by water in DMAc solution of PAA, and PAA is regarded as the acid catalyst. The reaction was kept for 24 h so that the hydrolysis could react completely. Second, the resulting homogeneous mixture was cast onto an aluminum substrate to prepare the PAA/silica hybrid film, and finally the polyimide/silica hybrid film was obtained by sequential heating to 270°C. After removal of the aluminum substrate by the treatment with an HCl aqueous solution, a transparent and flexible hybrid film was attained.

Table I summarizes the preparation recipe of the polyimide/silica hybrid films. The silica (SiO₂) content in the table denotes the value calculated by assuming that the sol-gel reaction proceeded completely. All the III series polyimide/silica hybrid films were obtained as transparent and flexible hybrid films with light yellow or no color. In most cases, the residual ash from TGA analysis is lower than the calculated silica content. This result can be explained by the fact that PAA is a weak acid to the alkoxy silane system in comparison to the strong, such as HCl, and some of unreacted TMOS were evaporated from the reaction system during the film casting.¹⁶

FTIR spectroscopy was used to confirm the structural features of the hybrid films. Figure 2 shows the typical FTIR spectra of polyimide/silica hybrid thin films of IIIa and III'a. The characteristic absorption bands of imide group are observed near 725, 1375, 1726, and 1778 cm⁻¹. The absorption bands at 454 and 1075 cm⁻¹ can be attributable to Si—O—Si bond formation.

Refractive indices and dielectric constants

The refractive indices including the transverse electric refractive indices (n_{TE}) and transverse magnetic refractive indices (n_{TM}) of the fluorine-containing

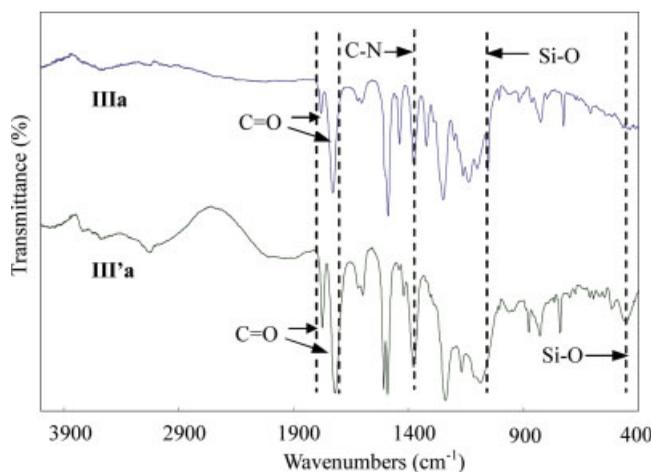


Figure 2 FTIR spectra of polyimide/silica hybrid thin films of IIIa and III'a. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hybrid films (III) and pure polyimide films (IV) at 633 nm are listed in Table II. The thickness of the polyimide/silica hybrid (III series) thin films on silicon wafer is in the range of 2.17–3.30 μm. The average refractive indices are in the range of 1.5562–1.5944 and 1.6020–1.6509 for the III and IV series films, respectively. A dielectric constant (ϵ) of a material at optical frequencies can be estimated from the refractive index n according to Maxwell's equation, $\epsilon = n^2$. The n_{AV} values of these polymer films can be translated into dielectric constants ranging from 2.42 to 2.73. Incorporation of silica results in a decrease in the refractive index and the estimated dielectric constant. In addition, the lower n and ϵ values of the 6FDA-produced films (III'f and IV'f) than the other ones in the same series can be attributed to

TABLE II
Refractive Indices and Birefringence of the Pure Polyimides and the Polyimide/Silica Hybrid Films

Polymer	Thickness (μm)	633 nm				ϵ^c
		n_{TE}	n_{TM}	N_{AV}^a	Δn^b	
IIIa	2.37	1.5904	1.5766	1.5858	0.0138	2.51
IIIb	2.57	1.5841	1.5759	1.5814	0.0082	2.50
IIIc	3.30	1.5772	1.5667	1.5737	0.0105	2.48
III'd	2.32	1.5977	1.5878	1.5944	0.0099	2.54
IIIe	2.17	1.5958	1.5893	1.5936	0.0065	2.54
III'f	3.26	1.5584	1.5517	1.5562	0.0067	2.42
IVa	3.45	1.6387	1.6021	1.6265	0.0366	2.65
IVb	4.15	1.6464	1.6210	1.6379	0.0254	2.68
IVc	4.02	1.6619	1.6290	1.6509	0.0329	2.73
IV'd	2.85	1.6517	1.6246	1.6427	0.0271	2.70
IVe	2.59	1.6351	1.6229	1.6310	0.0122	2.66
IV'f	1.71	1.6076	1.5909	1.6020	0.0167	2.57

^a Average refractive index: $n_{AV} = (2n_{TE} + n_{TM})/3$.

^b Birefringence: $\Delta n = n_{TE} - n_{TM}$.

^c Optically estimated dielectric constant: $\epsilon = n_{AV}^2$.

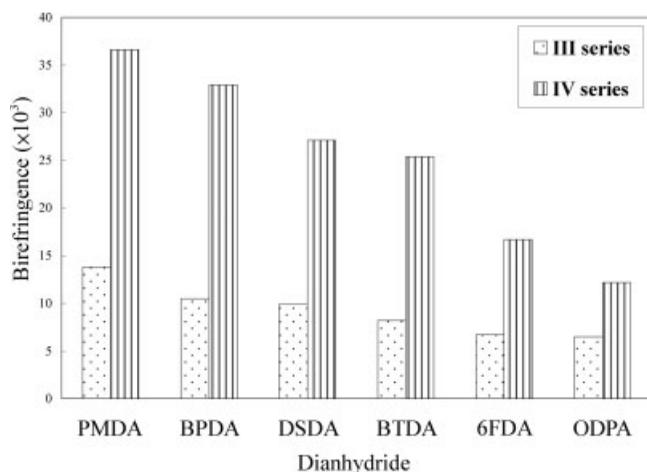


Figure 3 Comparison of the birefringence of polyimide/silica hybrid thin films **IIIa–f** and polyimide thin films **IVa–f** at 633 nm.

the low electronic polarizability and a large molecular volume of the hexafluoroisopropylidene group. Birefringence (Δn) of polyimides **IVa–f** and polyimide/silica hybrids **IIIa–f** are listed in Table II as well. Lower values of Δn were observed in **IIIa–f** compared with **IVa–f** since silica is a low birefringence material. The birefringence corresponds to the optical anisotropy of the thin films and thus depends on the structure of polymer backbones. For example, the polymer films derived from PMDA and BPDA showed higher Δn than those from 6FDA and ODPA. This could be explained by the fact that the polyimides based on PMDA and BPDA have a more planar rigid backbone than those derived from 6FDA and ODPA that enhances the ordering along the substrate, increasing the anisotropy and birefringence. Figure 3 compares the birefringence between **III** (polyimide/silica hybrids) and **IV** (pure polyimides). For the cases of the hybrid thin films of **IIIe** and **IIIf**, the decrease of birefringence due to silica hybridizing is not as marked as the others in the same series because the birefringence of the neat polyimides derived from 6FDA and ODPA is small.

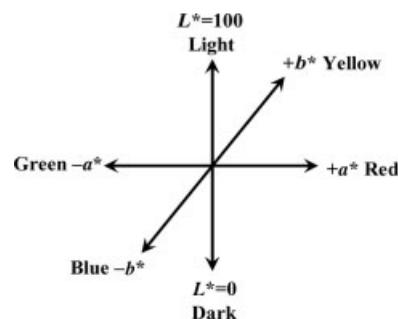
Color intensity and optical transparency

The color intensities of the polyimide/silica hybrid films were evaluated from the yellowness (b^*) or redness (a^*) indices observed by a colorimeter. The color coordinates of the hybrid films are given in Table III. It could be found all the **III** series films revealed a lower b^* value compared with the **III'** series analogs without CF_3 substituents. 6FDA and ODPA produced essentially colorless polyimide/silica hybrid films in contrast to other dianhydrides, and the result can be explained from the decreased intermolecular interactions. The transmission UV–vis spectra were measured for all the hybrid thin films. Figure 4

TABLE III
Color Coordinates and Cutoff Wavelength (λ_0) from UV–Vis Spectra of Polyimides and the Polyimide/Silica Hybrid Films

Polymer	Film thickness (μm)	Color coordinates ^a			λ_0 (nm)
		b^*	a^*	L^*	
Paper		1.1	−0.5	94.7	
IIIa	21	68.0	−9.2	83.5	374
IIIb	41	55.8	−12.4	87.0	386
IIIc	33	20.7	−7.4	87.9	362
IIId	43	32.5	−10.7	89.7	374
IIIe	33	15.9	−5.0	90.5	362
IIIf	41	9.8	−3.3	92.2	362
III'a	47	73.7	−12.7	76.8	398
III'b	54	69.9	−7.0	80.2	400
III'c	46	65.6	−6.9	83.4	398
III'd	52	68.5	−3.4	83.1	397
III'e	41	40.5	−9.0	87.7	366
III'f	43	29.0	−6.9	89.5	364

^a The CIE $L^*a^*b^*$ color scale:



shows the UV–vis spectra of the hybrid films, and the cutoff wavelength (absorption edge, λ_0) values from these spectra are listed in Table III. Almost all the hybrid films had λ_0 shorter than 400 nm and showed a high optical transparency ($> 80\%$ at 500 nm). In accordance with the results obtained from colorimeter, all the **III** series polyimide/silica hybrid films showed a shorter λ_0 than their respective nonfluorinated polyimide/silica hybrids (**III'**). The bulky and electron-withdrawing CF_3 group in

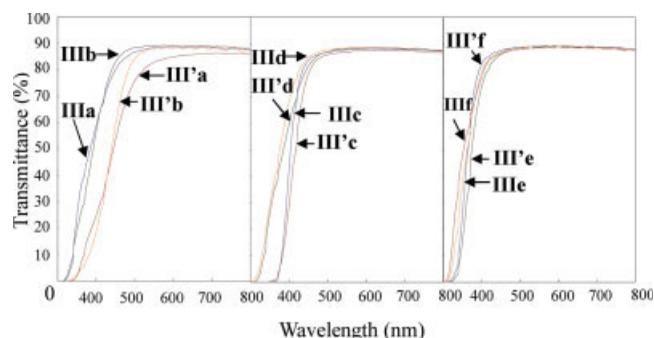


Figure 4 UV–vis spectra of polyimide/silica hybrid thin films (2–4 μm thick) on the glass.

TABLE IV
Tensile Properties of Polyimide/Silica Films^a

Polymer	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
IIIa	106	6	3.1
IIIb	114	7	2.9
IIIc	123	9	2.9
IIId	88	3	3.2
IIIe	98	5	2.8
III'f	94	5	3.0
III'a	95	6	3.0
III'b	103	8	2.2
III'c	120	14	2.6
III'd	118	8	2.5
III'e	120	15	2.1
III'f	90	4	2.8
IVa	97	26	1.8
IVb	108	11	2.0
IVc	119	33	1.9
IVd	98	9	2.1
IVe	114	38	1.8
IVf	101	10	2.1

the diamine components was presumably effective in decreasing charge-transfer complexes between polymer chains through steric hindrance and the inductive effect.

Mechanical properties

The tensile properties for all the polyimide films are summarized in Table IV. Polyimide/silica hybrid films (III and III') had strengths at break of 88–123 MPa, elongations to break of 3–15%, and initial moduli of 2.1–3.1 GPa. The pure polyimide films (IV) had strengths at break of 97–114 MPa, elongations to break of 9–38%, and initial moduli of 1.8–2.1 GPa. All these three series polyimide films exhibited high tensile strengths, especially for those derived from BPDA. In comparison with the pure polyimides, samples containing silica have higher initial modulus, but lower elongation to break. This can be attributed to the fact that the polymer/silica hybrid materials are organic and inorganic crosslinked networks. The aforementioned results showed that the polyimide/silica hybrid films (III and III') possess good mechanical properties such as high tensile strength and modulus because of the introduction of chemical bonding between the polyimide chain and the silica network.

Thermal properties

DSC and TGA were used to evaluate the thermal properties of the polyimide/silica hybrid films. The results are presented in Table V. Most of the III and III' series hybrid films revealed a clear T_g in the range of 251–282 and 258–294°C, respectively, by DSC. The hybrid films of IIIa, III'a, and III'c did not

show discernible transitions on their DSC curves possibly due to the rigid nature of the polymer matrix. Slightly lower T_g values for the III series in comparison with the III' series might be a result of reduced chain–chain interaction and increased free volume due to the pendant CF_3 groups. The T_g value of these polymers is dependent on the structure of the dianhydride component, and decreases with the increase in the flexibility of the polymer backbones. For example, the IIIe and III'e obtained from ODPA showed the lower T_g s because of the presence of a flexible ether linkage between the phthalimide units. In general, the T_g of polymer/silica hybrids should be notably increased since the motion of polymer chain is restricted by the formation of a silica network. In our study, the III series polyimide/silica hybrids only showed slightly higher T_g s than the pure IV series polyimides. One possible reason may be the reduction of T_g due to plasticizing effect by the incompletely crosslinked silica segments. The flexible segment (methylene groups) in the coupling agent (APrTMOS) also limits the significant increase in T_g .

The temperatures for 10% weight loss (T_{10}) and char yields were determined from original TGA thermograms and are also tabulated in Table V. In general, these polyimide/silica hybrid films had fairly high thermal stability; the T_{10} values of polyimide/silica hybrid films (IIIa–f and III'a–f) were all higher than 500°C and stayed within 527–615°C in nitrogen and within 535–597°C in air atmosphere. Almost all

TABLE V
Thermal Properties of Polyimide/Silica Hybrid Films

Polymer	T_g (°C) ^a	T_{10} (°C) ^b		Char yield (%) ^c
		In N ₂	In Air	
IIIa	–	580	548	61
IIIb	267	582	547	63
IIIc	278	586	560	68
IIId	282	527	544	63
IIIe	251	581	572	61
III'f	277	545	535	58
III'a	–	603	593	72
III'b	285	601	584	68
III'c	–	615	597	74
III'd	294	554	566	67
III'e	258	601	591	68
III'f	288	560	550	66
IVa	313	600	573	55
IVb	260	592	567	55
IVc	276	603	581	60
IVd	279	540	554	55
IVe	247	601	583	54
IVf	274	599	540	52

^a Baseline shift in the second heating DSC traces, with a heating rate of 15°C/min.

^b Temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20°C/min.

^c Residual weight (%) when heated to 800°C.

of them left more than 60% char yield at 800°C in nitrogen. The increased weight residue of the hybrid films compared with the pure polyimides is a result of the incorporation of thermally stable silica. However, when compared with pure polyimides (IV), the III hybrid films showed a lower T_{10} value. The weight loss occurred at lower temperatures for the films containing silica, possibly because of the further condensation of silica at elevated temperatures and/or the early decomposition of the less-stable aliphatic segment in the coupling agent.

CONCLUSIONS

A novel series of fluorinated hybrid polyimide/silica composites (III) were prepared by the sol-gel reaction and characterized. They were synthesized from diamine (I) with dianhydride to get viscous poly(amic acid)s, and then the hybrid composite films were obtained by the hydrolysis and polycondensation of APrTMOS and TMOS in DMAc, followed by solution casting and multistep heating. The non-fluorinated polyimide/silica hybrids (the III' series) and the pure polyimides (the IV series) without silica were also prepared, and their characteristics including optical, mechanical, and thermal properties were compared with the IV series. The fluorinated III series films generally showed a higher optical transparency and less color intensity. They exhibited a lower refractive index and birefringence than pure IV series polyimides. These hybrid films also showed excellent thermal stability and good tensile

properties. Thus, they are promising candidates for microelectronics and optoelectronics applications.

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