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Preparation, morphology, and ultra-low dielectric constants of benzoxazine-based polymers/polyhedral oligomeric silsesquioxane (POSS) nanocomposites

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ABSTRACT

Nanocomposites of benzoxazine-based polymers/polyhedral oligomeric silsesquioxane (POSS) have been prepared through copolymerization of furan-containing benzoxazine compounds and methylmethacrylate-POSS (MMA-POSS). Nanocomposites having MMA-POSS fractions of 0–70 wt% (POSS fractions of 0–28 wt%) are obtained. The high contents of MMA-POSS of the nanocomposites result in a reduction of their dielectric constants to 2.3. Moreover, some nanocomposites display POSS orientation into lamellar structures in nanometer sizes. The POSS orientation further reduces the dielectric constants of the nanocomposites to about 1.9. Hence, the prepared nanocomposites could be used as ultra-low-*k* materials for advanced microelectronics.

1. Introduction

Benzoxazines (Bz) are thermally curable compounds being capable of transformation to cross-linked polymers by means of ring-opening addition polymerization [1–4]. The benzoxazine-based polymers are phenolic-like, as Bz polymers and phenolic resins have similar precursors and chemical structures. Nevertheless, benzoxazine-based polymers have some favorable properties over conventional phenolic resins, including small shrinkage in curing, low water absorption, good thermal stability, high glass transition temperatures, and low-cost and versatile raw materials [4]. On the other hand, modification and functionalization of benzoxazine-based polymers still have received research attention to further enhance their properties. Some efforts with purposes of increasing cross-linking densities and glass transition temperatures [3,5–8], improvement thermal stability and flame resistance [9–11], enhance toughness and flexibility [12–15], and reduce dielectric constants [16–22] have been reported.

Low dielectric constant (low-*k*) polymers are expected for modern microelectronics and electrical products. Hence, reduction of the dielectric constants of benzoxazine-based polymers has attracted certain attention of researchers. Fluorination has successfully reduced the dielectric constants of benzoxazine-based polymers from 3.5 to about 2.2–2.4 [16–19]. Incorporation of dicyclopentadiene moieties to poly(benzoxazine)s could also effectively reduce their dielectric constants to around 3.1, owing to the low polarity of dicyclopentadiene moieties [20,21]. Fabrication of poly(benzoxazine)s into porous thin films is another effective approach to reduce their dielectric constants. Porous poly(benzoxazine) films with low dielectric constants of about 1.95 have been reported in Ref. [22]. The drawbacks of this approach are involving complicated preparation routes and sacrificing mechanical strengths of the obtained poly(benzoxazine) thin films. Moreover, the generated pores might be collapsed during thermal cycles in post process or utilization. Nanoporous cross-linked organosilicates have been developed to prevent the collapse of pores of the ultra-low dielectric materials [23–25]. Nevertheless, this methodology is not suitable for benzoxazine-based polymers.

Introduction of polyhedral oligomeric silsesquioxane (POSS) has been demonstrated as an effective approach to reduce the dielectric constants of polymers [26–32]. Formation of polymer/POSS nanocomposites could simultaneously lower the dielectric constants and enhances the mechanical properties of polymers. Nevertheless, over-loaded POSS might induce macro-phase separations in polymer/POSS nanocomposites because of the less compatibility between polymer-rich and POSS-rich domains. Hence, the POSS fractions of polymer/POSS nanocomposites as well as the reduction of their dielectric constants are within certain limits. As a result, the previous studies on poly(benzoxazine)/POSS nanocomposites focused on studying their thermal behaviors, mechanical properties, and morphologies [33–36]. Less attention has been paid to their dielectric constants.

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Multifunctional methylmethacrylate-POSS (MMA-POSS) possesses reactive methylmethacrylate groups which could undergo thermo-induced radical self-polymerization and Diels–Alder addition reaction with diene groups [37,38]. The features make MMA-POSS be a suitable reactive-additive for preparation of polymer/POSS nanocomposites. In our previous work [38], polymer/POSS nanocomposites have been prepared from MMA-POSS (as a dienophile) and a tri-functional furan compound (as a diene) through Diels–Alder reaction. Thermally curing the nanocomposite resulted in a highly cross-linked material, which showed a surprisingly low dielectric constant of 1.47. In the present study, furan-containing benzoxazine compounds have been utilized to react with MMA-POSS for the preparation of low-*k* poly(benzoxazine)/POSS nanocomposites. The morphologies and dielectric constants of the poly(benzoxazine)/POSS nanocomposites are studied. POSS-rich domains could self-assemble into lamellar structures in the poly(benzoxazine)/POSS nanocomposites. The POSS cages and their self-assembled lamellar structures result in a reduction of dielectric constant to about 2.0. The low dielectric constants of the prepared poly(benzoxazine)/POSS nanocomposites warrant their potential of applications for advanced microelectronics electrical products.

2. Experimental

2.1. Materials

Furan-containing benzoxazine compounds, 3-furfuryl-3,4-dihydro-2H-1,3-benzoxazine (Ph-FBz) and bis(3-furfuryl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BPA-FBz), were prepared according to the reported method [8]. Bismaleimide (BMI) was purchased from Aldrich Chemical Co. Poly(benzoxazine) (PBz) containing benzoxazine groups in the main chain has been prepared in the Lab. using BPA-FBz and BMI as monomers by means of Diels–Alder reaction. The preparation and characterization of PBz polymer has been reported in our previous paper [14]. MMA-POSS was purchased from Hybrid Plastics Co. (Fountain valley, CA). Tetrahydrofuran (THF) from TEDIA Chem. Co. and 1-methyl-2-pyrrolidinone (NMP) from Aldrich Chemical Co. were used as received.

2.2. Characterization

Scanning electron micrographs (SEM) were obtained using a Hitachi S-4800 field-emission SEM. Transmission electron micrographs were recorded using a Hitachi H-7500 TEM. Cross-linked samples were encapsulated with epoxy resin and then the samples were cured at 70 °C for 24 h in a vacuum oven. The samples were then microtoned (Leica Ultracut Uct) into slices with a thickness of about 80 nm. The slices were then placed on 200-mesh copper grids for TEM observation. Dielectric constants were measured according to the method described below. The capacitance of the films (dried at 120 °C under vacuum for 8 h prior to measurements) was measured on a Hewlett–Packard model 4280A material analyzer at a frequency of 1 MHz. The dielectric constants of the films can be calculated from their capacitances and thicknesses. Poly(tetrafluoroethylene) film has been taken as a reference for dielectric constant measurements. Refractive index was measured with an Abbe 5 Refractometer (at 589 nm) from the Bellingham and Stanley Company (UK). Thermal stability of samples was measured with a thermogravimetric analyzer (TGA, Thermal Analysis TGA-Q500) at a heating rate of 10 °C/min in nitrogen. The glass transition temperatures (T_g) of samples were measured with a dynamic mechanical analyzer (DMA, Thermal Analysis DMA-Q800). The peak temperature of the tan δ plot was taken as T_g of the sample.

2.3. Preparation of poly(benzoxazine)/POSS nanocomposites

Various series of poly(benzoxazine)/POSS nanocomposites have been prepared in this work using furan-containing benzoxazines and MMA-POSS as precursors. The method and reactions for the preparation of poly(benzoxazine)/POSS nanocomposites are shown in Table 1 and Fig. 1.

The method to prepare the nanocomposites of Ph-FBz and MMA-POSS is described below. Ph-FBz and MMA-POSS in various weight ratios were dissolved in THF (4.0 g in 20 mL). While the solutes completely dissolved, the solution was poured into a Teflon-coated stainless mold. The sample was heated at 80 °C for 30 min to remove the solvent. The residual was thermally cured at 160 °C for 1 h, 180 °C for 2 h, and 240 °C for 2 h. In the curing process, Ph-FBz and MMA-POSS polymerized by means of the ring-opening addition reaction of benzoxazine groups and the radical addition reaction of methylmethacrylate groups, respectively. The obtained products were coded as PPh-FBz/MMA-POSS-X, where X denotes the weight fraction of MMA-POSS of the sample. Samples with X = 0, 0.3, 0.5, and 0.7 have been prepared. Nanocomposites of BPA-FBz and MMA-POSS have been prepared using the same method. The products were coded as PBPA-FBz/MMA-POSS-Y, where Y denotes the weight fraction of MMA-POSS. Samples with Y = 0, 0.3, 0.5, and 0.7 have been prepared.

Moreover, another series of poly(benzoxazine)/POSS nanocomposite samples have also been prepared using the same precursors but different curing processes. First, the mixtures of benzoxazine and MMA-POSS were left to react at 160 °C for 36 h. In this stage, Ph-FBz (or BPA-FBz) reacted with MMA-POSS through Diels–Alder (DA) reaction between the furan (diene) groups of benzoxazines and the methylmethacrylate (dienophile) groups of MMA-POSS. After the DA reaction, the products were not taken out and were further cured at 180 °C for 2 h and 240 °C for another 2 h. At this stage, DA adducts of Ph-FBZ (or BPA-FBz) and MMA-POSS might break down to regenerate furan and methylmethacrylate groups through retro-DA reaction. Meanwhile, polymerization of benzoxazine and methylmethacrylate groups carried out to result in highly cross-linked samples. A prefix "DA-" has been added to code the nanocomposites prepared with this DA reaction method.

Table 1
Methods and reactions for preparation of poly(benzoxazine)/MMA-POSS nanocomposites.

Nanocomposite samples	Preparation method	Reactions
PPh-FBz/MMA-POSS or PBPA-FBz/MMA-POSS	Co-curing Ph-FBz (or BPA-FBz) and MMA-POSS at 160 °C for 1 h, 180 °C for 2 h, and 240 °C for 2 h.	Ring-opening addition reaction of benzoxazine ring of Ph-FBz (or BPA-FBz); Radical polymerization of MMA groups of MMA-POSS.
DA-PPh-FBz/MMA-POSS or DA-PBPA-FBz/MMA-POSS	Diels–Alder (DA) reaction between Ph-FBz (or BPA-FBz) and MMA-POSS at 160 °C for 36 h; Further curing the DA adducts at 180 °C for 2 h and 240 °C for another 2 h.	Diels–Alder (DA) reaction between Ph-FBz (or BPA-FBz) and MMA-POSS to result in DA adduct; Ring-opening addition reaction of benzoxazine ring of BPA-FBz; Radical polymerization of MMA groups of MMA-POSS.
PPBz/MMA-POSS	Co-curing PBz and MMA-POSS at 160 °C for 1 h, 180 °C for 2 h, and 240 °C for 2 h.	Ring-opening addition reaction of benzoxazine ring of BPA-FBz; Addition polymerization of maleimide groups; Radical polymerization of MMA groups of MMA-POSS.

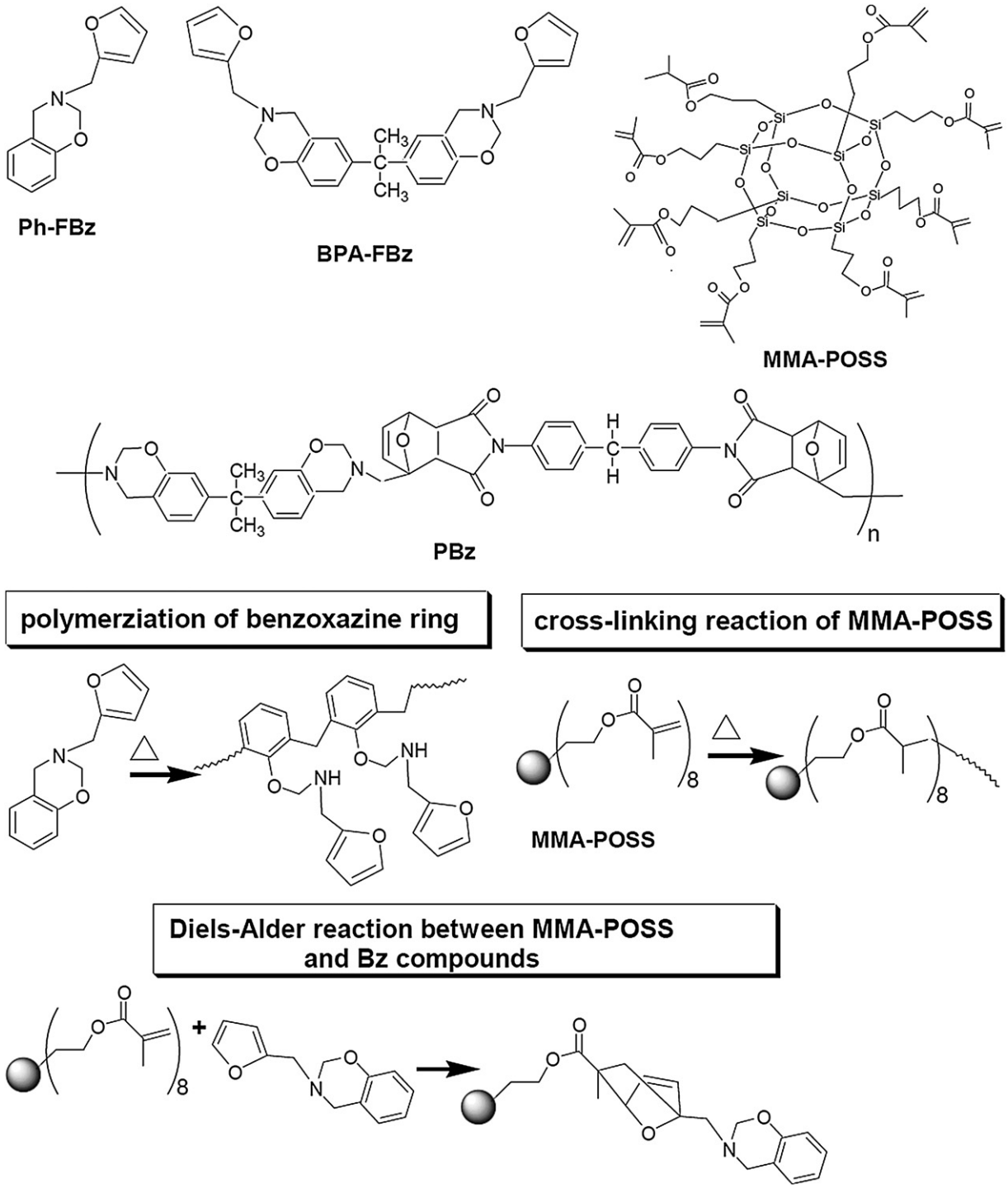

Fig. 1. Chemical structures and reactions of benzoxazine compounds and MMA-POSS.

For example, the PPh-FBz/MMA-POSS-0.5 nanocomposite which was prepared with the DA method has a code of DA-PPh-FBz/MMA-POSS-0.5.

Nanocomposites of PBz and MMA-POSS were also prepared. PBz and MMA-POSS in various weight ratios were dissolved in NMP (4.0 g in 20 mL). While the solutes completely dissolved, the solution was poured into a Teflon-coated stainless mold. The mixture was heated at 120 °C under a reduced pressure for 30 min to remove NMP. The residual was cured at 160 °C for 1 h, 180 °C for 2 h, and 240 °C for 2 h. The products were coded as PPBz/MMA-POSS-Z, where Z denotes the weight fraction of MMA-POSS. Samples with Z = 0, 0.1, 0.15, 0.3, and 0.5 have been prepared.

MMA-POSS possesses about 40 wt% of POSS [37]. Hence, the weight fraction of POSS in each of the prepared poly(benzoxazine)/POSS nanocomposite is equal to 40% of its weight fraction of MMA-POSS. For example, PBPA-FBz/MMA-POSS-0.7 contains 70 wt% of MMA-POSS, which corresponds to 28 wt% of POSS.

3. Results and discussion

3.1. Morphology and dielectric constants of poly(benzoxazine)/POSS nanocomposites

Poly(benzoxazine)/POSS nanocomposites have been prepared using furan-containing benzoxazines (Ph-FBz and BPA-FBz) and MMA-POSS as precursors (Table 1, Fig. 1). Both benzoxazine compounds and MMA-POSS could undergo thermally induced cross-linking reactions. Fig. 2 shows the DSC thermogram of the mixture of Ph-FBz/MMA-POSS. Only one exothermic peak appears in the thermogram. Hence, thermo-polymerizations of benzoxazine and MMA-POSS could simultaneously carry out in the temperatures of about 200–240 °C. Cross-linked poly(benzoxazine)/POSS nanocomposites have been obtained from thermally curing the mixtures of the precursors.

Fig. 3 shows the photographs of poly(benzoxazine)/POSS nanocomposites. All samples are highly transparent. As a result, macrophase separations do not occur between the poly(benzoxazine) and POSS domains of the nanocomposites. Neat poly(benzoxazines)s shows deep brown color. The colors of the poly(benzoxazine)/POSS nanocomposites are relatively light. Addition of MMA-POSS to poly(benzoxazines)s lightens their colors, as the color of neat MMA-POSS-based resin is light yellow [37]. Moreover, cracks do not happen to the nanocomposites containing MMA-POSS as high as 70 wt%, indicating their acceptable mechanical property.

The morphologies of the nanocomposites have been first investigated using SEM (Fig. 4). For poly(benzoxazine)/POSS nanocomposites, the POSS-rich domains has higher hardness compared to that of the polymer-rich domains. Hence, the POSS-rich domains display bright areas in the SEM micrographs of poly(benzoxazine)/POSS nanocomposites [29,33,36,38,39]. POSS-rich phases (the relatively bright areas) in various sizes and shapes appear in the SEM micrographs of PPh-FBz/MMA-POSS nanocomposites. The POSS-rich phases of PPh-FBz/MMA-POSS-0.3 are in round shapes and in sizes of about 60–80 nm. They homogeneously disperse in polymer-rich matrix without gathering together. The portions of the POSS-rich domains increase with increasing the MMA-POSS contents of the nanocomposites. While the nanocomposite contains 70 wt% of MMA-POSS, the POSS-rich phases become the major matrix of the nanocomposite. As it can be seen in the SEM image of PPh-FBz/MMA-POSS-0.7, the POSS-rich phases form pillar-like structures with somewhat regularity. The SEM micrographs of PBPA-FBz/MMA-POSS samples are also shown

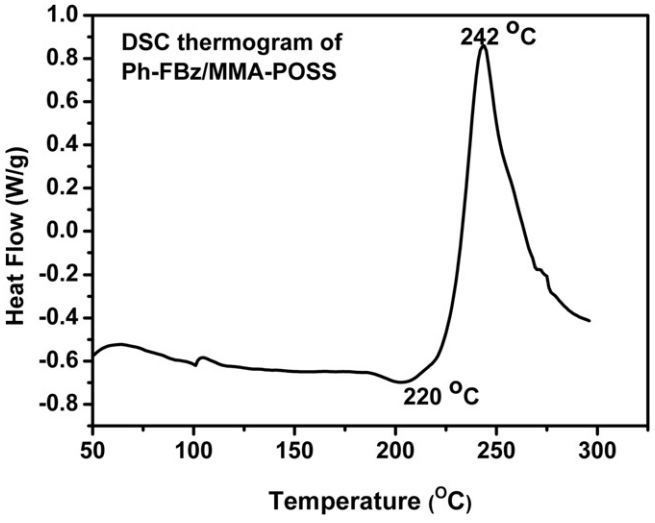

Fig. 2. DSC thermogram of Ph-FBz/MMA-POSS mixture.

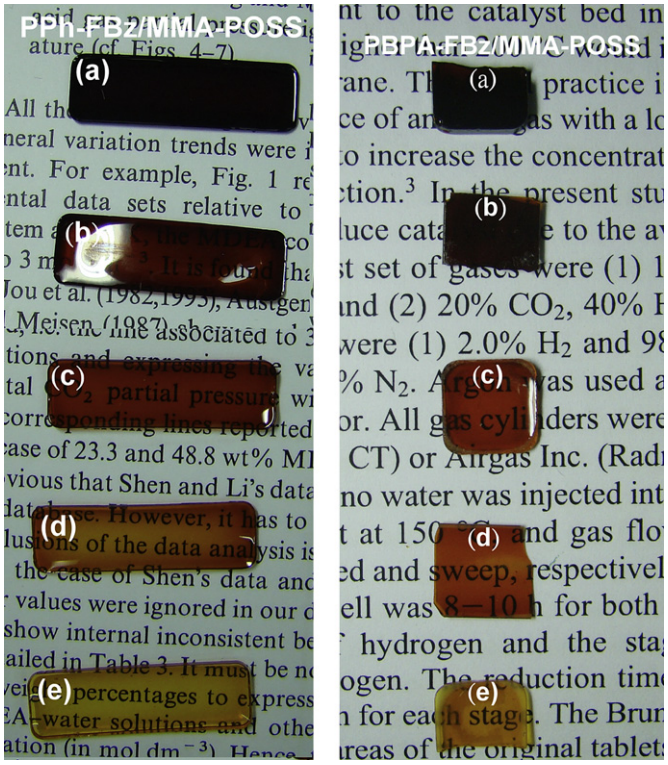

Fig. 3. Photographs of poly(benzoxazine)/MMA-POSS nanocomposites. The fractions of MMA-POSS of the nanocomposites are (a) 0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0.

in Fig. 4. Pristine PBPA-FBz shows a dense and homogeneous structure. POSS-rich phases appear in the SEM images of PBPA-FBz/MMA-POSS nanocomposites. The fractions and sizes of the POSS-rich domains increase with increasing the MMA-POSS contents of the nanocomposites. Like PPh-FBz/MMA-POSS-0.7, the POSS-rich domains become the major matrix of PBPA-FBz/MMA-POSS-0.7. Nevertheless, the dispersion patterns of the POSS-rich domains in PBPA-FBz/MMA-POSS samples are different from what in PPh-FBz/MMA-POSS nanocomposites. PBPA-FBz has higher cross-linking density compared to PPh-FBz [8]. As a result, PBPA-FBz is relatively rigid. The rigid structure of PBPA-FBz depresses POSS agglomeration in the preparation process of the PBPA-FBz/MMA-POSS nanocomposites. As a result, the POSS-rich domains in PBPA-FBz/MMA-POSS nanocomposites are relatively small and hazy.

Fig. 5 shows the dielectric constants of the samples measured at 1 MHz and 25 °C. The dielectric constants of PPh-FBz and PBPA-FBz are 3.2 and 3.4, respectively. The dielectric constants are close to the values reported in our previous paper [8]. Formation of nanocomposites with MMA-POSS results in a reduction of the dielectric constants of PPh-FBz/MMA-POSS-0.7 and PBPA-FBz/MMA-POSS-0.7 to be 2.4 and 2.3, respectively. Loading of MMA-POSS to poly(benzoxazine)s also reduces their refractive index from 1.58 to 1.51. The dielectric constants are comparable to the values reported to highly fluorinated poly(benzoxazine)s [16–19]. The reduction in the dielectric constants of the poly(benzoxazine)/POSS nanocomposites has been attributed to the presence of air captured in the POSS cages. The more POSS fraction the nanocomposite has, the lower dielectric constant it displays.

Some papers on poly(benzoxazine)/POSS nanocomposites have been reported [33–36]. Nevertheless, the dielectric constants of the prepared poly(benzoxazine)/POSS nanocomposites were not studied and reported in the papers because of the low POSS contents (below 10 wt%) of the nanocomposites [33–35]. Liu and Zheng [36] prepared poly(benzoxazine)/POSS nanocomposites

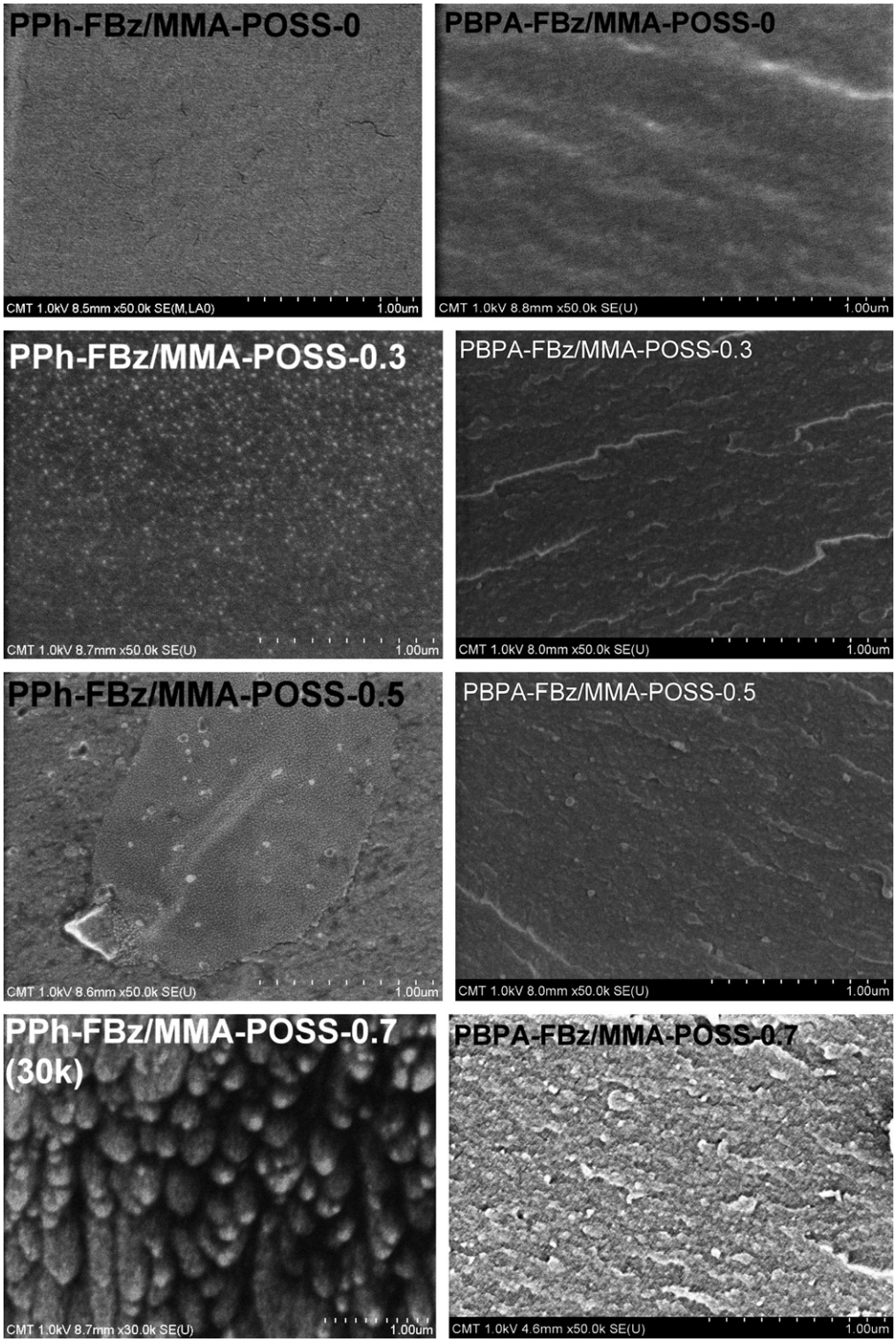

Fig. 4. Cross-sectional SEM micrographs of PPh-FBz/MMA-POSS and PBPA-FBz/MMA-POSS nanocomposites. The image of PPh-FBz/MMA-POSS-0.7 is given in a lower magnification to show its completed view.

containing 40 wt% of POSS compounds. They still did not report the dielectric constants of the products. In contrast to the previous works, here we have demonstrated the method to prepare highly POSS-loaded poly(benzoxazine)/POSS nanocomposites. The high POSS contents result in the low dielectric constants of the poly (benzoxazine)/POSS nanocomposites. Moreover, the preparation method could also be applied to other benzoxazine monomers as well as thermo-curable compounds, such as epoxy, maleimide, and phenolic resins.

3.2. POSS orientation in poly(benzoxazine)/POSS nanocomposites

The dielectric constant of composite materials depends not only on their fractions but also on the shape of the inorganic fillers. The

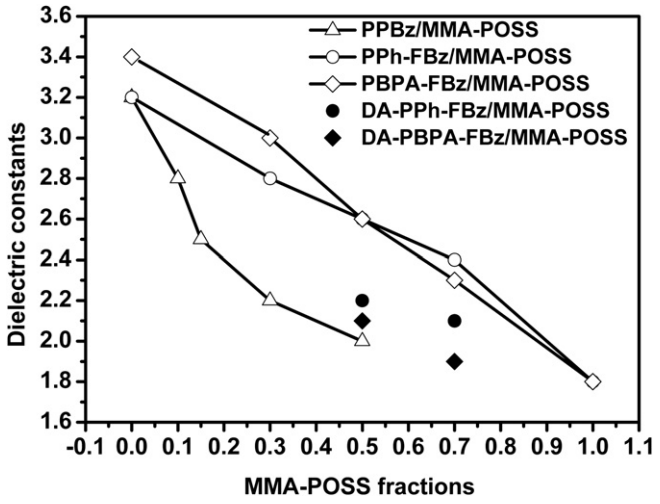

Fig. 5. Dielectric constants of poly(benzoxazine)/MMA-POSS nanocomposites.

shape effect of inorganic fillers on the dielectric constants of composite materials could be described with the power-law relationship [40]:

$$kc^{\beta} = \varphi k_1^{\beta} + (1-\varphi)k_2^{\beta} \quad (1)$$

where kc, k_1, and k_2 are the dielectric constants of the nanocomposite, inorganic filler, and polymer matrix respectively, φ is the volume fraction of inorganic filler and β is a parameter representing the shape and orientation of the inorganic filler. β approaches to -1.0 for the cases of the inorganic filler orienting perpendicular to the applied electrical field [40]. In this case Eq. (1) becomes

$$1/kc = \varphi/k_1 + (1-\varphi)/k_2 \quad (2)$$

Basing on Eq. (2), orientation of POSS into lamellar layers, which is perpendicular to the applied electrical field, would result in the dielectric constant of nanocomposite (kc) being close to the dielectric constant of POSS filler (k_1, which is much lower than k_2) over a wide range of POSS fraction (φ). Hence, with low POSS contents, orientation of POSS into lamellar layers could further reduce the dielectric constants of the POSS/polymer nanocomposites.

The dielectric constants of PPh-FBz/MMA-POSS-0.7 and PBPA-FBz/MMA-POSS-0.7 are 2.4 and 2.3, respectively. Nevertheless, the values are higher than the dielectric constants of MMA-POSS polymer (TP-MMA-POSS, 1.85) [37] and MMA-POSS/tri-furan nanocomposites (MMA-POSS/TF, 1.47) [41]. The ultra-low-k values of TP-MMA-POSS and MMA-POSS/TF have been attributed to the lamellar structures of POSS-rich domains oriented in the nanocomposites [37,41]. However, orientation and lamellar structures of POSS-rich domains are not observed in the TEM micrographs of PPh-FBz/MMA-POSS-0.7 and PBPA-FBz/MMA-POSS-0.7, as shown in Fig. 6.

Basing on the above discussion, the curing process for the preparation of poly(benzoxazine)/POSS nanocomposites have been modified to introduce POSS orientation and lamellar structures to the obtained nanocomposites. The mixtures of benzoxazine (Ph-FBz or BPA-FBz) and MMA-POSS were first to react at 160 °C for 36 h. In this stage of reaction, benzoxazine reacted with MMA-POSS through the Diels–Alder reaction between the furan groups of benzoxazine compounds and the methylmethacrylate groups of MMA-POSS [41]. Treatments of the DA product at higher temperatures carry out the polymerization of benzoxazines and MMA-POSS to result in highly cross-linked nanocomposite samples [14,41]. As it can be seen in Fig. 6,

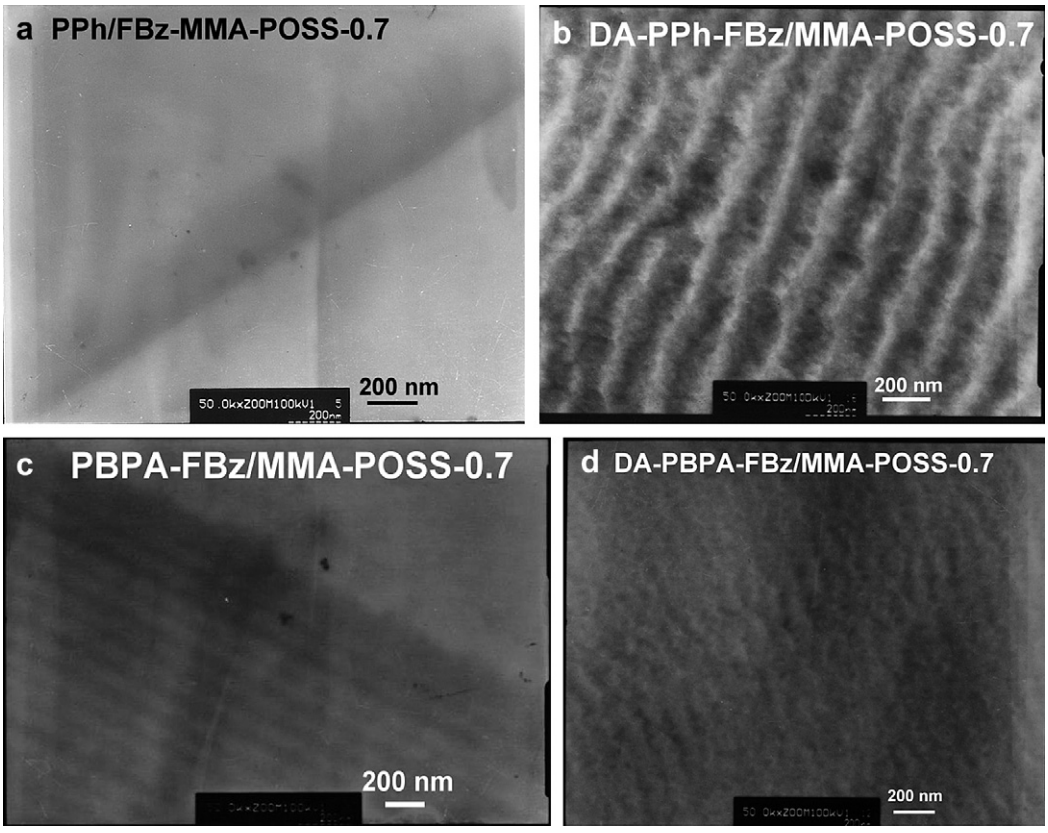

Fig. 6. TEM micrographs (×50 k) of poly(benzoxazine)/MMA-POSS-0.7 nanocomposites. The samples were prepared with different curing processes.

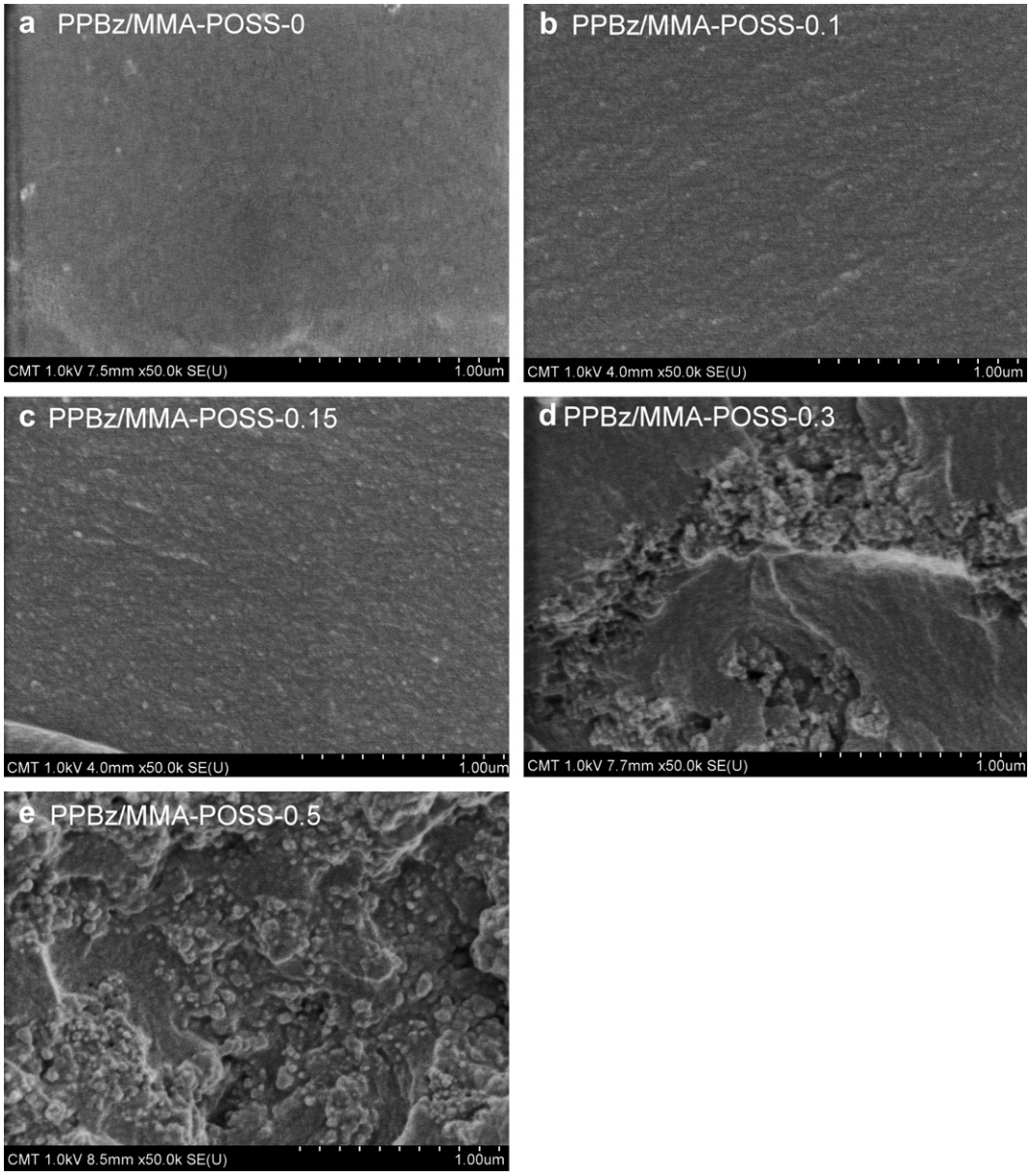

Fig. 7. Cross-sectional SEM micrographs of PPBz/MMA-POSS nanocomposites.

lamellar structures of POSS-rich domains appear in the TEM images of DA-PPh-FBz/MMA-POSS-0.7 and DA-PBPA-FBz/MMA-POSS-0.7. As a result, DA-PPh-FBz/MMA-POSS-0.7 and DA-PBPA-FBz/MMA-POSS-0.7 display dielectric constants of 2.1 and 1.9, respectively (Fig. 5). Their refractive indices are of about 1.49, which is approaching to the refractive index of MMA-POSS (1.47). Their dielectric constants are obviously lower than the values of their analogues, PPh-FBz/MMA-POSS-0.7 and PBPA-FBz/MMA-POSS-0.7. As PPh-FBz/MMA-POSS-0.7 and DA-PPh-FBz/MMA-POSS-0.7 have same POSS contents, the lower dielectric constant of DA-PPh-FBz/MMA-POSS-0.7 has been reasonably attributed to the POSS-orientated lamellar structures.

3.3. Morphology and dielectric constants of PPBz/MMA-POSS nanocomposites

In addition to small molecules, polymers containing benzoxazine groups in the main chains have also received research interests. In the previous work, we prepared PBz by means of Diels–Alder reaction using BPA-FBz and BMI as monomers [14]. PBz contains DA adducts and benzoxazine groups in main chains (Fig. 1). Under high temperatures, the DA adduct linkages of PBz break down to regenerate furan and maleimide groups by means of retro-DA reaction. Meanwhile, the benzoxazine groups polymerize through ring-opening addition reaction and the maleimide groups polymerize through addition reaction of C=C bonds [14]. All the reactions as well as the methylmethacrylate polymerization of MMA-POSS carry out in the curing process for the preparation of PPBz/MMA-POSS nanocomposites.

Fig. 7 shows the cross-sectional SEM images of PPBz/MMA-POSS nanocomposites. Neat PPBz resin displays a homogeneous fracture surface. POSS-rich domains could be seen in the SEM micrographs of PPBz/MMA-POSS nanocomposites. The portions of the POSS-rich domains increase with increasing the MMA-POSS contents of the nanocomposites. Phase-separation between the polymer-rich and POSS-rich domains does not appear. For PPBz/MMA-POSS-0.3 and PPBz/MMA-POSS-0.5, the POSS-rich domains appear as granules in the size of about 30–50 nm.

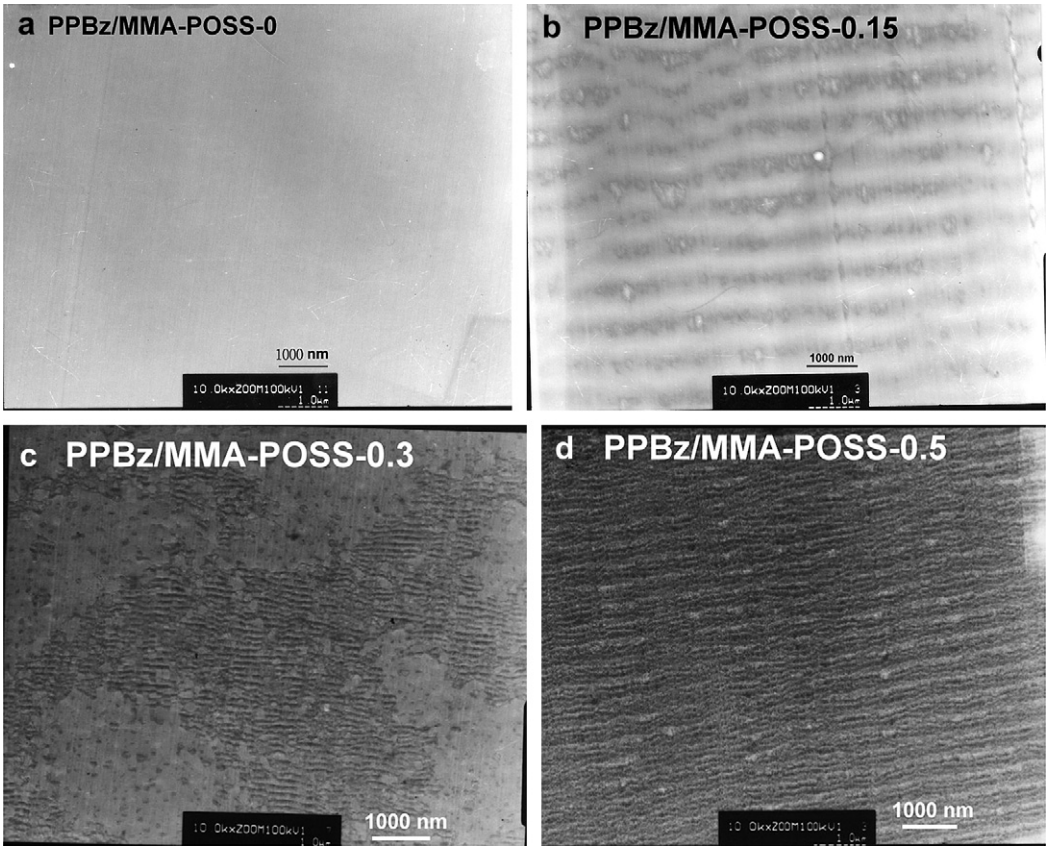

Fig. 8. TEM micrographs (×10 k) of PPBz/MMA-POSS nanocomposites.

The dielectric constants of PPBz/MMA-POSS nanocomposites are collected in Fig. 5. Incorporation of MMA-POSS significantly reduces the dielectric constants of PPBz. PPBz/MMA-POSS-0.3 to a dielectric constant of 2.2, which is lower than the values found for PPh-FBz/MMA-POSS-0.3 (2.8) and PBPA-FBz/MMA-POSS-0.3 (3.0). Among the nanocomposite samples having the same fractions of MMA-POSS, PPBz/MMA-POSS has displayed the lowest dielectric constants. Moreover, the dielectric constant of PPBz/MMA-POSS-0.5 is 2.0, which is comparable to the *k* values of DA-Ph-FBz/MMA-POSS-0.5 and DA-PBPA-FBz/MMA-POSS-0.5. The low-*k* value implies that PPBz/MMA-POSS-0.5 might possess POSS orientation and lamellar structures. This has been examined with TEM observation. Fig. 8 shows the TEM images of PPBz/MMA-POSS nanocomposites. Neat PPBz resin exhibits a dense and homogeneous structure. Nevertheless, lamellar structures of POSS orientation have been observed for PPBz/MMA-POSS-0.15, PPBz/MMA-POSS-0.3, and PPBz/MMA-POSS-0.5. However, the lamellar structures of the three samples are different. The amount of MMA-POSS has a significant effect on POSS orientation.

The lamellar structures in PPBz/MMA-POSS samples are worthy of notice. We have prepared the nanocomposites of polyimide and MMA-POSS and not observed POSS orientation in the nanocomposites [37]. The strong interactions between polyimide chains prevent POSS orientation and push POSS moving together. Loading too much MMA-POSS to polyimide makes POSS gathering together to result in phase-separation. Nevertheless, in this work PBz chains act a different role in formation of PPBz/MMA-POSS nanocomposites. PBz chains break down under heat through retro-DA reaction to generate furan and maleimide groups. The furan groups could react toward methylmethacrylate groups of MMA-POSS by means of Diels–Alder reaction. The maleimide groups could copolymerize with methylmethacrylate groups by means of radical addition reaction. These reactions establish chemical linkages between PPBz and MMA-POSS networks. As a result, the chemical linkages increase the compatibility of the polymer and POSS domains, consequently contributing to POSS orientation.

Self-assembled structures from POSS-containing block copolymers have been studied [42,43]. The polymer-rich and POSS-rich domains in the self-assembled structures have different etching characteristics, and the materials could be applied to the preparation of nano-structured silica [44]. The materials reported in this work could have potentials of application in this issue, as they show self-assembled long-range order [42]. The lamellar structures should not be negative characteristics to PPBz/MMA-POSS nanocomposites for their application in lithographic patterning, as the lamellae are parallel to the surface of the nanocomposite films. On the other hand, the POSS-rich domain sizes (30–50 nm) might bring some limit to the applications of PPBz/MMA-POSS nanocomposites to silicon-base integrated circuits (ICs). The low-*k* PPBz/MMA-POSS nanocomposites still have potential use as encapsulants of ICs, interlayer of printed circuit boards, and structural materials for electronics.

3.4. Thermal properties of poly(benzoxazine)/POSS nanocomposites

The thermal properties of some poly(benzoxazine)/POSS nanocomposites have been studied. Thermally cured MMA-POSS displays 5% weight loss at about 340 °C (T_{d5}, measured with TGA at a heating rate of 10 °C/min under nitrogen) [37]. The T_{d5} of PPh-FBz and PBPA-FBz are 336 and 347 °C, respectively [8]. Hence, addition of MMA-POSS to poly(benzoxazine)s should not reduce their thermal

stability. In fact, the poly(benzoxazine)/POSS nanocomposites show their T_{d5} at about 340–370 °C. Nanocomposites possessing high MMA-POSS contents exhibit improved thermal stability because that the thermally stable POSS cages could serve as a heat barrier to organic portions [45].

The glass transition temperatures (*Tg*) of poly(benzoxazine)/POSS nanocomposites are about 270–290 °C. Compared to the high *Tg*'s of PPh-FBz (315 °C) and PBPA-FBz (308 °C), addition of MMA-POSS to poly(benzoxazine)s reduces their *Tg*'s. This could be reasonable since thermally cured MMA-POSS has a *Tg* of 191 °C [37]. Nevertheless, the *Tg*'s of the nanocomposites are still high enough for utilization in microelectronics and electrical devices.

4. Conclusions

We have demonstrated that MMA-POSS is an effective nano-additive for the preparation of poly(benzoxazine)/POSS nanocomposites. The nanocomposites have wide range (0–70 wt%) of MMA-POSS fractions and low dielectric constants of about 2.3. Moreover, induction of orientation and lamellar structures of POSS could further decrease the dielectric constants of the poly(benzoxazine)/POSS nanocomposites to 1.9–2.1. The success of preparation of ultra-low-*k* poly(benzoxazine)-based nanocomposites has been demonstrated.

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