Novel Epoxy Nanocomposite of Low D_k Introduced Fluorine-Containing POSS Structure

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ABSTRACT: A nanoporous additives, polyhedral oilgomeric silisesquioxane containing eight functional hexafluorine groups, octakis(dimethylsiloxyhexafluoropropyl ether)-silsesquioxane (OF) has been synthesized and blended with the UV-cured epoxy resin. The OF containing (10%) epoxy has significantly lower dielectric constant (2.65) than the plain epoxy (3.71). The incorporation of fluorine containing additives is well-known to reduce dielectric constant due to lower its polarizability. In addition, the presence of the bulky POSS structure is able to create additional free space or pores and further reduces the dielectric constant of the epoxy matrix. ©2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 502–510, 2007
Keywords: POSS; dielectric constant; epoxy resin; nanocomposite

INTRODUCTION

Hybrid materials with both inorganic and organic components are interesting from the standpoint of increased performance capabilities relative to either of the nonhybrid counterparts. The polyhedral oligomeric silsesquioxanes (POSS) as modifiers of organic polymers have received a great deal of attention recently. One special feature of POSS particles of about 1.5 nm in diameter is comparable to that of polymer segments. Incorporation of POSS particles into linear thermoplastics or thermoset networks can be used to modify the composition. These modifications can ultimately affect the thermal, oxidative, and dimensional stabilities of many polymer resins, thus upgrade properties for numerous high performance engineering applications. These enhancements have been applied to a wide range of thermoplastics and a few thermoset systems, that is methacrylates,[1,2] styrenes,[3] norbornenes,[4] epoxies,[5–10] and siloxanes[11] and so forth. Therefore, many nanocomposites using functionalized POSS derivatives with traditional plastics and resins can be designed. It has been reported that the monofunctional or multifunctional POSS-epoxy can be incorporated into the backbone of epoxy resin to improve its thermal properties.[5–10]

The need for lower dielectric constant materials become more stringent as the size of electronic devices is reduced to avoid cross talk

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between conducting wires. Further expounding on the RC time delay, the delay time τ can be approximate as by eq 1[12]

$$\tau = RC = 2\rho\varepsilon\varepsilon_0\left[\frac{4L^2}{P^2}+\frac{L^2}{T^2}\right] \qquad (1)$$

where τ is the sign delay time, R is the resistance, C is the capacitance, ρ is the specific resistance of the conductor, ε is the dielectric constant of the insulating material, ε_0 is the dielectric constant of the vacuum, L is the length of the conductor, P is the distance between two conducting lines, and T is the thickness of the conductor. Based on eq 1, increased sign speed can be obtained in three ways[13]: changing the layout and/or the ratio of width to thickness of the metal lines, decreasing the specific resistance of the interconnect metal, and decreasing the dielectric constant of the insulating material (intermetal dielectric). Investigations of low dielectric constant polymers usually involve two approaches, introducing the fluorine atoms on backbone of polymers and incorporating porosities in polymers.[14–17] Among all bulk materials, poly(tetrafluoroethylene) and some of its derivatives have the lowest dielectric constant with the values of ε between 1.9 and 2.1.[18] Since to the C—F bond possesses the lowest electronic polarizability, fluorine containing polymers are potential candidates for low-k applications.[19] The incorporation of the free space or pores in polymeric matrix is another attractive approach to decrease the dielectric constant because the dielectric constant of gases is not much different from that of vacuum ($\varepsilon \sim 1$).

In our previous work,[20] we introduced the octafunctional POSS-epoxy (OG, nanoporous structure) compounds into the epoxy resin to form a low dielectric constant epoxy resin and the dielectric constant of resulted epoxy resin containing OG is 2.85. In this investigation, we synthesized an octafunctional POSS-fluoride compound possessing structure with nanoporosities and hexafluorine atoms that we would expect to possess even lower dielectric constant of the resulted epoxy resin than the OG containing epoxy resin under the same POSS content.

EXPERIMENTAL

Materials

The octakis(dimethylsiliyloxy)silsesquixoxane $(HMe_2SiOSiO_{1.5})_8$ and platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(dvs)] were purchased from the Aldrich of USA. The allyl 1,1,2,3,3,3-hexafluoropropyl ether (AHFPE) was purchased from the Lancaster of USA. The DGEBA (DER 331, EEW = 190 g/eq) was purchased from Dow Chemical Company of USA. The salt triarylsulfonium hexafluoroantimonate (UVI 6974, photoinitiator) was purchased from Union Carbide Company of USA. Chemical structures used in this study are illustrated in Scheme 1.

Octakis(dimethylsiloxyhexafluoropropyl ether)silsesquioxane

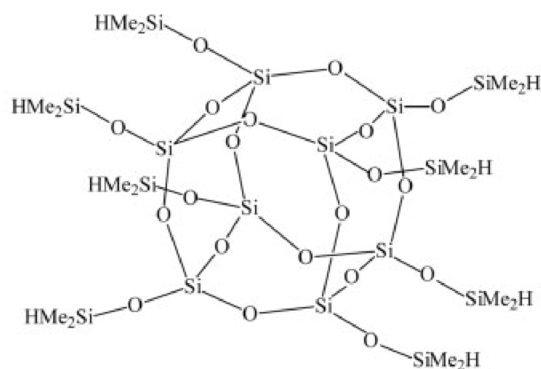
The preparation of the POSS-fluoride was carried out by adding the $(HMe_2SiOSiO_{1.5})_8$ (0.50 g, 0.49 mmol) in a magnetically stirred 25-mL Schlenk flask, toluene (5 mL) was added, and the solution was stirred for 5 min. AHFPE (0.62 mL, 3.92 mmol) was added and followed by adding 10 drops of 2.0 mM Pt(dvs). The mixture was stirred for 8 h at 80 °C, cooled, and dry activated charcoal added. After stirring for 10 min, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as 10 wt % clear solution. Solvents and unreactive AHFPE were removed in vacuum oven at 100 °C. It affords 1.05 g of an opaque viscous liquid (90% yield). The general synthetic reaction of OF is shown in Scheme 2.

Photopolymerization

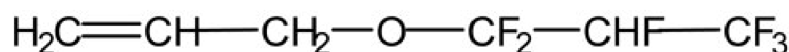
Table 1 shows codes and compositions used in this study. A typical process of photopolymerization was carried out by placing the desired reactant mixture onto a glass plate at a typical thickness of 300 μm. A 180 W medium-pressure arc lamp (λ_{max} = 366 nm) irradiated the sample at a distance of 10 cm for 70 min at room temperature. The UV-cured sample was then heated (for postcure) at 180 °C for 120 min.

Characterizations

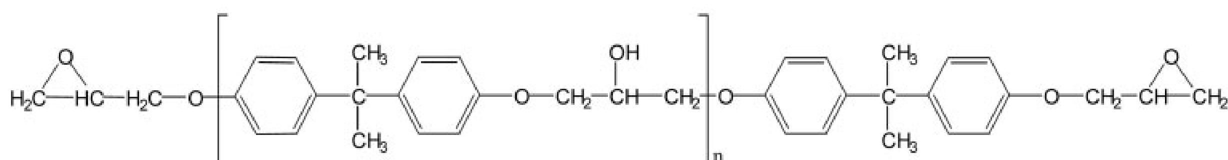
The sample was placed on a KBr pellet and FTIR spectra were obtained by using a Nicolet AVATAR 320 FTIR. ^{1}H-NMR experiments were performed at 500 MHz by using a Bruker AMX-500 FT NMR Spectrometer in $CDCl_3$. The glass transition temperature was obtained by a DuPont Dynamic Mechanical Analyzer (DMA Q800) and thermal stabilities were studied by a



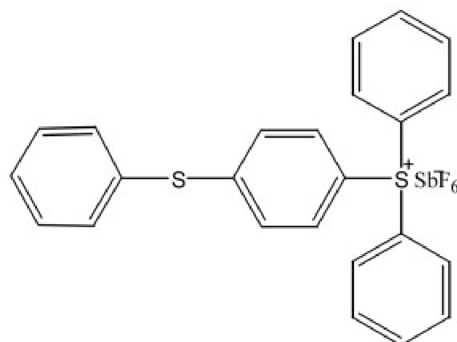
(A) $(HMe_2SiOSiO_{1.5})_8$



(B) Allyl 1,1,2,3,3,3-hexafluoropropyl ether



(C) DGEBA



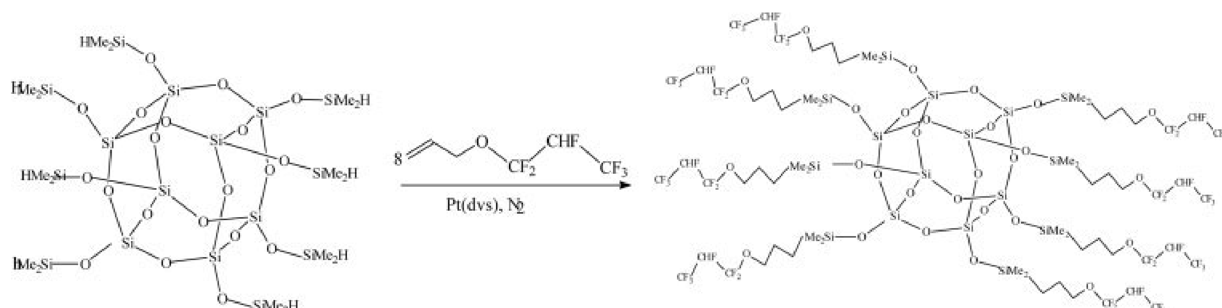
(D) UVI 6974

Scheme 1. Chemical structures of compounds used in this study.

DuPont Thermo-Gravimetric Analyzer (TGA Q50) under nitrogen flow. The dielectric constant was obtained by a DuPont Dielectric Analyzer (DEA 2970). The measured densities (d^{M}) of DGEBA-UVI 6974-OF system were obtained by dividing the weight of the films by their volume. At least three specimens were used for each density data point. The relative porosity increase was calculated based on eq 2.

$$\text{Relative porosity increase}(\phi_{\mathrm{r}}) = [(d^{\mathrm{T}} - d^{\mathrm{M}})/d^{\mathrm{T}}] \times 100\% + (0.048 \times V\%) \quad (2)$$

where d^{T} is the theoretical density of the DGEBA-UVI 6974-OF system estimated from the weight percentage of OF in the nanocompo-



Scheme 2. OF synthesis step.

site and the density of OF and epoxy (1.23 and 1.35 g/cm^3, respectively). *V%* is the volume percentage of OF in the nanocomposites. The scanning electron microscope (SEM) observations were performed on a JEOL 5300 apparatus. The samples were fractured in liquid nitrogen and the fracture surfaces were contrasted with gold.

RESULTS AND DISCUSSIONS

Characterizations of Octakis(dimethylsiloxyhexafluoropropyl ether)silsesquioxane

The cube structure of OF was characterized by FTIR and ^{1}H-NMR. The FTIR spectra of pure POSS, AHFPE, and OF (POSS-fluoride) are shown in Figure 1. Figure 1(A) shows a sharp, strong, and symmetric Si—O—Si stretching peak at ~1100 cm^{-1} typical of silsequioxane cages and a relatively smaller Si—H stretching peak at ~2140 cm^{-1}.[21,22] The AHFPE shows a small CH_2=CH— stretching peak at ~1640 cm^{-1} as shown in Figure 1(B). Figure 1(C) shows that both Si—H and CH_2=CH peaks are disappeared, implying that the allyl group of AHFPE has reacted with Si—H of POSS to form a covalent bond in the POSS structure while the —CF_2—, —CHF— and —CF_3 peaks of AHFPE are still present on Figure 1(C).[23] Figure 2(A) shows the chemical shifts of ^{1}H-NMR of POSS for —CH_3 group at 0.11 ppm and —Si—H group at 4.71 ppm. Figure 2(B) shows the chemical shifts of the AHFPE where the CH_2=CH— groups are at 5.90, 5.35, and 5.25, ppm, respectively. Figure 2(C) shows chemical shifts of the OF where the CH_2=CH— group of AHFPE is converted into —CH_2—CH_2— group of OF by shifting chemical shifts of 5.90, 5.35, and 5.25 ppm into two peak groups, group one at 0.6 and 1.70 ppm and group two at 0.85 and 1.30 ppm. The ratios of integrated areas of group one and group two is 4:1. Therefore, the chemical structures of OF are approximately 80% in the form of structure (i) and 20% in the form of structure (ii)as indicated in Figure 2(C). Both Figure 2(B) and Figure 2(C) show the chemical shifts of the —CHF— group at 4.73 and 4.81 ppm. The —Si—H of POSS chemical shift at 4.71 ppm is disappeared in Figure 2(C). Therefore, the POSS reacting with AHFPE

Table 1. Codes and Compositions of Materials Prepared in This Study

Codes	Components
F0	DGEBA:UVI 6974:OF = 100:5:0 (phr)
F3	DGEBA:UVI 6974:OF = 100:5:4 (phr)
F5	DGEBA:UVI 6974:OF = 100:5:6.7 (phr)
F10	DGEBA:UVI 6974:OF = 100:5:13.3 (phr)
F15	DGEBA:UVI 6974:OF = 100:5:20.5 (phr)

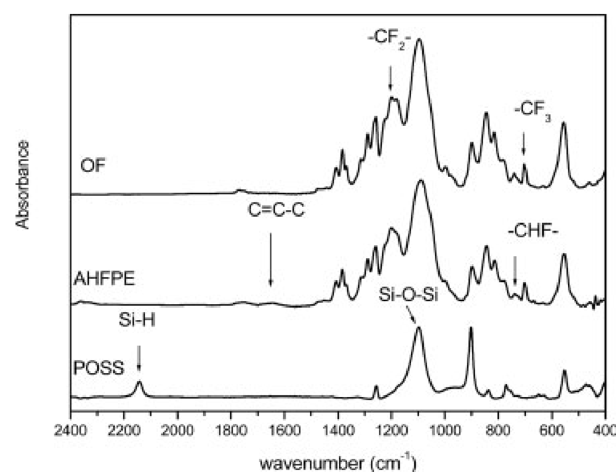


Figure 1. FTIR spectra of the POSS, AHFPE, and OF.

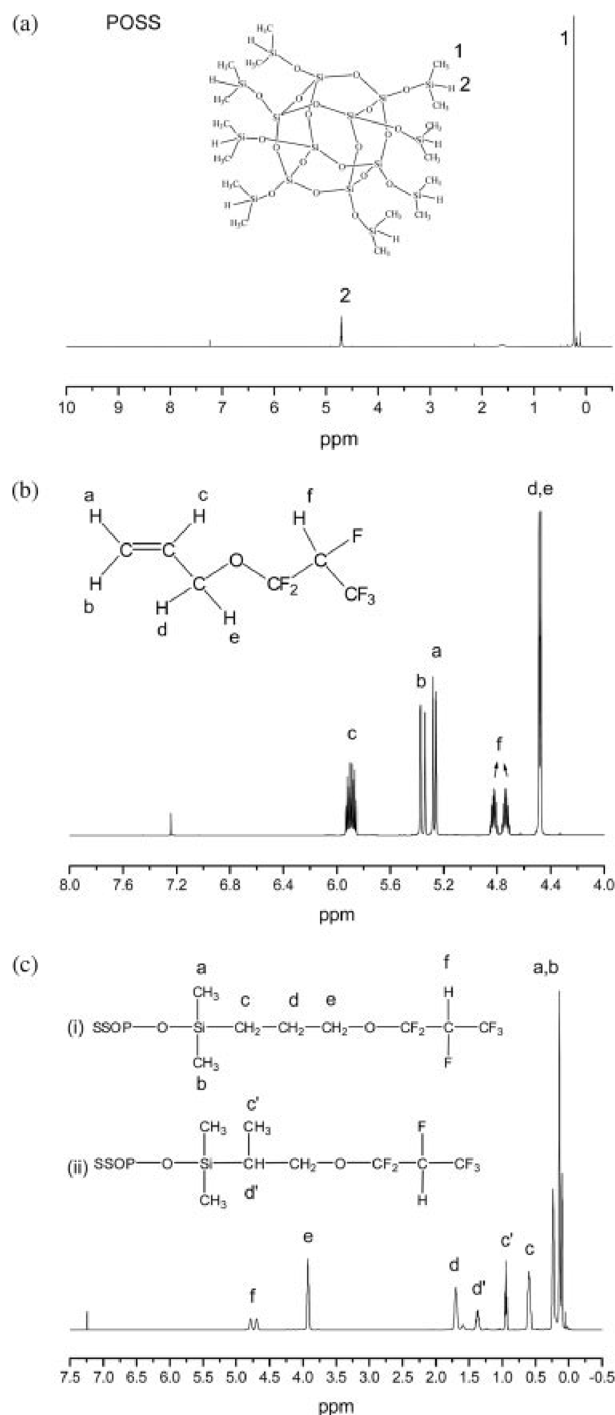


Figure 2. ^{1}H-NMR spectra of the (A) POSS, (B) AHFPE, and (C) OF.

through hydrosilylation[24] has been positively verified by FTIR and ^{1}H-NMR.

Thermal Properties of OF

Both of FTIR and ^{1}H-NMR results confirmed the OF structure. The thermal properties of OF were characterized by DSC and TGA. Figure 3 shows the DSC thermogram of OF under nitrogen atmosphere and the results are summarized in Table 2. The glass transition temperature of OF is at –79.5 °C. Figure 4(A) shows the typical TGA thermogram of OF and Figure 4(B) shows the DTG thermogram of OF under nitrogen atmosphere and the results are listed in Table 2. The 5% mass loss temperature is 281.4 °C and the char yield of 31.3% at 750 °C. The DTG result indicated that the OF has three decomposed steps and the peaks maximum of DTG are at 320.4, 435.2, and 501.8 °C, respectively.

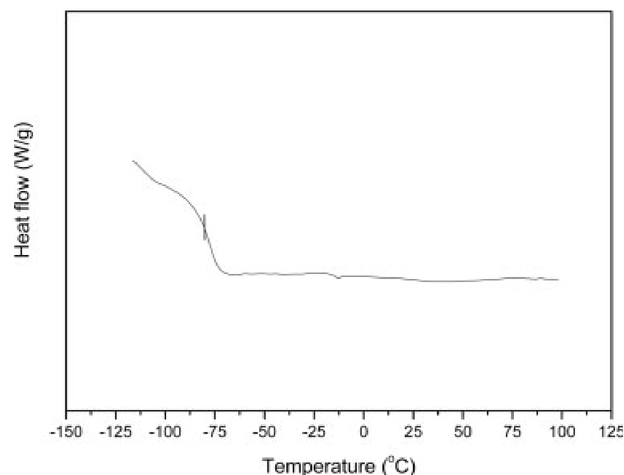


Figure 3. DSC thermogram of OF under an N_2 atmosphere.

Thermal Properties of DGEBA-UVI 6974-OF System

The glass transition temperature of OF epoxy was characterized by DSC. Figure 5 shows the

Table 2. Thermal Properties of DGEBA-UVI 6974-OF System

Code	T_g (°C)	T_{dec} (°C, 5% loss)	Char Yield (%) at 700 °C
OF	−79.5	281.4	31.3
F0	132.1	398.4	12.0
F3	86.7	366.6	12.8
F5	82.5	356.7	13.4
F10	77.0	355.5	15.7
F15	71.3	339.6	18.2

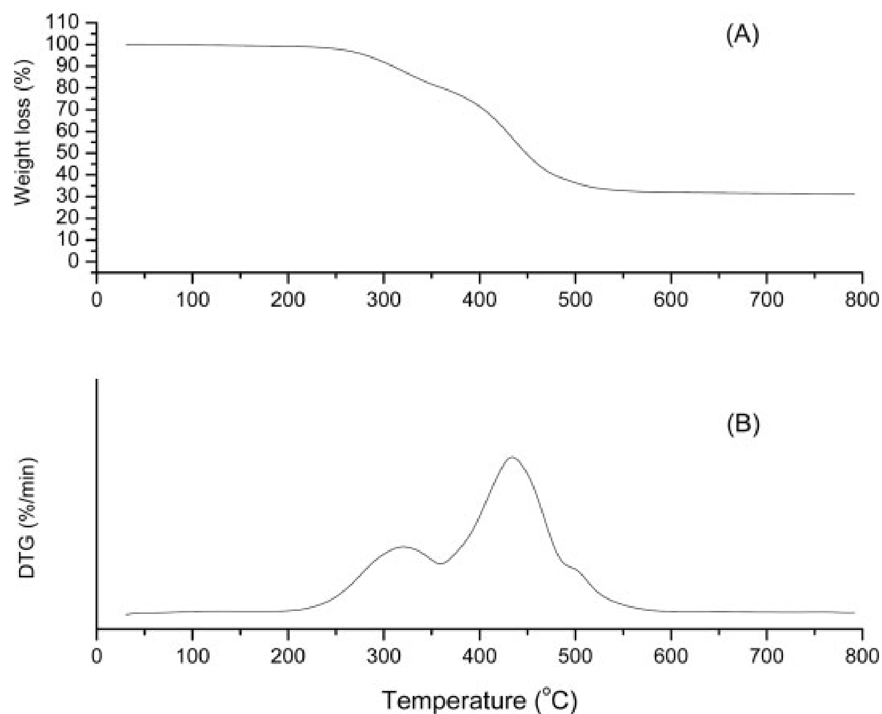


Figure 4. TGA thermogram of OF under an N_2 atmosphere.

DSC thermograms of cured epoxies containing various contents of OF and the results are summarized in Table 2. It clearly shows that the glass transition temperature of OF containing epoxy is lower than the plain epoxy. The presence of OF tends to hinder epoxy curing reaction and causes lower crosslinking density and thus lower T_g as would be expected. In addation, the presence of OF can act as a plasticizer to further decrease the glass transition temperature of the epoxy resin.

The thermal stabilities investigated by TGA. The TGA thermograms of epoxy resins containing different OF contents under a N_2 atmosphere are shown in Figure 6 and Table 3. The trend clearly shows that the 5% mass loss tem-

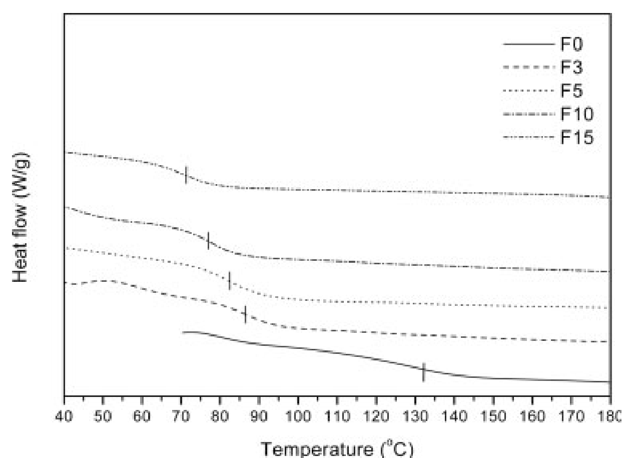


Figure 5. DSC thermogram of DGEBA-UVI 6974-OF system under an N_2 atmosphere.

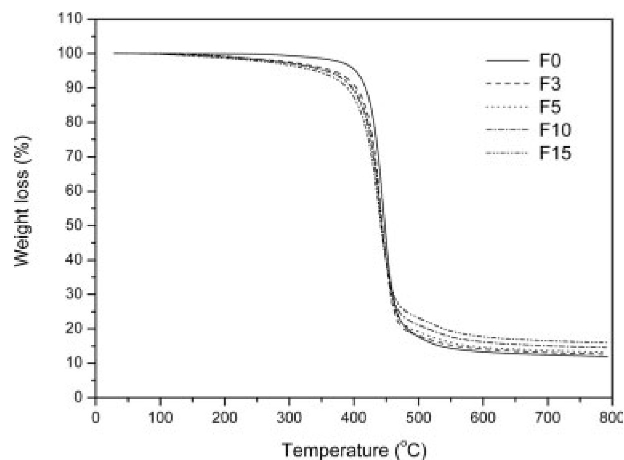


Figure 6. TGA thermograms of DGEBA-UVI 6974-OF system under an N_2 atmosphere.

Table 3. Dielectric Property and Density of DGEBA-UVI 6974-OF System

	Dielectric Permittivity at 25 °C	Theoretical Density[a] (d^T) (g/cm^3)	Measured Density (d^T) (g/cm^3)	Relative-Porosity-Increase (φr) (%)	Density of Epoxy Resin in Nanocomposite (d^N) (g/cm^3)	Fraction Free Volume (FFV)
F0	3.71 ± 0.03	1.35	1.35	0	1.35	0.36
F3	3.12 ± 0.01	1.35	1.26	7.16	1.25	0.37
F5	2.91 ± 0.02	1.34	1.24	9.69	1.24	0.38
F10	2.80 ± 0.02	1.34	1.22	10.33	1.21	0.39
F15	2.65 ± 0.02	1.33	1.17	14.18	1.15	0.41

[a] Theoretical density (d^T): estimated from the weight percentage of OF in the nanocomposite and the density of OF and Epoxy (1.22 and 1.35 g/cm^3).

peratures (T_{dec}) of epoxy containing OF system are lower than the plain epoxy. The OF possesses lower T_{dec} (281.4 °C) and its presence tends to decrease the epoxy crosslinking density. Therefore, the T_{dec} of epoxy resin decreases with increasing OF content. The char yield increases with increasing OF content. A POSS structure is thermally degraded, silica and SiO_2 are typically formed to contribute higher char yield. Therefore, greater OF content results in higher char yield as would be expected.[6,22]

Morphology of DGEBA-UVI 6974-OF System

The morphology of the DGEBA-UVI 6974-OF system was investigated by scanning electron microscopy (SEM). Figure 7 presents SEM images of the fracture surface of specimens created by freezing in liquid nitrogen. Figure 7(A) shows that a smooth fracture surface is formed from the neat epoxy without OF. The spherical OF particles increase with the increase of the OF content due to immiscibility OF and the cured epoxy.

Dielectric Constant of DGEBA-UVI 6974-OF System

Dielectric constants of the epoxy resins containing OF were studied at 100 kHz by DEA and the results are summarized in Table 3. The dielectric constant of the epoxy decreases steadily with the increase of the OF content. In this system, two factors are responsible for the lower dielectric constant of the resulted epoxy resin. The incorporation of fluorine atoms is particularly effective in lowering the polarizability [25] due to their high electronegativity leading to tight binding of electrons. The relative porosity increase (ϕ_r) shown in Table 3 is defined as the sun of increased external porosity due to the incorporation of OF molecules in epoxy resin and the intrinsic nanoporosity of OG molecules calculated based on eq 1. The ϕ_r of DGEBA-UVI 6974-OF system is increased with the increase of OF content. The increase of ϕ_r is partially attributed from the nanoporosity in cores of POSS molecules.[26,27] The external porosity of DGEBA-UVI 6974-OF system introduced by tethering OG to epoxy resin is another factor to decrease its dielectric constant.

Therefore, the dielectric constant of the epoxy decreases steadily with the increase of the nonreactive OF content and it is more effective to decrease the dielectric constant of epoxy resin than the reactive OG under the same POSS content.

CONCLUSIONS

A new epoxy blended with a fluorinated POSS containing additives (OF) is able to significantly reduces its dielectric constant of the UV-cured epoxy resin. At 10% OF content, the dielectric constant is 2.65, which is substantially lower than the plain epoxy at 3.71. The glass transition temperature (T_g) and thermal decomposition temperature (T_{dec}) of OF containing epoxy are lower than the plain epoxy. However, the char yield of OF containing epoxy is higher because the POSS structure is degraded into silica and SiO_2.

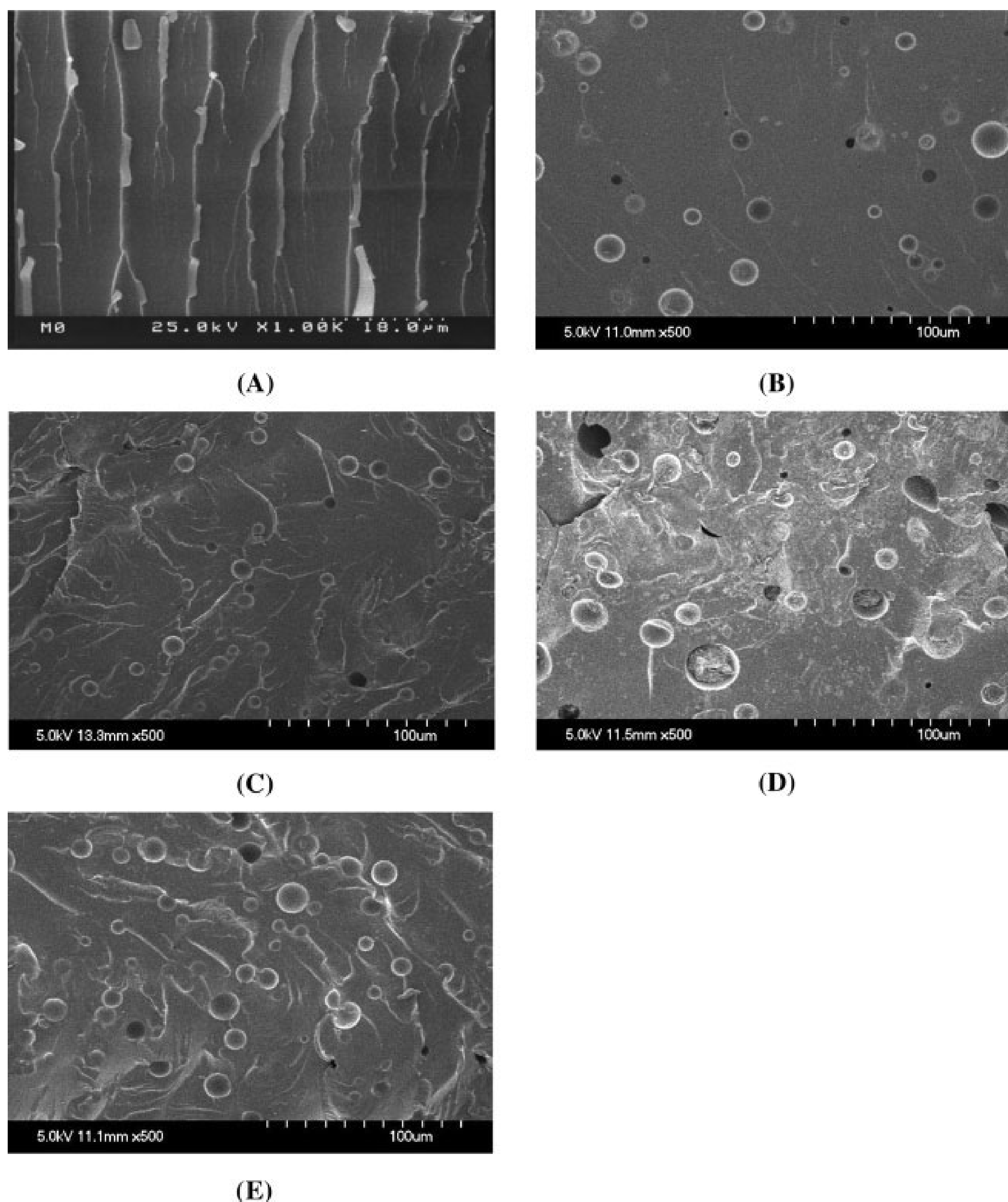


Figure 7. The SEM micrographs of cross section of DGEBA-UVI 6974-OF system (A) F0; (B) F3; (C) F5; (D) F10; (E)F15.

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