Available online at www.sciencedirect.com

SCIENCE DIRECT®

polymer

Polymer 46 (2005) 173–181

www.elsevier.com/locate/polymer

Polyimide and polyhedral oligomeric silsesquioxane nanocomposites for low-dielectric applications

Yuan-Jyh Lee[a], Jieh-Ming Huang[b], Shiao-Wei Kuo[a], Jian-Shing Lu[a], Feng-Chih Chang[a,*]

[a]*Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan ROC*
[b]*Department of Chemical Engineering, Van Nung Institute of Technology, Chung-Li 32054, Taiwan ROC*

Received 28 May 2004; received in revised form 13 September 2004; accepted 5 October 2004
Available online 19 November 2004

Abstract

A novel polyimide (PI) hybrid nanocomposite containing polyhedral oligomeric silsesquioxane (POSS) with well defined architecture has been prepared by copolymerization of octakis(glycidyldimethylsiloxy)octasilsesquioxane (Epoxy–POSS), 4,4′-oxydianiline diamine (ODA), and 4,4′-carbonyldiphthalic anhydride (BTDA). In these nanocomposite materials, the equivalent ratio of the Epoxy–POSS and ODA are adjustable, and the resultant PI–POSS nanocomposites give variable thermal and mechanical properties. More importantly, we intend to explore the possibility of incorporating POSS moiety through the Epoxy–POSS into the polyimide network to achieve the polyimide hybrid with lower dielectric constant (low-*k*) and thermal expansion. The lowest dielectric constant achieved of the POSS/PI material (PI-10P) is 2.65 by incorporating 10 wt% Epoxy–POSS (pure PI, $k=3.22$). In addition, when contents of the POSS in the hybrids are 0, 3, 10 wt% (PI-0P, PI-3P, PI-10P), and the resultant thermal expansion coefficients (TEC) are 66.23, 63.28, and 58.25 ppm/°C, respectively. The reduction in the dielectric constants and the resultant thermal expansion coefficients of the PI–POSS hybrids can be explained in terms of creating silsesquioxane cores of the POSS and the free volume increase by the presence of the POSS–tethers network resulting in a loose PI structure.
© 2004 Elsevier Ltd. All rights reserved.

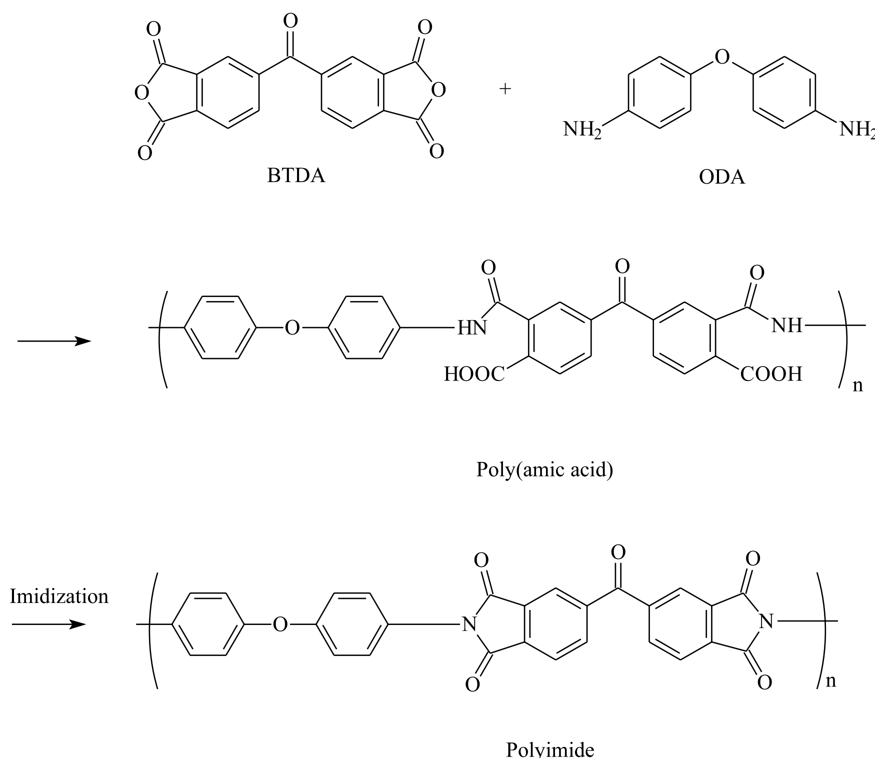
Keywords: Polyimide; POSS; Low-*k*

1. Introduction

Aromatic polyimides (PI) are widely used in electronics and aerospace because of their excellent thermal, electrical, and mechanical properties. Polyimides are usually prepared through a two-step reaction between aromatic diamines and aromatic tetracarboxylic dianhydrides in commercially available *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMAc) solution to give soluble polyamic acids (PAAs), and followed by thermal imidization (Scheme 1). Recently, PIs possessing lower dielectric constant and higher dimensional stability than SiO_2 that have been extensively applied to the microelectronics industry [1–6]. However, polyimides most resistant to thermal decomposition and mechanical deformation are those incorporating aromatic or other double bonds, which tend to increase the electronic polarizability of these materials. Polyimides usually containing a large number of carbon double bonds can be expected to have a large polarization due to the increased mobility of the π electrons. The rigidity and thermal stability of the polyimide is in part due to the dense molecular packing. Unfortunately, the high-energy bond and material density in polyimide leads to a larger electronic polarizability, and therefore a higher dielectric constant in a modern electronic device. In order to decrease the dielectric constant of polymers, several research groups [7–11] have explored the possibility of incorporating various nanoforms into polymer matrixes to take the advantage of low dielectric constant of air ($k=1$). Current studies on nanoforming are based on two routes, by the thermal decomposition of blends or by block copolymers or blends made up of a high thermally stable polymer and an unstable one [7–9] and by the evaporation of the dissolved

* Corresponding author. Tel.: +886-3-5727077; fax: +886-3-57195-07.
E-mail address: changfc@cc.nctu.edu.tw (F.-C. Chang).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.10.003



Scheme 1. Chemical reactions and structures of typical polyimide.

supercritical CO_2 [10–11]. The dissolved CO_2 escaping from a polymer is considered non-polluting.

A low dielectric constant material can also be made by incorporating silica cage like polyhedral oligomeric silsesquioxane (POSS) into the polyimide matrix [12,13]. Recently, a novel class of organic/inorganic hybrid materials based on POSS has been developed which contains an inorganic Si_8O_{12} core (1 nm) surrounded by eight or seven organic hydrocarbon groups and a functional group. POSS has an unique and well defined structure that can be used for preparing hybrid materials with well defined structure [14–16]. In this nanocomposite material, the mole ratio of POSS is adjustable, and the resultant POSS nanocomposite possesses improved thermal and mechanical properties [17–19]. In this study, excess oxydianiline diamine (ODA), was reacted initially with 4,4′-carbonyldiphthalic anhydride (BTDA) and the residual terminal amines of the polyamic acid (PAA) were then reacted with octakis(glycidyldimethylsiloxy)octasilsesquioxane (Epoxy–POSS). By varying equivalent ratio of the ODA, polyamic acids with different molecular weights and different morphologies of thers nanocomposites were obtained. The reduction in the dielectric constant of the PI–POSS hybrids can be expected and the free volume increase by the presence of the rigid silsesquioxane cores and large POSS–tethers network resulting in a loose PI structure. Such a loose polyimide network structure due to the Epoxy–POSS incorporation can be visualized from Scheme 2. The void formation and the free volume increase of the PI/POSS nanocomposite can be qualitatively verified by its density. Furthermore, we intend to explore the possibility of incorporating POSS moiety through epoxy-functionalized POSS into the polyimide network hoping to achieve the resulted polyimide hybrid with lower dielectric constant and lower thermal expansion coefficient.

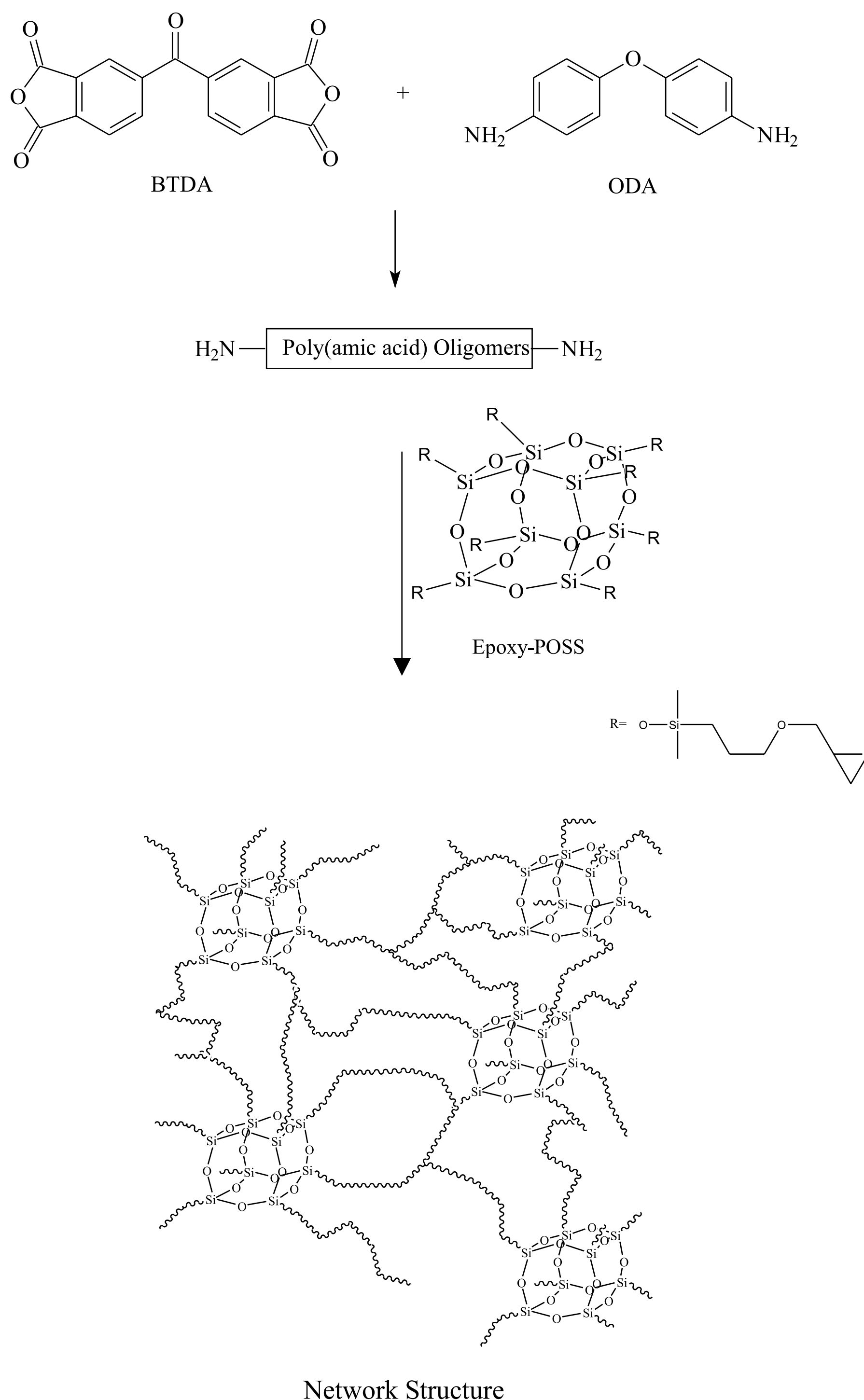
2. Experimental

2.1. Materials

All materials are commercially available and were used as received. The ultrapure 4,4′-carbonyldiphthalic anhydride (BTDA, 98.5%) and 4,4′-oxydianiline (ODA, 98%) were purchased from the Chriskev Inc. of USA. The *N,N*′-dimethylacetamide (DMAc, HPLC grade) was purchased from Aldrich. Octakis(glycidyldimethylsiloxy)octasilsesquioxane (Epoxy–POSS) was bought from Hybrid Plastics Company and used without further purification.

2.2. Characterizations

Fourier transform infrared spectroscopy (FT-IR). Infrared spectroscopic measurements were performed using a Nicolet Avatar 320 FT-IR Spectrophotometer in the range 4000–400 cm^{-1} at a resolution of 1.0 cm^{-1}. All sample preparations were performed under a continuous flow of nitrogen to ensure minimal oxidation or degradation of the



Scheme 2. Preparation and morphology of PI–POSS nanocomposite. The mole ratio of the terminal amine ($-NH_2$) to the epoxy group is 1:1.

sample. Molecular weights were determined by gel-permeation chromatography (GPC) using a SUPER CO-150 apparatus equipped with an LC gel column and an RI detector. Polystyrene samples were used as standards and DMF was used as the eluent at a flow rate of 1 ml/min.

Thermal and viscoelastic properties. Thermal and viscoelastic properties of these hybrids were characterized by thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). TGA was carried out with a TA Instruments TGA 2050 Thermogravimetric Analyzer at

a heating rate of 10 °C from room temperature to 700 °C under a continuous nitrogen flow. Dynamic mechanical analysis (DMA) measurements were performed using a TA Instruments DMA Q800 (DuPont) in a tension mode over a temperature range from 30 to 390 °C. Data acquisition and analysis of the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were recorded automatically by the system. A sample with 14 mm in length, 6 mm in width, and 0.2 mm in thickness was used. The heating rate and frequency were fixed at 2 °C/min and 1 Hz, respectively.

Dielectric constant and thermal expansion coefficient. The thermal expansion coefficient (TEC) parallel to the surface direction was measured in an extension mode using a TMA 2940 Thermomechanical Analyzer (Du Pont) with a force of 0.05 N. The dielectric constant and dielectric loss were determined with a heating rate of 1 °C/min from 25 to 50 °C with scan frequencies ranging from 1 to 10^5 Hz by a DEA 2970 Dielectric Analyzer (Du Pont). All tests were conducted under a nitrogen flow 20 ml/min and the specimen thickness was controlled between 0.2 and 0.5 mm.

Morphology analysis. The surface morphology was recorded using the 'easy scan' contact mode of an atomic force microscopy (AFM) system (Nanosurf AG). The spring constant of the cantilever was 5 N/m and the feedback loop bandwidth was 12 kHz. All images were recorded at room temperature. Cross-sectional images of the PI/POSS nanocomposite films (0.2–0.4 mm) were studied by SEM. The SEM images were obtained using a Hitachi-S4700I microscope operating at an acceleration voltage of 15 kV.

2.3. Preparation of PI/POSS hybrid films

In a three-necked flask equipped with a mechanical stirrer, 2.072 g of ODA (0.0104 mol) was added in 28.23 ml DMAc and cooled in an ice-water bath under a nitrogen atmosphere. After the ODA was dissolved completely, 3.22 g (0.01 mol) of BTDA was added and stirred at room temperature for 1 h. A solution of 0.1633 g Epoxy–POSS (8.98×10^{-5} mol, 3 wt% in the hybrid) dissolving in 2 ml DMAc was added with continuous stirring at room temperature for 12 h to yield a 24.2 wt% DMAc solution of the polyamic acid (PAA) as shown in Scheme 2. The obtained DMAc solution of the PAA/POSS hybrid was coated by a doctor blade on a glass plate using an automatic film applicator at a rate of 0.34 mm/min, and subsequently heated at 60, 80, 100, 150, 200 °C under a nitrogen atmosphere and the prepared sample was named PI-3P. The film was then peeled off from the glass plate to obtain the PI/POSS hybrid film with a thickness of 200 μm (for tests on dielectric and mechanical properties). When contents of the POSS in the hybrids are 0, 0.405, 0.597 g (0, 7, 10 wt%), and the adjustable ODA of these hybrids are 2.00, 2.176, and 2.263 g. Codes of various hybrids with different compositions and molecular weights are listed in Table 1.

3. Results and discussion

3.1. Preparation of polyimide/POSS nanocomposites

In this study, we have developed a synthetic method to copolymerize Epoxy–POSS, BTDA and ODA. This approach provides a new route to design a series of polyimide–POSS nanocomposites with a wide range of dielectric and mechanical properties. Recently, the Epoxy–POSS and diamine network architecture and their curing behavior have been characterized carefully by Laine group [17–19]. In this work, excess diamine (ODA) was reacted initially with BTDA and the terminal amino groups of the polyamic acids (PAAs) were then reacted with Epoxy–POSS. The equivalent ratio of the terminal amine of the PAA to epoxy group of the POSS was 1:1. Table 1 gives the concentrations of the Epoxy–POSS and the molecular weight results of the PAAs without POSS content. Furthermore, by varying molar ratios of the ODA, PAAs with different molecular weights and showed broader molecular weight distributions. The different morphologies of the resulted network of polyimide–POSS nanocomposites after imidization were obtained as shown in Scheme 2.

3.2. FT-IR

FT-IR spectra of the pure polyimide, pure Epoxy–POSS,

Table 1
Component and molecular weight analysis of PI–POSS nanocomposites

Sample	Epoxy–POSS in feed		Molecular weights[a]				Elemental analysis		
	wt%	mol%	M_n	M_w	M_w/M_n		N%	C%	H%
PI-0P	0	0	50122	75776	1.51		6.02	70.97	3.52
						cal.	6.14	71.31	2.87
PI-3P	3	0.0017	14335	26867	1.87		5.88	69.56	3.71
						cal.	5.51	67.34	3.25
PI-7P	7	0.0038	6797	17643	2.60		5.68	68.32	3.87
						cal.	4.82	65.32	3.68
PI-10P	10	0.0056	3567	13321	3.73		5.65	67.86	4.09
						cal.	4.34	60.91	3.96

[a] Polyamic acid (PAA) without POSS content, DMF was used as an eluent.

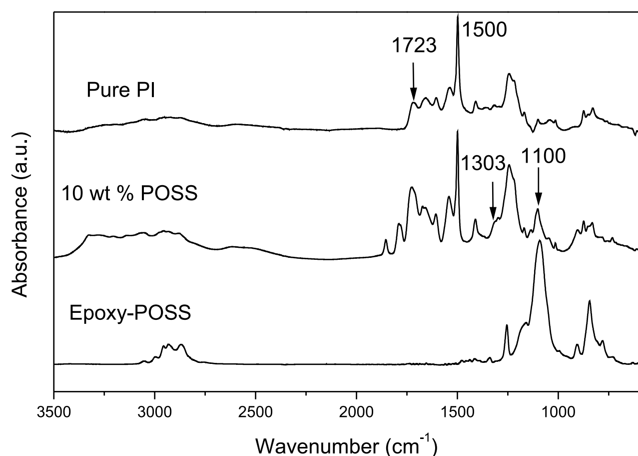


Fig. 1. FT-IR spectra of each components.

and 10 wt% Epoxy–POSS nanocomposite are shown in Fig. 1. A sharp and strong peak due to Si–O–Si stretching of the silsesquioxane cage appears at 1100 cm^{-1}. The characteristic imide group band at 1723 cm^{-1} and the symmetric/asymmetric N–H peaks disappear almost completely at 3300 cm^{-1} in the pure polyimide implies a fully imidized structure. In addition, the polyimide derived C=C aromatic ring absorption at 1500 cm^{-1} is present in both pure PI and the 10 wt% PI–POSS nanocomposite. For the 10 wt% PI–POSS nanocomposite, O–H and N–H bands in the composite appear strongly at 3200–3500 cm^{-1}. It is because the terminal amino groups (–NH_2) in the polyimide react with epoxy group of the POSS to form new O–H and N–H bond at 3200–3500 cm^{-1}, while the aromatic C=C band remains.

3.3. Thermal and mechanical properties of PI–POSS nanocomposites

Fig. 2 presents TGA thermograms of Epoxy–POSS, pure PI and various polyimide/POSS nanocomposites under nitrogen atmosphere. A slight decrease in the decomposition temperature (T_d) was found for PI–POSS nanocomposites relative to the pure PI due to lower degradation temperature of POSS organic segments. Char yields of these PI–POSS hybrid material remain essentially the same as the pure PI due to the component of the POSS and the polyimide in the composite PI–POSS material. The POSS fraction is small and the char yield is similar to the pure polyimide (Table 2).

More detailed information can be found from the dynamic mechanical properties of the film as a function of temperature as shown in Figs. 3 and 4. Fig. 3 shows the temperature dependence of the storage, loss modulus, and tan δ for the pure

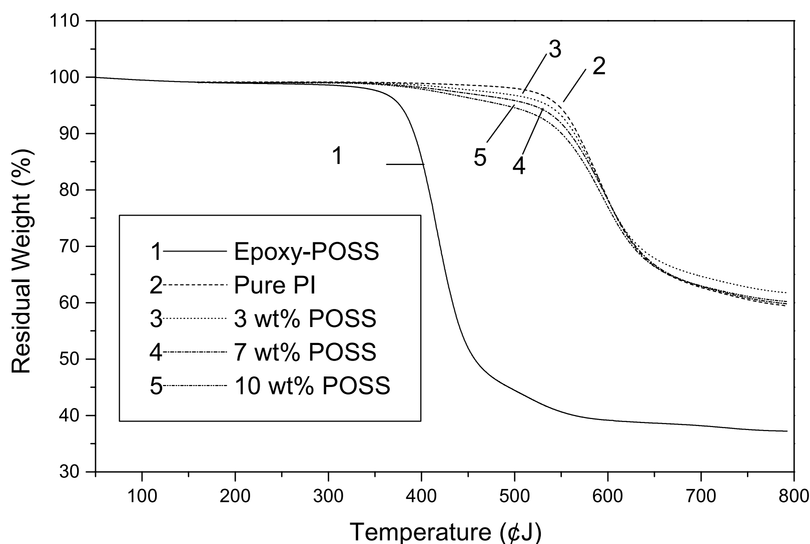


Fig. 2. TGA thermograms of PI–POSS nanocomposites having varying Epoxy–POSS content.

Table 2
Summary of the thermal properties of PI–POSS nanocomposites

Sample	Epoxy–POSS in feed		T_g (°C)[a]	5 wt% loss temperature (°C, in N_2)	Char yield in N_2 (wt%, 800 °C)
	wt%	mol%			
PI-0P	0	0	310	562	58.2
PI-3P	3	0.0017	308	558	62.2
PI-7P	7	0.0038	305	542	59.3
PI-10P	10	0.0056	302	533	60.4

[a] Detected by DMA.

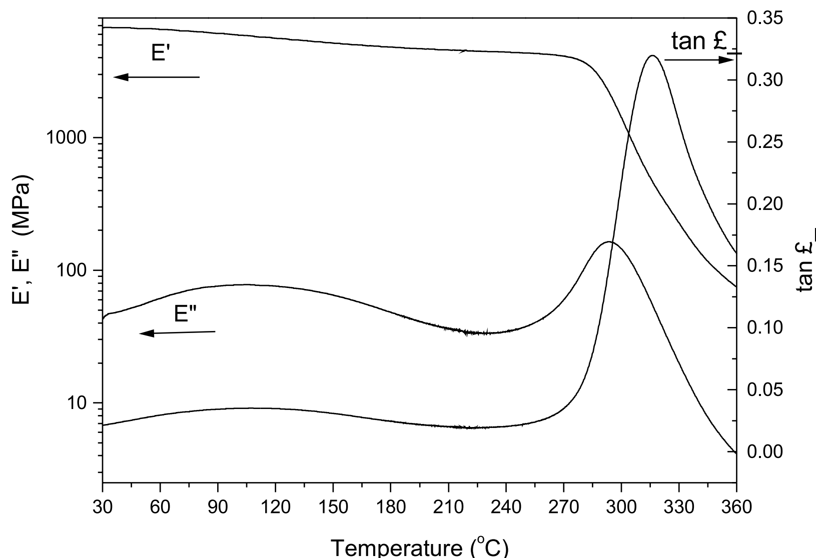


Fig. 3. Dynamic mechanical analysis curves for pure polyimide at a heating rate of 2 °C/min.

polyimide. Two relaxations appear at ca. 120 and 310 °C based on tan δ peaks. The subglass relaxation at 120 °C is a typical β transition for polyimides along with a steady decrease in E'. Such a transition has generally been accounted for the rotation or oscillation of the phenyl groups within the diamine moiety of the polyimide [20,21]. As shown in Fig. 3, the T_g of the polyimide is 293.5 °C based on the maximum of loss modulus or 310.5 °C based on the maximum of tan δ peaks. Fig. 4 presents the mechanical relaxation spectra of the pure polyimide and polyimide/POSS 97/3 and 90/10 nanocomposites. It is clear that the storage modulus, E', decreases slightly with increasing POSS content in the nanocomposites. The low-temperature subglass relaxation appeared nearly at ca. 120 °C in all three samples. However, the T_g based on the maximum E'' decreases with increasing POSS content. This is due to the presence of POSS organic tether segments within the polyimide network and thus increases the free volume of the polyimide matrix.

3.4. Dielectric constant, thermal expansion, and density of PI/POSS nanocomposites

Lower dielectric constant is one of the most desirable properties for next generation electronic devices. Table 3 gives the dielectric constant of various PI–POSS composites with different POSS contents. The dielectric constant of the hybrid decreases as the amount of POSS is increased. The measured dielectric constant of the pure BTDA-ODA PI

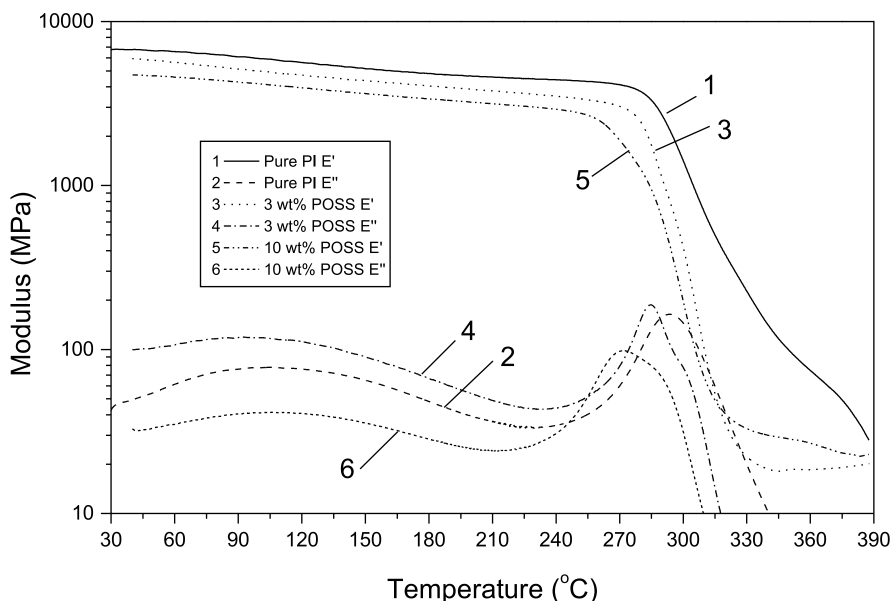


Fig. 4. Dynamic mechanical analysis curves for pure polyimide and varying Epoxy–POSS content at a heating rate of 2 °C/min.

Table 3
Summary of the dielectric constant and of PI–POSS nanocomposites

Sample	Epoxy–POSS in feed		Dielectric constant (k)[a]	TEC (ppm, 50–250 °C)	measured density (g/cm^3)
	wt%	mol%			
PI-0P	0	0	3.22	66.23	1.38
PI-3P	3	0.0017	2.88	63.28	1.31
PI-7P	7	0.0038	2.73	61.37	1.26
PI-10P	10	0.0056	2.65	58.25	1.12

[a] 1 °C/min from 25 to 50 °C, with scan frequencie 10^5 Hz by a DEA.

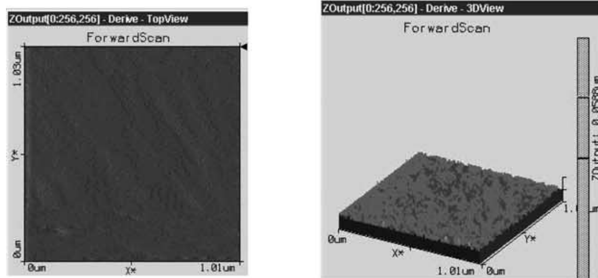
(PI-0P) is 3.22, while the lowest dielectric constant of the POSS/PI is 2.65 by incorporating 10 wt% Epoxy–POSS (PI-10P). The reduction in the dielectric constant of the PI–POSS hybrids can be explained in terms of creating the porous silsesquioxane nanocores of the POSS and the free volume increase by the presence of the rigid and large POSS structure resulting in a loose PI network. The void formation and the free volume increase of the PI/POSS nanocomposite can be qualitatively verified by its density. The density of the pure PI-0P is 1.38 while the density of the PI-10P is 1.12. Such a loose polyimide network structure due to the Epoxy–POSS incorporation can be visualized from Scheme 2.

There are a few possible causes for the reduction in the dielectric constant. Because the porosities of these nanocomposite are difficult to measure, we adopt to measure the densities to compare the relative porosities of these films [12]. The relative porosity increase (ψ_r) is defined as the increased external porosity due to the incorporation of POSS in polyimide matrix and the porosity of POSS themselves. At least three specimens were used for each density data point. The relative porosity increase was calculated by a equation as follows

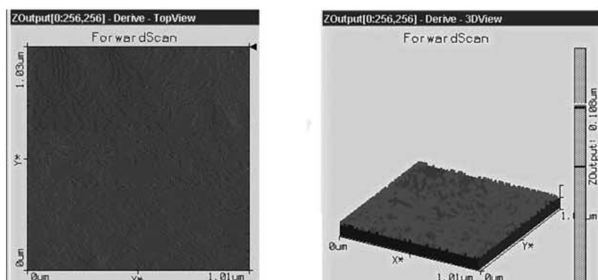
$$\psi_r = [(d_T - d_M)/d_T] \times 100\% + (0.048 \times V\%) \quad (1)$$

where ψ_r is the relative porosity increase, d_T and d_m are the measure densities and theoretical densities of the PI and POSS nanocomposites. The density of pure polyimide and POSS are 1.38 and 1.10 g/cm^3. V% is the volume percentage of POSS in the nanocomposites and the nanoporosity core of POSS represents 4.8 vol % of the total POSS volume as provided by the Hybrid Plastics company. Table 4 presents the components, POSS volume fractions, densities, and relative porosity increase of PI/POSS nanocomposites. The relative porosity increases, as the amount of POSS increases, and the dielectric constant of the hybrid decreases as the amount of POSS is increased. The measured dielectric constant of the PI-0P is 3.22, while the lowest dielectric constant of the POSS/PI is 2.65 by incorporating 10 wt% Epoxy–POSS (PI-10P). This is also means that the free volume for polyimide in the nanocomposites increase with the tethered Epoxy–POSS. The increase in the free volume of polyimide corresponds

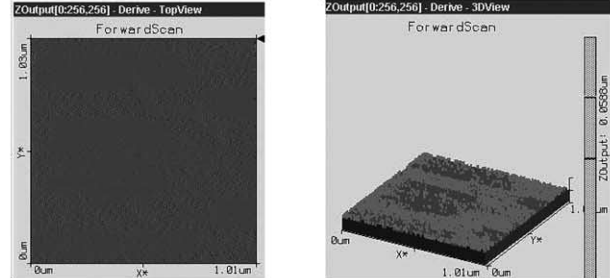
(a) PI-0P



(b) PI-3P



(c)PI-7P



(d) PI-10P

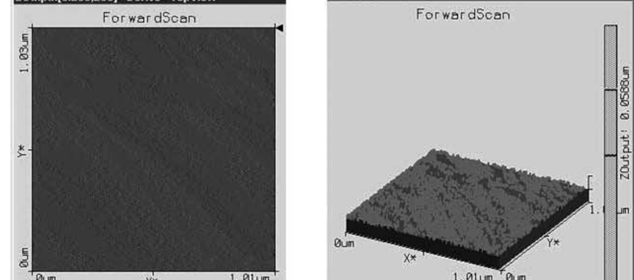


Fig. 5. AFM surface analysis of PI–POSS hybrid materials (a) PI-0P, (b) PI-3P, (c) PI-7P, (d) PI-10P.

Table 4
Summary of the relative porosity increase of PI–POSS nanocomposites

Sample	Epoxy–POSS in feed		Theoretical density (d_T, g/cm^3)	Measured density (d_M, g/cm^3)	Relative porosity increase (ψ, %)
	wt%	V%			
PI-0P	0	0	1.38	1.38	0
PI-3P	3	3.57	1.37	1.31	5.11
PI-7P	7	8.48	1.36	1.21	11.25
PI-10P	10	12.03	1.35	1.12	17.47

quite well to the fact that the modulus (E') and the glass transition temperature (T_g) of the polyimide with POSS is lower than the pure polyimide.

Reducing the high thermal expansion coefficient (TEC) of the pristine PI in order to match the relatively lower TEC of silica or metal such as copper is another main object of this research. Table 3 gives the TEC of PI–POSS hybrids measured below glass transition temperature has smaller TEC than the pure PI. When contents of the POSS in the hybrids are 0, 3, 10 wt% (PI-0P, PI-3P, PI-10P), and the resultant TEC of these hybrids are 66.23, 63.28, and 58.25 ppm/°C, respectively. Essentially all PI/POSS hybrids possess lower TEC than that of the pristine PI. POSS with inorganic silsesquioxane core has a substantially lower TEC than that of the PI. Therefore, the TEC of the PI/POSS hybrid is expected to be lower than that of the neat PI.

3.5. AFM and SEM analysis

We studied the surface morphologies of PI–POSS nanocomposites by AFM and SEM. Fig. 5 displays the AFM images of hybrids having various PI–POSS ratios. In

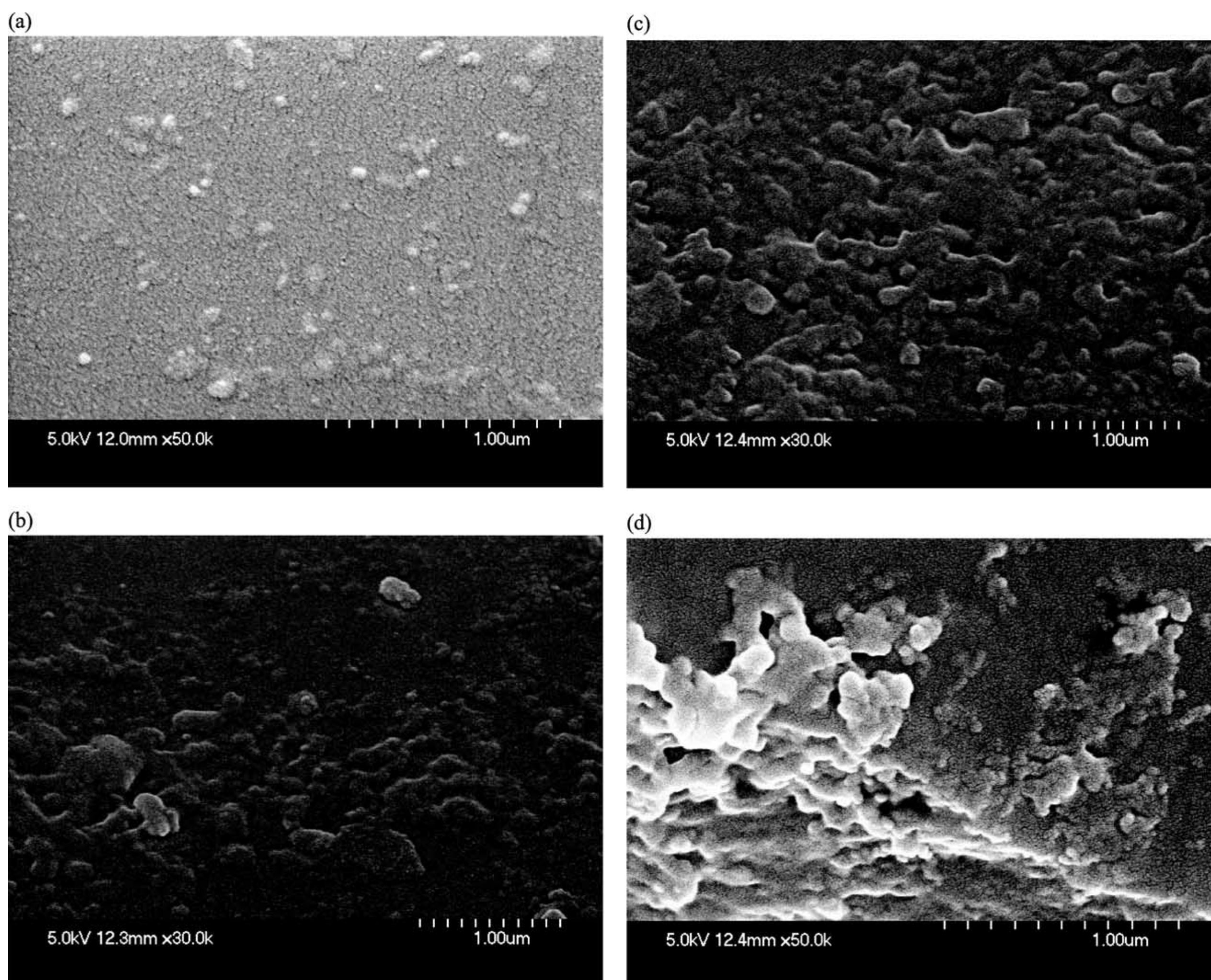


Fig. 6. SEM cross-section analysis of PI–POSS hybrid materials (a) PI-3P, (b) PI-7P, (c) PI-10P. (d) Fractured cross-section surface of the PI-10P.

Fig. 5(a)–(d), we observe that the degree of roughness of the PI and POSS hybrid films do not increase apparently upon increasing the POSS content. The Epoxy–POSS nanoparticles are well distributed and do not aggregate even at higher contents (10 wt%). The phase morphologies of PI–POSS network structures were also investigated by SEM analyses. Fig. 6(a)–(d) displays the cross section images obtained by SEM with various Epoxy–POSS contents. The hybrid materials with different POSS contents have various morphologies obtained by SEM. In this study, excess diamine (ODA) was reacted initially with BTDA and the terminal amine groups of the polyamic acid were then reacted with Epoxy–POSS. By varying equivalent ratio of the ODA, polyamic acids with different molecular weights and different morphologies of thers nanocomposites were obtained. The reduction in the dielectric constant of the PI–POSS hybrids can be explained and the free volume increase by the presence of the rigid and large POSS structure resulting in a loose PI network. Such a loose polyimide network structure due to the Epoxy–POSS incorporation can be visualized from Fig. 6(d).

4. Conclusions

A novel PI and POSS hybrid has been developed with well defined architecture through copolymerization. The reduction in the dielectric constant of these PI–POSS hybrids can be explained in terms of creating porous silsesquioxane nanocores of the POSS and the free volume increase by the presence of the rigid and large POSS structure resulting in a loose PI network. The PI–POSS hybrid film possesses lower thermal expansion coefficient than the pure PI film. With this approach, the dielectric constant and thermal expansion coefficient of the nanocomposite can be further reduced by increasing the POSS content.

References

[1] Auman BC, Myers TL, Higley DP. J Polym Sci, Part A: Polym Chem 1997;35:2441.
[2] Miwa T, Okabo Y, Ishida M. Polymer 1997;38:4945.
[3] Wilson D, Strenzenberger HD, Hergenrother PM. Polyimide. New York: Blackie; 1990.
[4] Numata S, Ohara S, Imaizumi J, Kinjo N. Polym J 1985;17:981.
[5] Sysel P, Pulec R, Maryska M. Polym J 1997;29:607.
[6] Mascia L, Kioul A. J Mater Sci Lett 1994;13:641.
[7] Carter KR, McGrath JE. Chem Mater 1997;9:105.
[8] Carter KR, DiPietro RA, Sanchez MI, Swanson SA. Chem Mater 2001;13:213.
[9] Mikoshiba S, Hayase SJ. Mater Chem 1999;9:591.
[10] Krause BR, Mettinkhof NF. Macromoleculars 2001;34:874.
[11] Krause BR, Mettinkhof NF. Adv Mater 2002;14:1041.
[12] Leu CM, Chang YT, Wei KH. Macromoleculars 2003;36:9122.
[13] Leu CM, Chang YT, Wei KH. Chem. Mater 2003; 15, p. 3721.
[14] Feher FJ, Newman DA. J Am Chem Soc 1990;112:1931.
[15] Lei Z, Farris RJ, Coughlin EB. Macromolecules 2001;34:8034.
[16] Patrick TM, Hong GJ. Macromolecules 1999;32:1194.
[17] Choi J, Yee AF, Laine RM. Macromolecules 2003;36:5666.
[18] Choi J, Harcup J, Yee AF, Zhu Q, Laine RM. J Am Chem Soc 2001; 123:11420.
[19] Tamaki R, Choi J, Laine RM. Chem Mater 2003;15:793–7.
[20] Bernier GA, Kline DE. J Appl Polym Sci 1968;12:593.
[21] Perena JM. Angew Makromol Chem 1982;106:61.