

Effect of Organosilica Isomers on the Interfacial Interaction in Polyimide/Aromatic Organosilica Hybrids

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ABSTRACT: We report the effect of organosilica precursor isomers on the interfacial interaction between polyimide and organosilica in polyimide/organosilica hybrid composite films. Poly(4,4'-oxydianiline biphenyltetracarboxamic acid) (BPDA-ODA PAA) was used as the polyimide precursor, while the organosilica was made using o-substituted, m-substituted, and p-substituted phenyl organosilica precursor isomers. For the preparation of precursor hybrid films, BPDA-ODA PAA and organosilica precursors were mixed and then the organosilica precursors were converted to corresponding organosilica via sol-gel process. Finally, these precursor films were converted to corresponding polyimide/organosilica hybrid films by the thermal imidization of BPDA-ODA PAA, which results in poly(4,4'-oxydianiline biphenyltetracarboximide) (BPDA-ODA PI). The

polyimide/organosilica hybrid films were characterized using three distinctive nuclear magnetic resonance spectroscopies (¹H NMR, ¹³C-CPMAS-NMR, and ²⁹Si-MAS-NMR), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), and peel strength measurement. We found that the m-substituted phenyl organosilica shows poorer interfacial interaction with BPDA-ODA PI than do the o- or p-substituted phenyl organosilicas. It was observed, however, that the peel strength of the hybrid films against an aluminum substrate increased with increasing contents of organosilicas, regardless of the nature of the organosilica isomers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2507–2513, 2007

Key words: organic/inorganic hybrid; organosilica; polyimide; interfacial interaction; small-angle X-ray scattering

INTRODUCTION

Organic/inorganic hybrid composites have attracted great interest because of their expected benefit in properties by combining the strong and useful characteristics of organic and inorganic materials.¹ Recently, these hybrid materials have found many applications in areas such as abrasive resistant coatings,² contact lenses,³ optically active films,⁴ and membranes.⁵ In the hybrid composites the inorganic components are made normally by the sol-gel process consisting of a two-step reaction, viz. hydrolysis of metal alkoxides to produce corresponding hydroxyl groups, followed by the polycondensation of the hydroxyl groups and residual alkoxy groups to form a three-dimensional network. However, organic components, whether small molecules⁶ or polymers,^{2–5} are just embedded in the hybrid composites or are further subjected to

individual reaction processes depending on the types of materials or functional groups.

For the polymer based organic/inorganic hybrid composites, polyimides have been applied, particularly, as a matrix polymer for aerospace and microelectronics applications because of their excellent electrical, thermal, and physical (mechanical) properties. As an inorganic component, silica has been widely used in the hybrid composites for achieving specific properties that are required for various applications.^{7–12} In addition, a keen interest has recently been drawn to polysilsesquioxane (PSSQ), which has similar structure to silica but possesses high free volume, for the application of low-k dielectrics (insulators) in microelectronic devices^{13,14} and novel reinforcing elements for hybrid composites.^{15,16} This is due to its extremely low dielectric constant and high thermal stability. In this regard, the polyimide/silica or polyimide/PSSQ hybrid composites have been widely reported,^{17–23} but the interfacial interaction between polyimide and silica or PSSQ has not been well researched so far.

In this work, we have attempted to apply organosilica as an inorganic component because of its resemblance to PSSQ. To study the interfacial interaction between polyimide and organosilica, three types of organosilica precursor isomers were synthesized: o-substituted phenyl organosilica, m-substituted phe-

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nyl organosilica, and p-substituted phenyl organosilica. These isomers give us the influence of chemical configuration on the interfacial interaction between polyimide and organosilica, because the chemical composition is the same for all isomers. As the polyimide, poly(4,4'-oxydianiline biphenyltetracarboximide) (BPDA-ODA PI) was chosen because of its versatile applications in microelectronic devices.^{24,25} The polyimide/organosilica hybrid composites were prepared from their corresponding precursor hybrid films through the sol-gel reaction of organosilica precursors and the thermal imidization of poly(4,4'-oxydianiline biphenyltetracarboxamic acid) (BPDA-ODA PAA). The prepared polyimide/organosilica hybrid films were characterized using nuclear magnetic resonance spectroscopies, X-ray diffraction and scattering, and peel strength measurement.

EXPERIMENTAL

Materials

1,2-Phenylene diamine (99.5%), 1,3-phenylene diamine (99+%), 1,4-phenylene diamine (99.5+%), 3-(triethoxysilyl)propylisocyanate (95+%), *N,N*-dimethylacetamide (DMAc, HPLC grade), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 97%), and 4,4'-oxydianiline (ODA, 97%) were purchased from Aldrich (St. Louis, MO) and used as received.

Synthesis of organosilica precursors (isomers)

o-Substituted phenyl organosilica precursor (op)

1,2-Phenylene diamine (0.01 mol, 1.11 g) and 3-(triethoxysilyl)propylisocyanate (0.02 mol, 5 mL) were refluxed in tetrahydrofuran (THF) (20 mL) at 70°C for a day under nitrogen environment. The solvent (THF) was removed by using a rotary evaporator. The resulting solid (yellow wax) was washed twice with 100 mL of *n*-hexane. The product, **op**, was dried in a vacuum oven at 60°C for a day (see the chemical structure of **op** in Fig. 1). The yield from the synthesis was 74%. The characterization details are as follows. ¹H NMR (300 MHz, CDCl₃, 30°C): δ (ppm) = 1.22 (t, *J* = 6.3, 18H, OCH₂CH), 3.82 (q, *J* = 7.3, 12H, OCH), 5.52 (m, *J* = 5.8, 4H, NH), 7.21–7.63 (m, 4H, Ph–H), 3.21 (q, *J* = 7.5, 4H, NCH), 1.6 (m, *J* = 7.0, 4H, NCH₂CH), 0.61 (t, *J* = 5.1, 4H, SiCH). ¹³C-CP MAS-NMR (400 MHz): 8.5 ppm (C1'), 18.6 ppm (C2'), 43.4 ppm (C3'), 157.6 ppm (C4'), 58.3 ppm (C5'), 24.4 ppm (C6'), 137.2 ppm (C2, C3), 129.1/127.0 ppm (C1, C4), 123.4 ppm (C5, C6).

m-Substituted phenyl organosilica precursor (mp)

1,3-Phenylene diamine (0.01 mol, 1.11 g) and 3-(triethoxysilyl)propylisocyanate (0.02 mol, 5 mL) were

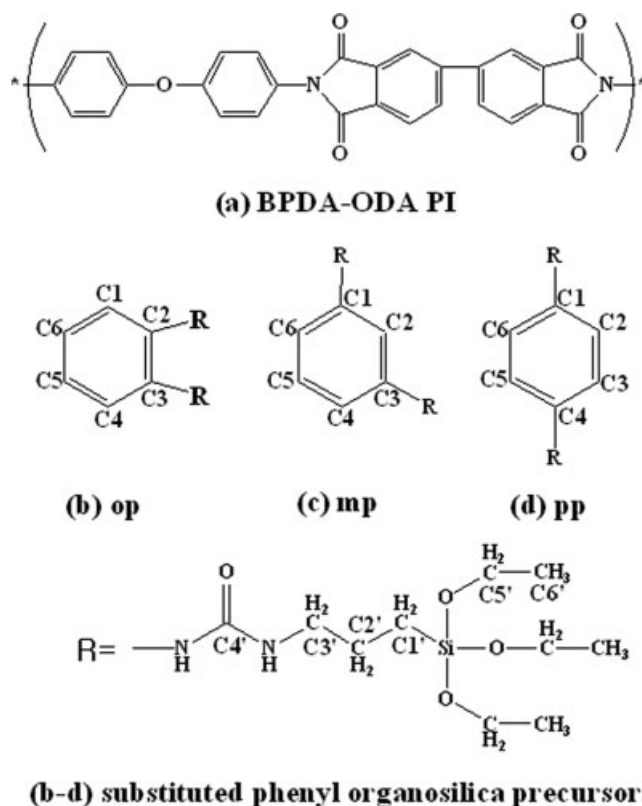


Figure 1 Chemical structure of BPDA-ODA PI (a) and organosilica precursors (b–d): o-substituted (b), m-substituted (c), and p-substituted (d).

refluxed in THF (20 mL) at 70°C for a day under nitrogen. Like the o-substituted product, the solvent was removed by using rotary evaporator. The resulting solid (dark brown powder) was washed twice with 100 mL of *n*-hexane. The product, **mp**, was dried in a vacuum oven at 60°C for a day. The yield from the synthesis was 47% (see the chemical structure of **mp** in Fig. 1). The characterization details are as follows. ¹H NMR (300 MHz, CDCl₃, 30°C): δ (ppm) = 1.14 (t, *J* = 6.3, 18H, OCH₂CH), 3.77 (q, *J* = 7.3, 12H, OCH), 6.23–6.38 (m, *J* = 5.1, 4H, NH), 7.04–7.63 (m, 4H, Ph–H), 3.12 (q, *J* = 7.8, 4H, NCH), 1.57 (m, *J* = 7.1, 4H, NCH₂CH), 0.55 (t, *J* = 5.5, 4H, SiCH). ¹³C-MAS-NMR (400MHz): 8.5 ppm (C1'), 18.6 ppm (C2'), 43.4 ppm (C3'), 157.6 ppm (C4'), 58.3 ppm (C5'), 24.4 ppm (C6'), 138.2 ppm (C1, C3), 131.1/129.7 ppm (C2), 121.2 ppm (C4, C6), 118.1 ppm (C5).

p-Substituted phenyl organosilica precursor (pp)

1,4-Phenylene diamine (0.01 mol, 1.11 g) and 3-(triethoxysilyl)propylisocyanate (0.02 mol, 5 mL) were stirred in THF (20 mL) at room temperature for an hour under nitrogen. Like the o- and m-substituted products, the solvent was removed by using rotary evaporator. The resulting solid (pale pink powder)

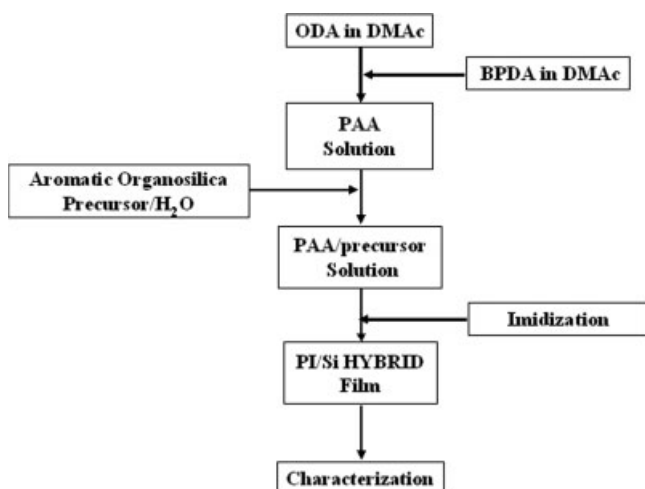


Figure 2 Schematic diagram for the preparation process of BPDA-ODA PI/organosilica hybrid composite films.

was washed twice with 100 mL of *n*-hexane. The product, **pp**, was dried in a vacuum oven at 60°C for a day. The yield was 81% (see the chemical structure of **pp** in Fig. 1). The characterization details are as follows. ¹H NMR (300 MHz, CDCl₃, 30°C): δ (ppm) = 1.19 (t, *J* = 6.1, 18H, OCH₂CH), 3.80 (q, *J* = 7.2, 12H, OCH), 6.4 (m, *J* = 5.7, 4H, NH), 7.52–7.61 (m, 4H, Ph–H), 3.1 (q, *J* = 7.2, 4H, NCH), 1.59 (m, *J* = 6.9, 4H, NCH₂CH), 0.58 (t, *J* = 5.4, 4H, SiCH). ¹³C-MAS-NMR (400MHz): 8.5 ppm (C1'), 18.6 ppm (C2'), 43.4 ppm (C3'), 157.6 ppm (C4'), 58.3 ppm (C5'), 24.4 ppm (C6'), 134.7 ppm (C1, C4), 124.4 ppm (C2, C3, C5, C6).

Preparation of polyimide/organosilica hybrid films

First, ODA was dissolved in DMAc by stirring for 2 h in a three-necked round-bottomed flask under nitrogen environment, and then BPDA was added to the ODA-dissolved DMAc solution. This polymerization reaction was carried out for 12 h at room temperature, leading to a BPDA-ODA PAA solution. To this poly(amic acid) solution, corresponding organosilica precursors were added and stirred for 1 h to obtain a homogeneous solution. Next, deionized water was dropped into the poly(amic acid)/organosilica precursor solutions and stirred for 12 h to complete the sol-gel reaction. The mixture solutions, after the sol-gel reaction, were spin-coated onto a glass slide, and soft-baked at 80°C for 3 h. The solid concentration was fixed as 10 wt % for all precursor solutions. These hybrid softbaked films were thermally imidized by a stepwise imidization process under nitrogen for 1 h at 130, 180, and 250°C. Figure 2 summarizes the whole process for preparing hybrid films. Table I shows the monomer amount and corresponding sample names used for the hybrid films.

Measurements

¹H NMR spectra were recorded using an NMR spectrometer (GEMINI 2000, 300 MHz, Varian). ¹³C-CP MAS and ²⁹Si-MAS-NMR spectra were obtained using an NMR spectrometer (DSX, 400 MHz, Bruker Analytische GmbH). Wide-angle X-ray diffraction (WAXD) patterns were measured using an X-ray diffractometer (Rigaku Corp., Cu Kα, λ = 1.5418 Å), while small-angle X-ray scattering (SAXS) patterns were measured using synchrotron X-ray source of Pohang Accelerator Laboratory (PAL, South Korea): Co Kα (λ = 1.608 Å) radiation with an energy range of 4–16 keV (energy resolution (ΔE/E) = 5 × 10⁻⁴, photon flux = 10¹⁰–10¹¹ ph/s, beam size = 1 mm²). The SAXS scan range was fixed as 0.0012 nm⁻¹ < *q* < 0.3316 nm⁻¹. Fourier transform infrared (FTIR) spectra were obtained using a spectrometer (React IRTM 1000, Applied System, ASi). Refractive indices were recorded using a variable angle spectroscopic ellipsometry (VESA, J.A. Woollam Co.) which was equipped with a He-Ne laser (wavelength = 630 nm). Using the Maxwell relation, ε = *n*², where ε and *n* are dielectric constant and refractive index, respectively. The dielectric constant of hybrid films was calculated from the refractive index measured by the ellipsometer.²⁶ The density of hybrid films was measured at 25°C using a flotation method of increasing concentrations in aqueous solutions of sodium iodide (NaI).²⁷ The adhesion property of the hybrid films against an Al substrate (2 cm × 2 cm) was measured according to ASTM D 897-01, which is the 180° peel test of the composites films performed at a peel rate of 1 mm/min using a universal testing machine (Instron 5582).

RESULTS AND DISCUSSION

The FTIR spectra in Figure 3 clearly show the characteristic peaks of both the symmetric and asymmetric C=O stretchings of the imide group at 1710 and 1770 cm⁻¹, respectively, for pristine polyimide and

TABLE I
Monomer Mole Ratio to Prepare the Polyimide and Hybrid Thin Films

Sample	BPDA (mmol)	ODA (mmol)	Precursor (mmol)		
			op	mp	pp
PI	6	6	0	–	–
op5	6	6	0.252	–	–
op10	6	6	0.504	–	–
op20	6	6	1.008	–	–
mp5	6	6	–	0.252	–
mp10	6	6	–	0.504	–
mp20	6	6	–	1.008	–
pp5	6	6	–	–	0.252
pp10	6	6	–	–	0.504
pp20	6	6	–	–	1.008

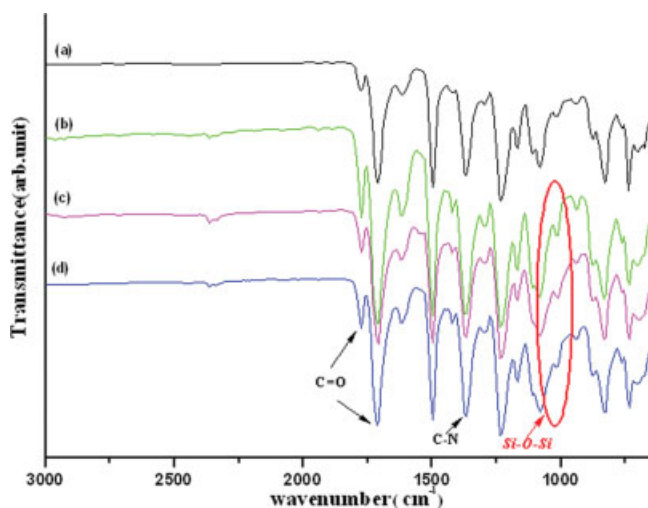


Figure 3 FTIR spectra of pristine BPDA-ODA PI (a) and hybrid films having *o*-substituted phenyl organosilica (b–d): (b) **op5**, (c) **op10**, (d) **op20**. For sample notations, see Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hybrid composite films. This indicates that the thermal imidization was successfully carried out for all films. The bands at 1370 and 737cm^{-1} are attributed to the C–N–C bond and the imide ring deformation, respectively, while the band at 1497cm^{-1} is assigned to the vibration of benzene ring in both PI and organosilica. For the hybrid films the weak band at 1019cm^{-1} corresponds to the vibration of silica networks (Si–O–Si). As shown in the IR spectra, the intensity of this peak gradually increases with increasing organosilica contents, confirming the formation of the three-dimensional Si–O–Si network in the hybrid films.^{28–30} Similar trends were observed for polyimide/organosilica hybrid composite films that have different types of polyimide.³¹

The influence of the organosilica isomers on the formation of the resulting organosilica in the hybrid composite films was measured using ^{29}Si -MAS NMR spectra (see Fig. 4). The peaks at around -59 and -68 ppm indicate the resonance of silicon atoms in positions of $(\equiv\text{SiO})_2\text{Si}(\text{OH})\text{R}$ and $(\equiv\text{SiO})_3\text{SiR}$, which are typically denoted as T^2 and T^3 , respectively.^{32–34} (Note that the presence of T^3 and T^2 resonances/functionalities indicates the existence of covalent bond (linkage) between organic groups and silica group.³⁴) In particular, the intensity ratio of T^2 to T^3 peak is higher for *o*-substituted phenyl organosilica than for other organosilicas. This difference might be due to the relatively higher steric hindrance of *o*-substituted phenyl organosilica than the other organosilicas because the *o*-substituted phenyl structure results in the bond angle of only 60° between the substituted moieties (see R in Fig. 1). Therefore, the higher steric hindrance between R groups could influence on the formation of $(\equiv\text{SiO})_3\text{SiR}$.

As shown in Figure 5, the pristine polyimide (BPDA-ODA PI) is characterized with the major diffraction peak at $2\theta = 17^\circ - 40^\circ$ and the weak peak at $2\theta = 10^\circ - 50^\circ$,³⁵ indicative of a poorly developed crystal structure that is due to the kink effect of oxygen unit of ODA.³⁶ However, the major peak shows a clear split as the organosilica content increases in the hybrid films for all isomers of organosilicas. This result indicates that the organosilica particles in the hybrid films play a role in improving the ordering (crystallization) of BPDA-ODA PI chains during the thermal imidization process. However, the exact mechanism for this improved ordering is unclear at the moment.

In addition to the crystal and ordering characteristics (see Fig. 5), the nanostructure of hybrid composite films can be analyzed from the Lorentz-corrected SAXS patterns (see Fig. 6).^{35,37,38} All films show a broad and single SAXS peak at $0.01 \leq q \leq 0.10\text{ \AA}^{-1}$, which is attributed to the mean long period of BPDA-ODA PI ($\sim 139\text{ \AA}$ for pristine film). Although the size and distribution of organosilica particles formed in the hybrid films were not examined quantitatively, these SAXS results indicate that various sized organosilica particles were made during sol-gel process and they affected the mean long period of the polyimide. For instance, the long period of the hybrid film hav-

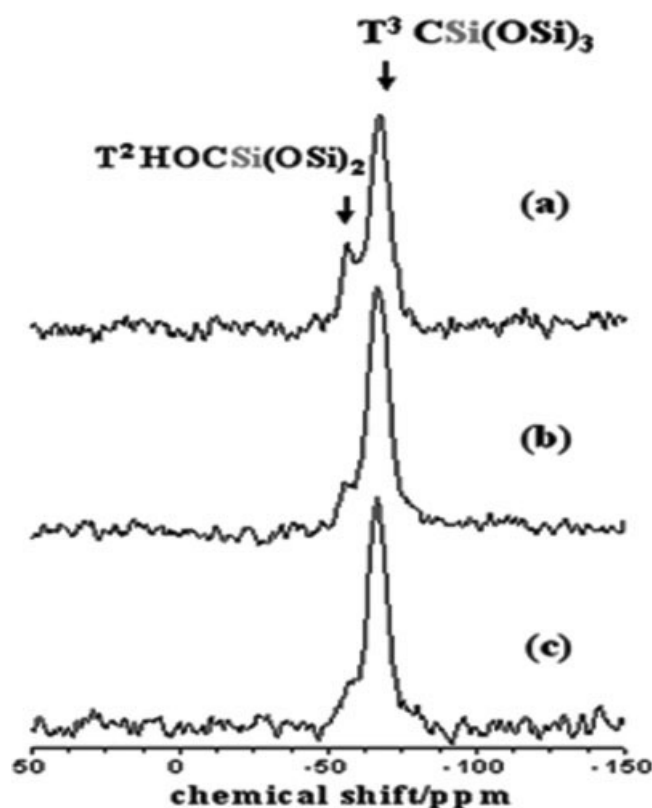


Figure 4 ^{29}Si NMR spectra of hybrid films: (a) **op10**, (b) **mp10**, (c) **pp10**. For sample notations, see Table I.

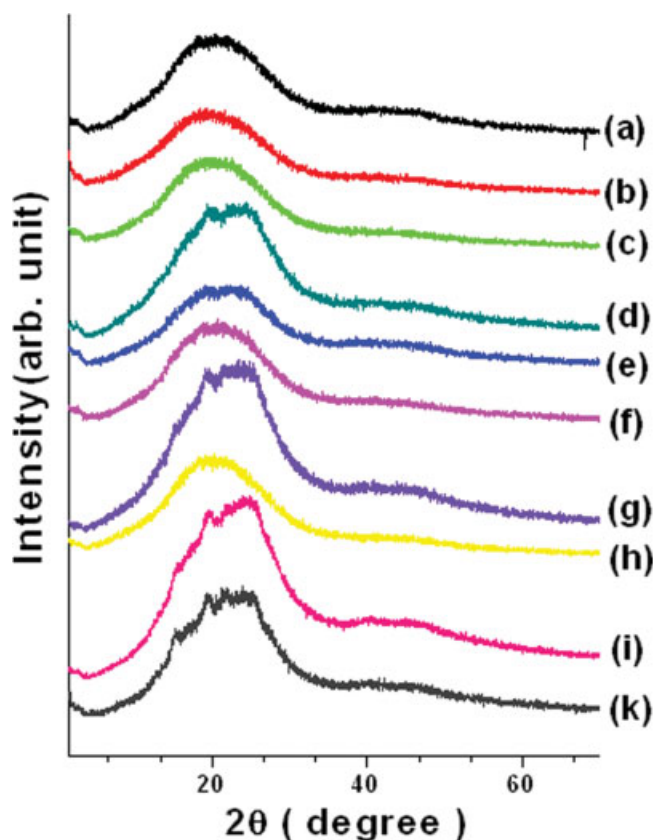


Figure 5 Wide-angle X-ray diffraction patterns of pristine BPDA-ODA PI (a) and hybrid films (b–j): (b) op5, (c) op10, (d) op20, (e) mp5, (f) mp10, (g) mp20, (h) pp5, (i) pp10, (j) pp20. For sample notations, see Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing m-substituted phenyl organosilica is larger up to 10 wt % of organosilica content than that of the pristine polyimide film, whereas the long period of the hybrid films containing o-substituted or p-substituted phenyl organosilicas is smaller than that of the pristine polyimide film. This indicates that the m-substituted phenyl organosilica plays a critical role in increasing the long period of polyimide. However, above this content of organosilica, the long period decreased, irrespective of the isomer types.

Basically, the increased long period can be attributed to the increased size of crystal or phase domains. Therefore, the m-substituted phenyl organosilica is considered to make bigger domains in the BPDA-ODA PI phases of hybrid film when compared with o-substituted or p-substituted phenyl organosilica. This indicates that m-substituted phenyl organosilica has lower interfacial interaction (less compatible or less miscible) with the BPDA-ODA PI than do other organosilicas, leading to the formation of larger organosilica nanoparticles ($> \sim 35$ nm)³⁹ than for o-substituted or p-substituted phenyl organosilica. In this regard, although the exact effects of the organosilica contents are not clearly

understood, it is of no doubt that the m-substituted phenyl organosilica exhibits different, possibly worse, interaction with BPDA-ODA PI, than does o- or p-substituted phenyl organosilica. Kim et al.³⁹ reported that for the BPDA-PDA/silica hybrid films the peak corresponding to the mean long period of BPDA-PDA PI was weakened with increasing loading of tetraethoxysilane, which is a precursor of silica, because of the interfacial interaction of silica and BPDA-PDA PI. Considering the previous³⁹ result of BPDA-PDA PI/silica hybrid films, the present result for BPDA-ODA PI/organosilica hybrid films suggests that the interfacial interaction between organosilicas and BPDA-ODA PI is a lot weaker than the interaction between BPDA-PDA PI and silica, confirming the authors' previous result indi-

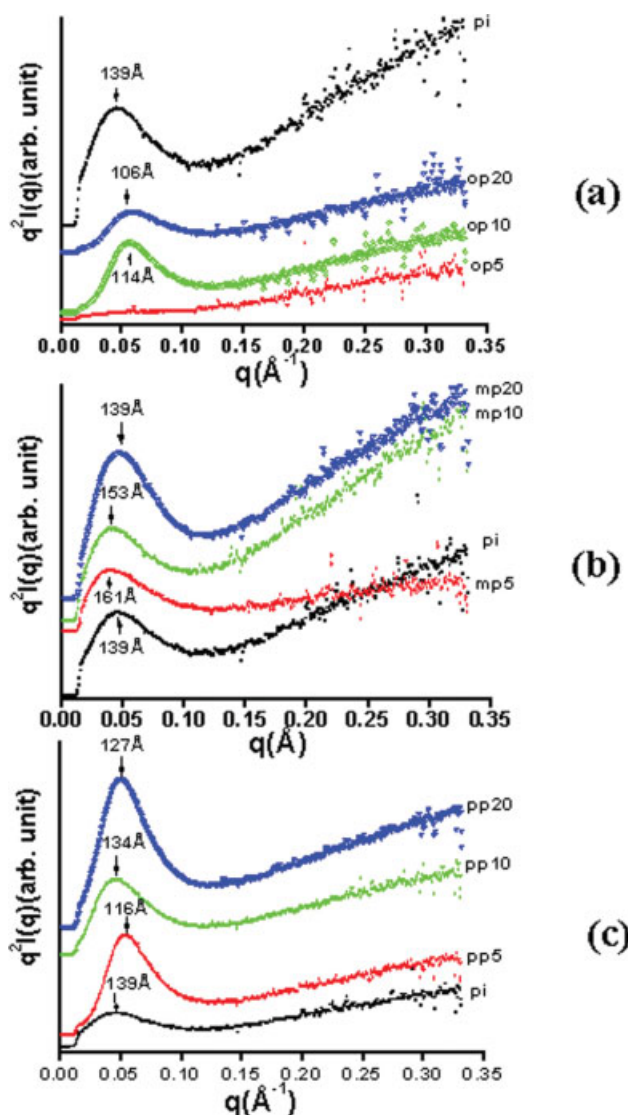


Figure 6 Lorentz-corrected SAXS patterns of pristine BPDA-ODA PI and hybrid films. For sample notations, see Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Optical and Dielectric Properties of the Polyimide Hybrid Films

Sample	Refractive index	Dielectric constant	Density (g/mL)
PI	1.78	3.17	1.385
op5	1.75	3.06	1.382
op10	1.73	2.99	1.383
op20	1.75	3.06	1.384
mp5	1.77	3.13	1.389
mp10	1.75	3.06	1.383
mp20	1.76	3.10	1.385
pp5	1.74	3.03	1.380
pp10	1.77	3.13	1.388
pp20	1.75	3.06	1.383

cating the fact that BPDA-ODA PI has worse interfacial interaction with silica than does the BPDA-PDA PI.¹¹

In our previous work,⁴⁰ we investigated the miscibility of blends of poly(vinyl methyl ether) (PVME) and styrene-containing copolymers. In the work, the styrene copolymers have the same chemical structures for the position of the methyl group, i.e., *o*-methylstyrene, *m*-methylstyrene, and *p*-methylstyrene. We concluded that the *m*-methylstyrene containing copolymer has the least miscibility with PVME, though the exact reason was not explained at that time. Comparison of the previous work with the present work indicates the fact that the interfacial interaction is affected sensitively by the chemical nature (isomer type) of the organosilicas (this work) in the hybrid materials as well as of styrene derivatives in the copolymers (previous work).⁴⁰ Therefore, it is obvious that the *m*-substituted phenyl unit has a stronger influence in reducing the interfacial interaction of organosilica with BPDA-ODA PI than do the *o*-substituted or *p*-substituted phenyl units.

To examine the effect of nanoparticle size on the optical property and porosity of the hybrid films, the refractive index and density were measured, as shown in Table II. The refractive index of the hybrid films was reduced by 0.1–0.05 from that of pristine polyimide film, which is in agreement with the result of refractive index change for BPDA-PDA PI/silica hybrid composite films, earlier reported.⁴¹ The resulting dielectric constants of hybrid films varied between 2.99 and 3.13, which is slightly lower than 3.17 recorded for the pristine polyimide film. However, no trends in the refractive index are observed with the organosilica contents and isomer types for the hybrid films, which is consistent with the density changes (see Table II). Consequently, this result indicates a lack of correlation between the nanoparticle size and the optical (porosity) property.

Finally, we have measured the peel strength between hybrid composite films and aluminum sub-

strate to investigate the influence of organosilica isomers on the adhesion property. As shown in Figure 7, the peel strength increases with increasing organosilica contents for all types of isomers. This improvement in the peel strength is ascribed to the specific interaction between aluminum and the functional groups (—OH or —NH) in organosilicas. However, the peel strength of the hybrid films was not much different with the isomer types, indicating that the adhesion property is independent of the type of organosilica isomers. This similar adhesion property can be supported by the similar surface nanomorphology of hybrid films for different isomer types as shown in AFM images (see Fig. 8), though this should be discussed with the interface nanomorphology measured for the contact surface of hybrid films on the aluminum substrate.

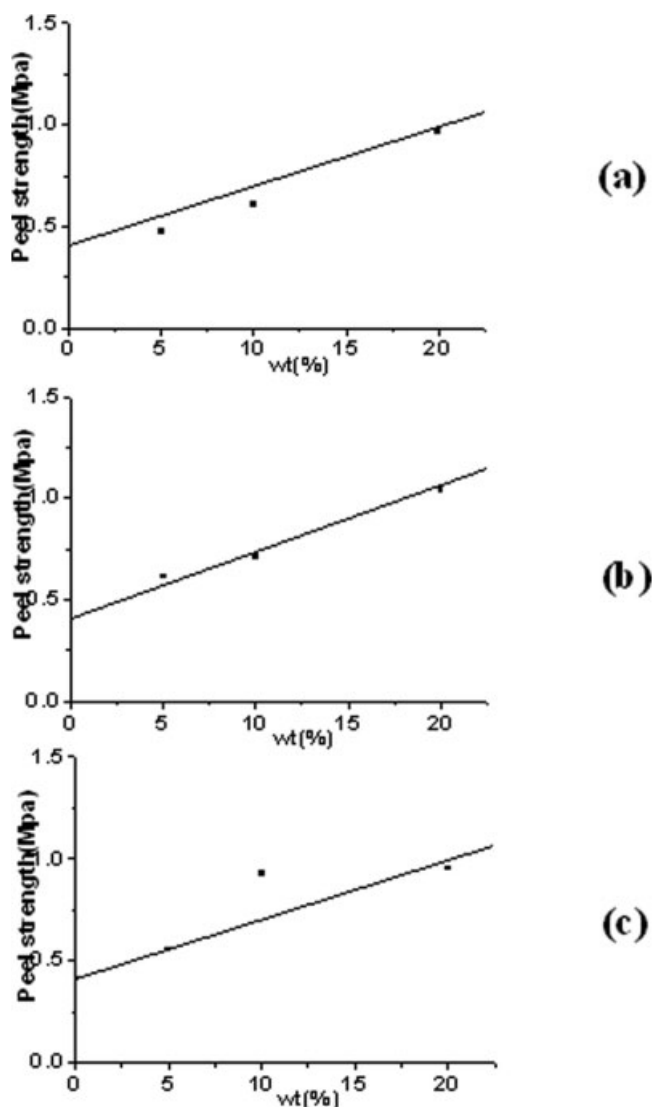


Figure 7 Peel strengths of pristine BPDA-ODA PI and hybrid films: (a) **op** series, (b) **mp** series, and (c) **pp** series. For sample notations, see Table I.

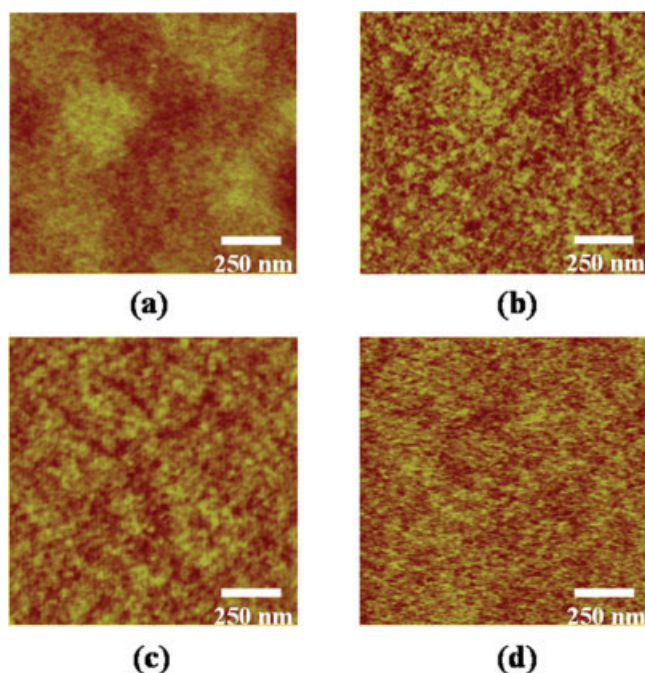


Figure 8 AFM images of pristine BPDA-ODA PI (a) and hybrid films (b–d): (b) **op5**, (b) **mp5**, and (c) **pp5**. For sample notations, see Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

The ^{29}Si NMR result showed that the *o*-substituted phenyl organosilica limits the perfect sol–gel reaction because of the steric hindrance effect of substituted moieties. From the WAXD results the organosilicas are considered to have an influence in improving the fine ordering/crystallization because the major diffraction peaks were split into several fine peaks with increasing the organosilica contents irrespective of the isomer types. The SAXS results showed that the long period of polyimide (BPDA-PDA PI) is affected by the presence of organosilicas in the hybrid films and the *m*-substituted phenyl organosilica is considered to have poorer *nanoscale* interfacial interaction with the polyimide than do other isomers. However, this difference in the *nanoscale* interfacial interaction was not observed for the bulk adhesion property against the aluminum substrate, although the overall peel strength improved as the organosilica content increased, irrespective of the isomer types.

The SAXS measurements at Pohang Accelerator Laboratory, Korea, are appreciated.

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