

Low- κ Nanocomposite Films Based on Polyimides with Grafted Polyhedral Oligomeric Silsesquioxane

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ABSTRACT: Nanocomposites of polyimides (PI) with covalently grafted polyhedral oligomeric silsesquioxane ($R_7R'Si_8O_{12}$ or POSS) units were prepared by thermally-initiated free-radical graft polymerization of methacrylcyclopentyl-POSS (MA-POSS) with the ozone-pretreated poly[N,N' -(1,4-phenylene)-3,3',4,4'-benzophenonetetracarboxylic amic acid] (PAA), followed by thermal imidization. The chemical composition and structure of the PI with grafted methacrylcyclopentyl-POSS side chains (PI-g-PMA-POSS copolymers) were characterized by nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The POSS molecules in each

grafted PMA side chain of the amorphous PI films retained the nanoporous crystalline structure, and formed an aggregate of crystallites. The PI-g-PMA-POSS nanocomposite films had both lower and tunable dielectric constants, in comparison with that of the pristine PI films. Dielectric constants (κ 's) of about 3.0–2.2 were obtained. The present approach offers a convenient way for preparing low- κ materials based on existing PI's. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2226–2232, 2006

Key words: graft copolymers; dielectric properties; polyimides; nanocomposites; NMR

INTRODUCTION

The demand for low dielectric constant (low- κ) materials in the microelectronics industry has recently led to considerable interest in the porous materials, in particular, the nanoporous low- κ materials.^{1–5} Polyimides (PI's) have been widely used as dielectric and encapsulating materials in the microelectronics industry because of their good mechanical, thermal, and dielectric properties.^{6–10} However, with dielectric constants in the range of 3.1–3.5, the conventional PI's are insufficient in meeting the requirement of $\kappa < 2.5$ for the dielectrics of the near future, and the ultra-low- κ of less than 2.2 for the technology nodes below 130 nm.¹¹ Low- κ materials can be prepared by introducing voids into the bulk to take advantage of the low dielectric constant of air ($\kappa \sim 1$). Homogeneous and closed pores with size in the nanometer range are preferred from the point of view of preserving the electric and mechanical properties of the material. The introduction of air gaps into interconnect structures and nanopores into polymers to reduce their dielectric constants have become an attractive approach.^{12–16}

The approaches to the preparation of porous PI films have included microwave processing¹⁷ and incorporation of foaming agents^{16,18} and hollow micro-

spheres.^{19,20} An alternative approach to the preparation of porous low- κ PI's is through the creation of voids by thermal degradation of the poly(propylene oxide) block of a phase-separated polyimide-poly(propylene oxide) block copolymer.^{21,22} Yet another approach to the preparation of nanoporous low- κ PI films was via thermally-induced graft copolymerization of poly(amic acid) with a vinyl monomer, followed by side chain decomposition after thermal imidization.^{23–25}

One class of the inorganic component—polyhedral oligomeric silsesquioxanes (POSS), e.g., the octameric form ($R_7R'Si_8O_{12}$) consists of a rigid cubic silica core and a nanopore of about 0.3–0.4 nm in size.²⁶ Polymer films based on polysilsesquioxanes with low- κ has been prepared.^{27,28} POSS has been shown to reduce the dielectric constant, without significantly affecting the mechanical properties, of the PI's when chemically incorporated into the PI's.^{28–31} The nanoporous POSS was covalently tethered to the prefunctionalized PI chain ends or pendant groups, resulting in organic-inorganic nanocomposite materials with much lower dielectric constants than that of the pristine PI. Alternatively, the methacryl functional group of methacrylcyclopentyl-POSS (MA-POSS) may be expected to undergo graft copolymerization with the PI chains when free radicals are generated on the PI chains. Free radicals can be readily produced on the parent polymer chains when the chains are exposed to ionizing radiation, or a free-radical initiator.^{32,33} Peroxide

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groups can also be introduced onto the parent polymer by ozone pretreatment to serve as the initiation sites for free-radical graft copolymerization with a monomer.^{34–36}

In the present study, a simple approach to the synthesis of PI with MA-POSS polymer (PMA-POSS) side chains via thermally-induced graft copolymerization of MA-POSS with the ozone-pretreated poly[*N,N'*-(1,4-phenylene)-3,3',4,4'-benzo phenonetetra-carboxylic amic acid] (PAA), followed by thermal imidization, was carried out. By adjusting the molar ratio of grafted PMA-POSS in the copolymer, PI-g-PMA-POSS nanocomposites with tunable dielectric constants were prepared.

EXPERIMENTAL

Materials

The poly(amic acid) precursor, poly[*N,N'*-(1,4-phenylene)-3,3',4,4'-benzophenone tetracarboxylic amic acid], was purchased from Aldrich Chemical Co., Milwaukee, WI, in powder form and was used as received. Methacrylcyclopentyl-POSS (MA-POSS) was obtained from Hybrid Plastics Co., Fountain Valley, CA. The solvent, *N,N*-dimethylformamide (DMF), was purchased from Fisher Scientific Co. Leics, UK, and was used as received. Tetrahydrofuran (THF, from Aldrich Chemical Co.) was distilled under nitrogen with sodium benzophenone ketyl.

Graft copolymerization

The PAA powders were dissolved in DMF to a concentration of 75 g/L. A continuous stream of O₃/O₂ mixture was bubbled through 14 mL of the solution at 25°C. The O₃/O₂ mixture was generated from an Azcozon RMU 16–04EM ozone generator. The gas flow rate was adjusted to 300 L/h to give rise to an ozone concentration of about 0.027 g/L of the gaseous mixture. A typical treatment time of about 10 min was used. This pretreatment time gave rise to a peroxide content of about 8×10^{-5} mol/g of the polymer. The dependence of peroxide concentration and molecular weight of PAA on the ozone treatment time under similar experimental conditions had been reported earlier.³⁷ The number average molecular weight of PAA decreased, while the polydispersity increased, with the ozone treatment time. In this case, the molecular weights (\bar{M}_n 's) of PAA before and after ozone-pretreatment for 5 min are 81,300 and 65,600, respectively. The degradation of the PAA chains probably had also resulted in the formation of active sites on the chains for the subsequent reaction with oxygen to form the peroxides and the oxidized species. The ozone-pretreated PAA solution (containing about 1 g of PAA) was transferred to an ampoule. About 20 mL

of DMF and 20 mL of a THF solution of MA-POSS were then introduced into the ampoule. The amount of MA-POSS in the THF solution ranged from 1 to 3 g, giving rise to a concentration of 18 mM to 54 mM in the reaction mixture. The ampoules were degassed with three freeze-evacuate-thaw cycles. They were then sealed and kept at 70°C for 20 h. After the desired reaction time, the reaction ampoules were cooled in an ice bath. Each PAA-g-PMA-POSS copolymer sample was precipitated in an excess amount of *n*-hexane, and recovered by filtration. The copolymer sample was purified thrice by redissolving in DMF and reprecipitating in hexane. It was further purified by washing in excess hexane for another 48 h. Since hexane is a good solvent for MA-POSS and its homopolymer, the unreacted MA-POSS and the PMA-POSS generated during the free-radical graft copolymerization process should have been extracted completely. Finally, the copolymer samples were dried by pumping under reduced pressure overnight at room temperature.

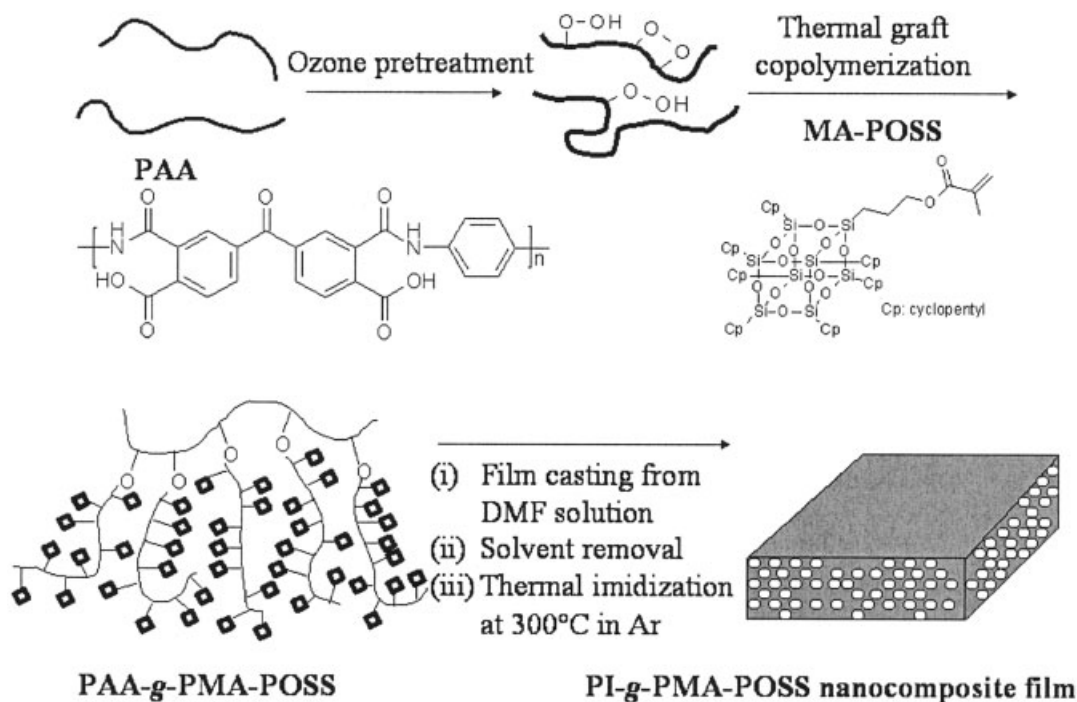
Preparation of the PI-g-PMA-POSS films

The graft copolymer was dissolved in DMF to a concentration of 20 wt %. The PAA-g-PMA-POSS film was prepared by casting the copolymer solution on a polished silicon substrate (Si(100) wafer). The film was heated initially in a vacuum oven at 90°C for 1 h under atmospheric pressure, before the imidization step. It was then heated at 150°C for 1 h, at 200°C for 1 h, at 250°C for 0.5 h, and finally at 300°C for 0.5 h in a vacuum oven, prepurged with argon, to complete the imidization process. The resulting nanoporous PI-g-PMA-POSS composite film had a thickness of about 200 μm. The overall process is shown in Scheme 1.

Characterization

Proton nuclear magnetic resonance (¹H-NMR) studies of the copolymers was performed on a Bruker ARX 300 instrument. Fourier transform infrared (FTIR) spectra of KBr disks were recorded on a Bio-Rad FTS 135 FTIR spectrophotometer. Differential scanning calorimetry (DSC) studies were conducted on a DSC 822e (Mettler Toledo Co., Switzerland) apparatus at a heating rate of 10°C/min under a nitrogen atmosphere. The X-ray diffraction (XRD) study of the samples was carried out on a Shimadzu XRD-6000 X-ray diffractometer, operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54 \text{ \AA}$) and at a scanning rate of 1°/min.

The morphology of the PI-g-PMA-POSS films was studied by field emission scanning electron microscopy (FESEM) on a JEOL JSM-6700F FESEM at an accelerating voltage of 5 kV. The film was fractured under liquid nitrogen and mounted on the sample stud by means of double-sided adhesive tape for the cross-sectional view. A thin layer of platinum was



Scheme 1 Schematic illustration of the thermally-initiated graft copolymerization of methacrylcyclopentyl-POSS with the ozone-preactivated poly(amic acid) and the preparation of the PI-g-PMA-POSS nanocomposite film.

sputtered onto the cross-sectional surface before the FESEM measurement.

The density of the PI-g-PMA-POSS films was measured on a top-loading electronic Mettler Toledo balance (model AP250D, equipped with a density kit), according to the Archimedeian principle. The sample was weighed in air and then in doubly distilled water at room temperature. The dielectric constant of the film was measured on an RF impedance/capacitance material analyzer (Hewlett-Packard model 4291B) in the frequency range of 1 MHz to 1.8 GHz and at 50% relative humidity (25°C) under ambient conditions.

RESULTS AND DISCUSSION

The chemical structure of the PAA-g-PMA-POSS copolymer was first characterized by $^1\text{H-NMR}$ spectroscopy. The chemical shifts at 7.5–7.7 and 8.2–8.4 ppm are attributable to the aromatic protons of PAA. Graft polymerization of MA-POSS with PAA has resulted in the appearance of chemical shifts at 4.6 ppm, and in the region below 1.9 ppm, attributable, respectively, to the COOCH_2 group and the aliphatic hydrogen associated with the PMA-POSS. The mole percentage of the MA-POSS units in the copolymer (sum of the MA-POSS units and the amic acid repeat units of PAA) was determined from the NMR peak integrals. The volume percentage of MA-POSS in PI-g-PMA-POSS was calculated by taking into account the densities of PMA-POSS and PI (1.12 and 1.43 g/cm³,

respectively). The results are presented in Table I. The $^1\text{H-NMR}$ spectrum of the PAA-g-PMA-POSS copolymer containing 23.5 mol % MA-POSS is shown in Figure 1. The resonances labeled s_n are peaks associated with the deuterated DMF solvent.

Figure 2 shows the FTIR spectra of the pristine PI (part a) and the PI-g-PMA-POSS copolymers with different PMA-POSS contents (part b–e). The characteristic absorption bands of the imide group at 1786 and 1725 cm^{-1} suggest the presence of an imidized structure.⁷ The FTIR spectra of the PI-g-PMA-POSS copolymers show the presence of an aliphatic C–H stretching band between 2850 and 2950 cm^{-1} (attributable to cyclopentyl groups in PMA-POSS), confirming the presence of PMA-POSS molecules in the PI. The averaged molecular weight of the graft chains was estimated from the peroxide concentration of the ozone-preactivated PAA and the graft concentration. The M_n 's of the graft chains so calculated are also shown in Table I and are in range of 3600–9200 (Table I).

The thermal properties of the graft copolymers were studied by differential scanning calorimetry (DSC, Table I) in nitrogen. The pristine (ungrafted) PI has a T_g of about 317°C. The T_g of the graft copolymer decreases with the increase in graft concentration, as shown in Table I. Graft copolymerization with MA-POSS reduces the structural rigidity of the PI backbone and increases the molar-free volume of the polymer, resulting in the lowering of T_g .

TABLE I
Characteristics of the PAA-g-PMA-POSS Graft Copolymers and the Resulting PI-g-PMA-POSS Films

	PAA-g-PMA-POSS				PMA-POSS		PI-g-PMA-POSS			Dielectric constant ^e
	Mol % of a MA-POSS		Graft chain ^a	T_g^b (°C)	wt % ^g	vol % ^h	Theoretical density ^c (δ) (g/cm ³)	Measured density (d) (g/cm ³)	Increase in relative porosity ^d (p_r) (%)	
Pristine ⁱ	—	—	—	317	—	—	1.43	1.43	0	3.52
1	29.5	10.8	3600	308	24.0	28.7	1.34	1.31	3.6	3.01
2	40.1	16.3	5800	301	—	33.7	39.4	1.30	1.24	6.5
3	45.6	8.9	6900	294	37.8	43.7	1.29	1.20	9.1	2.35
4	55.7	23.5	9200	288	44.5	50.6	1.27	1.15	11.9	2.21

^a Averaged molecular weight of grafted chains was calculated from the peroxide concentration of the ozone-pretreated PAA (8×10 mol/g) and the graft concentration.

^b The glass transition temperature.

^c The theoretical density was estimated from the weight percentage of PMA-POSS in the nanocomposites and the densities of PMA-POSS and PI.

^d The increase in relative porosity was calculated from the equation stated in the text.

^e The dielectric constant was obtained at 1 MHz and 50% relative humidity under the ambient atmosphere.

^f Calculated from the ¹H NMR peak integrals.

^g Derived from the NMR data and converted to the mass basis.

^h The volume percentage of PMA-POSS in the nanocomposites was calculated based on the densities of PMA-POSS and PI (1.12 and 1.43 cm³, respectively).

ⁱ Pristine poly(amic acid) or corresponding polyimide.

Figure 3 shows the XRD curves of the MA-POSS (part a), PI-g-PMA-POSS nanocomposites with different PMA-POSS contents (part b-e), and PI (part f). There are five distinct diffraction peaks at $2\theta = 8.2^\circ$, 11.1° , 12.3° , 19.2° , and 24.9° for the MA-POSS, corresponding to d -spacings of 10.7, 7.9, 7.1, 4.6, and 3.6 Å, respectively. The peak corresponding to the d -spacing of 10.7 Å is caused by the size of the POSS molecule. The remaining peaks are produced by the rhombohedral crystal structure of the POSS molecules.³⁸ No

XRD peak is discernible for the pristine PI. A small, but distinct peak at $2\theta = 8.2^\circ$ is also observed in the diffraction patterns of the PI-g-PMA-POSS nanocomposites, indicating that POSS crystals with one dimension approximately equal to 1 nm remain in the copolymer.

The morphology of the fractured surfaces of the pristine PI and two PI-g-PMA-POSS nanocomposite films is revealed by the field-emission scanning electron microscopy (FESEM) images of Figure 4(a-c). The

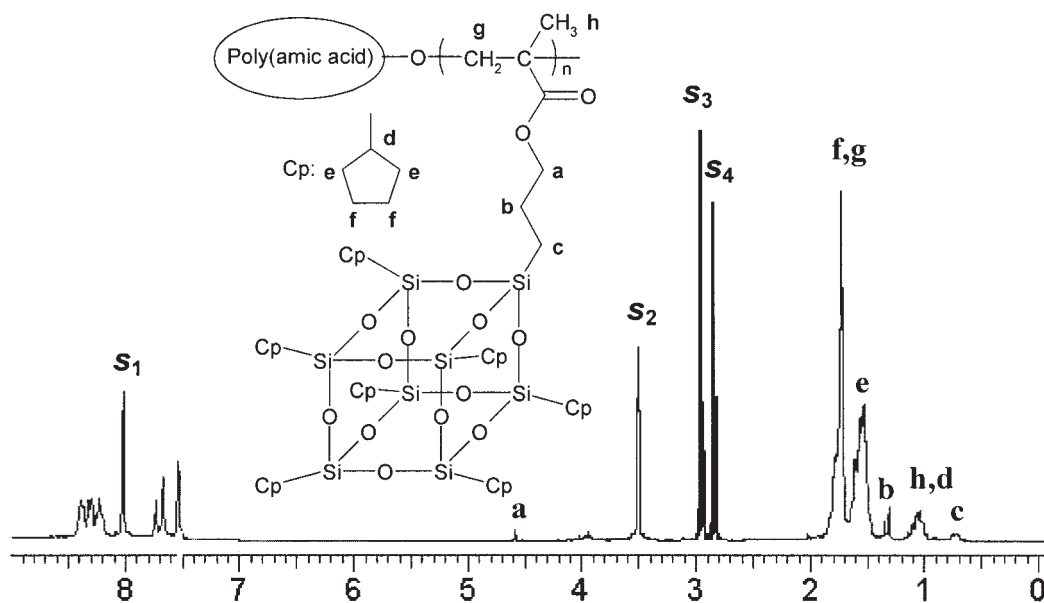


Figure 1 300 MHz ¹H-NMR spectrum of the PAA-g-PM-POSS copolymer containing 23.5 mol % MA-POSS. Resonances labeled s_n are solvent peaks associated with the deuterated solvent DMF.

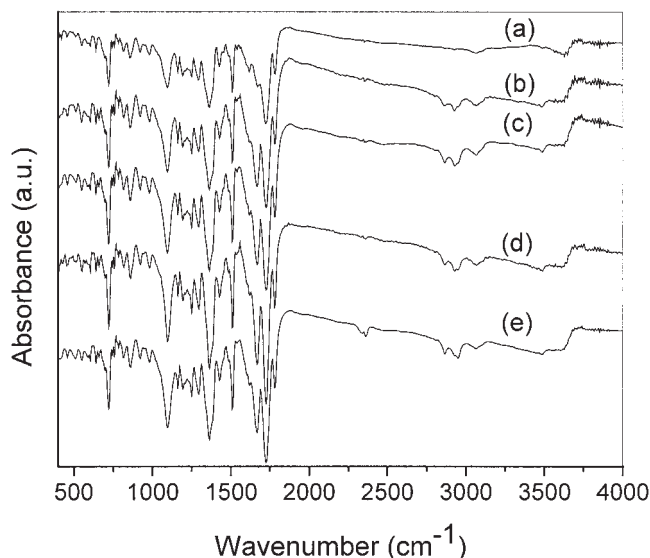


Figure 2 FTIR spectra of (a) the pristine PI, and the PI-g-PMA-POSS nanocomposites containing (b) 10.8 mol %, (c) 16.3 mol %, (d) 18.9 mol %, and, (e) 23.5 mol % MA-POSS.

pristine PI film has a dense (nonporous) morphology [Fig. 4(a)] For the copolymer containing 23.5 mol % MA-POSS [Fig. 4(b)] the light-gray spots of about 15–25 nm in size distributed across the dark background are probably the crystalline aggregates of the grafted PMA-POSS. For the copolymer with lower (18.9 mol %) content of MA-POSS, the concentration of aggregates decrease accordingly [Fig. 4(c)] The voids (dark spots) of about 15–20 nm in size in Figure 4 (b, c) are probably associated with the external porosity,

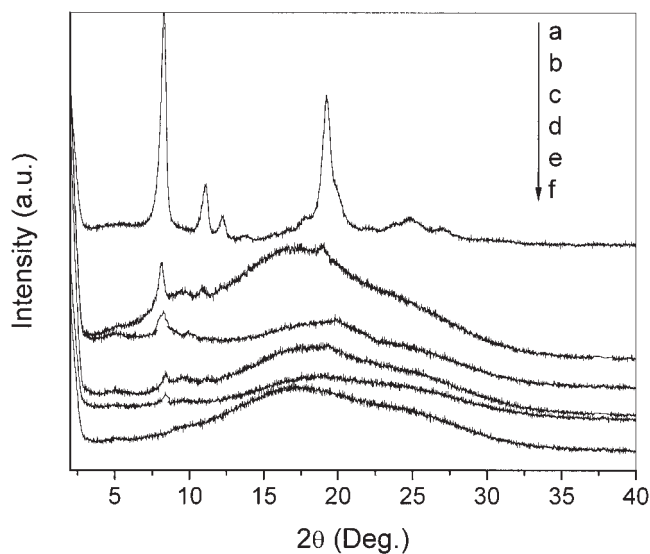


Figure 3 X-ray diffraction curves of (a) the methacrylcyclopentyl-POSS, the PI-g-PMA-POSS nanocomposites containing (b) 23.5 mol %, (c) 18.9 mol %, (d) 16.3 mol %, and (e) 10.8 mol % MA-POSS, and (f) the pristine PI.

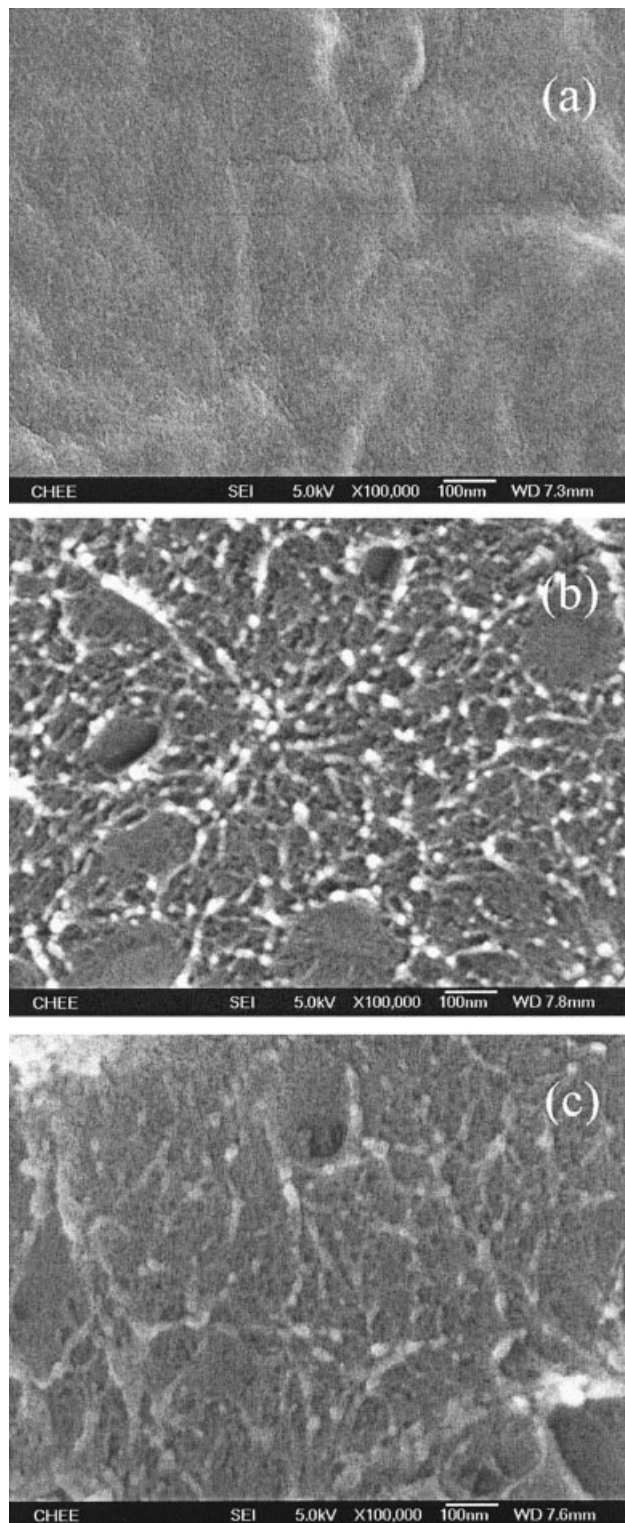


Figure 4 Field-emission scanning electron micrographs of fractured surface of (a) the pristine PI film, and the PI-g-PMA-POSS nanocomposite films containing (b) 23.5 mol % and (c) 18.9 mol % MA-POSS.

arising from the stacking of the PMA-POSS side chains and PI main chains.

Table I shows the dielectric constants (κ) and densities (d) of the PI-g-PMA-POSS nanocomposites. The

dielectric constant of the nanocomposites decreases as the amount of grafted PMA-POSS is increased. The lowest dielectric constant (measured at 1 MHz) of the PI-g-PMA-POSS nanocomposites containing 23.5 mol % MA-POSS is about 2.2, in comparison with the dielectric constant of 3.5 for the pristine PI film. Pure POSS macromolecules have been shown to have very low dielectric constants of 2.1–2.7, due to the inherent nanoporosity in the POSS molecules.²⁷ The ultimate κ value of the nanoporous PI-g-PMA-POSS films is governed by the intrinsic κ value of the PI matrix, and the changes in morphology and porosity introduced by the PMA-POSS side chains. Since the porosity of these nanocomposite films are difficult to measure (the size distribution of pores cannot be detected, for example, by small-angle X-ray scattering), a simple method was adopted to measure the relative porosity of these films. The increase in relative porosity (p_r) is defined as the sum of the increase in bulk porosity (p_b) due to stacking of the PMA-POSS side chains and the PI main chains, and the inherent nanoporosity (p_i) of the POSS molecules. It is calculated from eqs. (1) and (2):

$$p_b = [(\delta - d) / \delta] \times 100\% \quad (1)$$

$$p_i = 0.048 \times V\% \quad (2)$$

where the measured density (d) of PI-g-PMA-POSS nanocomposite film is obtained by dividing the weight of the film by its volume. The theoretical density (δ) of the PI-g-PMA-POSS nanocomposites is estimated from the weight percentage of PMA-POSS in the nanocomposite and the density of PMA-POSS and PI (1.12 and 1.43 g/cm³, respectively). $V\%$ is the volume percentage of MA-POSS in the nanocomposite. The nanoporous core of the POSS molecule, with a dimension of 0.54 nm in a POSS molecule of about 2 nm in size, represents only about 4.8 vol % of the total POSS volume.²⁶ The p_r for the 23.5 mol % PMA-POSS-grafted PI is about 11.9%.

The dielectric constant of the nanocomposites can be assumed to be a linear function of the molar concentration of the two components. For the PI-g-PMA-POSS copolymer containing 23.5 mol % MA-POSS, the dielectric constant, calculated from the linear concentration dependence, is 3.26. However, the dielectric constant of this sample was measured to be about 2.21. Therefore, the nanoporosity arising from the cores of the POSS molecules cannot solely account for the observed reduction in the dielectric constant of the nanocomposites. The reduction is most likely due to a combined contribution of the nanoporosity of the POSS molecules and the bulk porosity introduced by the grafting of PMA-POSS to the PI chains, as evidenced by the decrease in density and the increase in p_r value for the nanocomposite film when the amount

of PMA-POSS in the film is increased (Table I). The increase in the overall porosity of the nanocomposite film as a result of grafting of the PMA-POSS molecules can, in turn, be interpreted as an increase in the free volume of the nanocomposites arising from steric interactions of the PI main chains and the bulky PMA-POSS side chains. The increase in free volume of the PI matrix is consistent with the fact that the glass transition temperature (T_g) of the PI in the graft copolymer is lower than that of the pristine PI and decreases with the increase in PMA-POSS graft concentration.

CONCLUSIONS

Nanocomposites consisting of polyimide with POSS have been successfully synthesized by thermally-initiated free-radical graft copolymerization of methacrylcyclopentyl-POSS (MA-POSS) with the ozone-preactivated poly(amic acid), followed by thermal imidization. The dielectric constants of the resultant nanocomposites are lower than that of the pristine polyimide because of the increase in free volume arising from the bulky side chains, the less polar nature of the MA-POSS molecules, and the nano-voids inherent in the POSS molecules. The dielectric constants of the film can be tuned by varying the molar ratio of the grafted PMA-POSS side chains in the copolymer. Copolymers with dielectric constants approaching 2.2 could be achieved in the PI-g-PMA-POSS film containing 23.5 mol % MA-POSS. The crystalline structure of the POSS molecules in the grafted side chains was retained in the form of nano-aggregates in the composite films. Graft polymerization of MA-POSS with poly(amic acid) by the free-radical process provides a relatively simple and effective approach to the preparation of nanocomposites with low and tunable dielectric constants and well-preserved polyimide backbones.

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