Effect of Polyhedral Oligomeric Silsesquioxane on Water Sorption and Surface Property of Bis-GMA/TEGDMa Composites

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ABSTRACT: 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (Bis-GMA), one of the most important light-curable dimethacrylate resins, is widely used as dental restorative material. However, one problem of Bis-GMA is the high water sorption due to the hydrophilic hydroxyl (–OH) group, resulting in a short life in actual application. In this study, to overcome the drawback stated above, novel organic–inorganic dimethacrylate monomer containing polyhedral oligomeric silsesquioxanes (POSS), Bis-GMA-*graft*-POSS, is synthesized via the nucleophilic addition reaction of isocyanate functionalized POSS (IPOSS) and pendent hydroxyl group of Bis-GMA. Then the as-synthesized Bis-GMA-*graft*-POSS, of which hydroxyl group was substituted by hydrophobic POSS, is also introduced into the Bis-GMA/TEGDMA matrix to prepare a series of methacrylate-based hybrids for dental materials under visible light with camphorquinone and ethyl-4*N,N*-dimethylaminobenzoae (EDMAB) as initiator and coinitiator, respec-
tively. Compared to Bis-GMA/TEGDMA composites, water sorption of modified composites can be significantly reduced with the addition of Bis-GMA-*graft*-POSS. Moreover, the Bis-GMA/TEGDMA/POSS hybrids show hydrophobic surfaces, leading to much higher water contact angles than that of Bis-GMA/TEGDMA composites. The morphology of hybrids containing POSS was furthermore studied by X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS). The results show that POSS disperses in the matrix in noncrystalline form and tend to migrate to the surface of the modified composites that lead to the lower water sorption and higher water contact angles. These results are very useful for design of novel methacrylate monomers and clinical application. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3334–3340, 2012

Key words: Polyhedral oligomeric silsesquioxane; dental polymers; Bis-GMA; water sorption; surfaces; XPS

INTRODUCTION

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (Bis-GMA) is one of the most preferred dimethacrylate-based monomer for dental materials due to many advantages, such as esthetics, low health risks, and good handling properties.[1–5] Composites materials based on Bis-GMA matrix resin along with silane-coated inorganic fillers are extensively used in dentistry in a variety of application. The above composites possess excellent mechanical properties, esthetic quality, and ability to bond to enamel surface. However, Bis-GMA contains hydroxyl group within its backbone. Because of these polar groups, dental materials made with

monomer tend to be somewhat hydrophilic and elute unreacted monomers from composites, which may stimulate the growth of bacteria around the restoration and promote allergic reactions in some patients.[6–8] The water ingress into polymers can decrease the life of resin composites by silane hydrolysis and microcrack formation. Excess water uptake can promote breakdown of the bond between silane and filler particles, filler-matrix debonding, or even hydrolytic degradation of the fillers. Thus, it is important to reduce the water sorption behavior of polymeric dental materials containing inorganic fillers, such as SiO_2 and hydroxyapatite. Much research has been performed on reducing the hydrophilicity of Bis-GMA-based dental materials. Some of these methods include capping the hydroxyl group of Bis-GMA with more hydrophobic substitutes and synthesis of new aliphatic and aromatic dimethacrylates, which can prevent the forming of hydrogen bond.[9]

In recent years, polyhedral oligomeric silsesquioxanes (POSS) have received considerable attention as they possess a synergistic combination of constituent properties of organic and inorganic materials. POSS is an amazing nanofiller and considered as the next general biomedical materials.[10–21] Generally, inorganic nanoparticles need to be modified before they are used due to their poor miscibility with the organic matrix. Unlike conventional inorganic fillers, POSS nanofillers offer the advantages of monodisperse size, low density, and synthetically well-controlled functionalities. Typically POSS nanoparticle is a 3D cage-like siloxane structure surrounded by eight organic R groups ($RSiO_4$), where R can be reactive organic group, such as epoxy,[22,23] methacrylate,[24] norbornyl,[25,26] vinyl,[27] styryl,[28] amines,[29]. A number of studies have been performed on the modification of methacryl-based monomer with POSS, e.g., Gao[30] used three different methods to prepare Bis-GMA/POSS hybrids via light-cured technique. The results showed that with the incorporation of POSS into Bis-GMA system, the shrinkage of methacrylate-based neat resin can be reduced efficiently. Amerio[31] prepared hybrid nanocomposites containing POSS based on multifunctional POSS and they found that with the introduction of POSS, the thermal stability, hardness, and mechanical properties can be greatly improved. However, few studies have been done on the effect of POSS on the water sorption and surface properties on the methacrylate-based dental materials.

In this study, to reduce the water sorption, POSS is grafted onto Bis-GMA to prepare (Bis-GMA-*graft*-POSS), and then Bis-GMA-*graft*-POSS is introduced to Bis-GMA/TEGDMA matrix to prepare Bis-GMA/TEGDMA/POSS organic–inorganic hybrids. In addition, the effect of POSS on surface properties of Bis-GMA/TEGDMA is also investigated.

EXPERIMENTAL

Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (Bis-GMA, 99%), camphorquinone (CQ, 97%) and ethyl-4*N*,*N*-dimethylaminobenzoate (EDMAB, 99%) were obtained from Aldrich Co. and were used directly. Aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) was purchased from Hybrids Plastic Co.. Triethylene glycol dimethacrylate (TEGDMA, 99%) and isophorone diisocyanate (IPDI, 99%) were donated by Sartomer Chemical Co. and Bayer Co., German, respectively. They were used as received without further purification. Tetrahydrofuran (THF) from Beijing Regent Co. was thoroughly dried by CaH_2 and freshly distilled prior to use. The structures of main chemicals employed in this study are illustrated in Scheme 1.
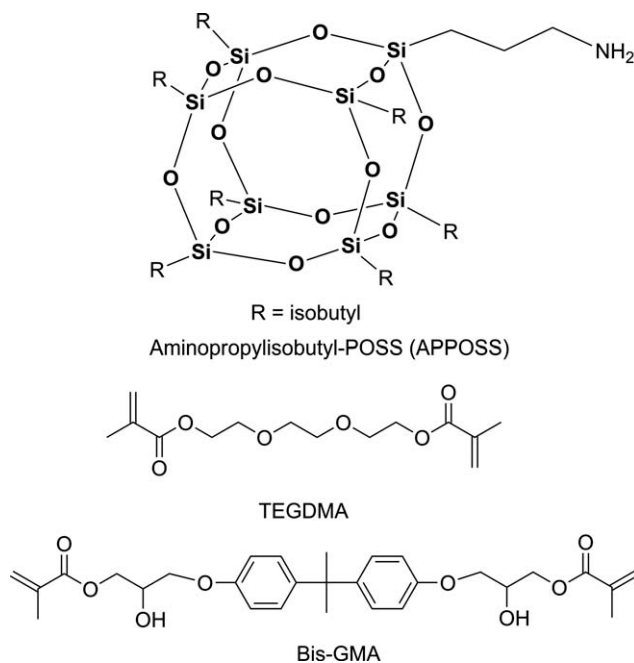
Scheme 1 Chemical structure of APPOSS and dimethacrylate monomer (TEGDMA and Bis-GMA).
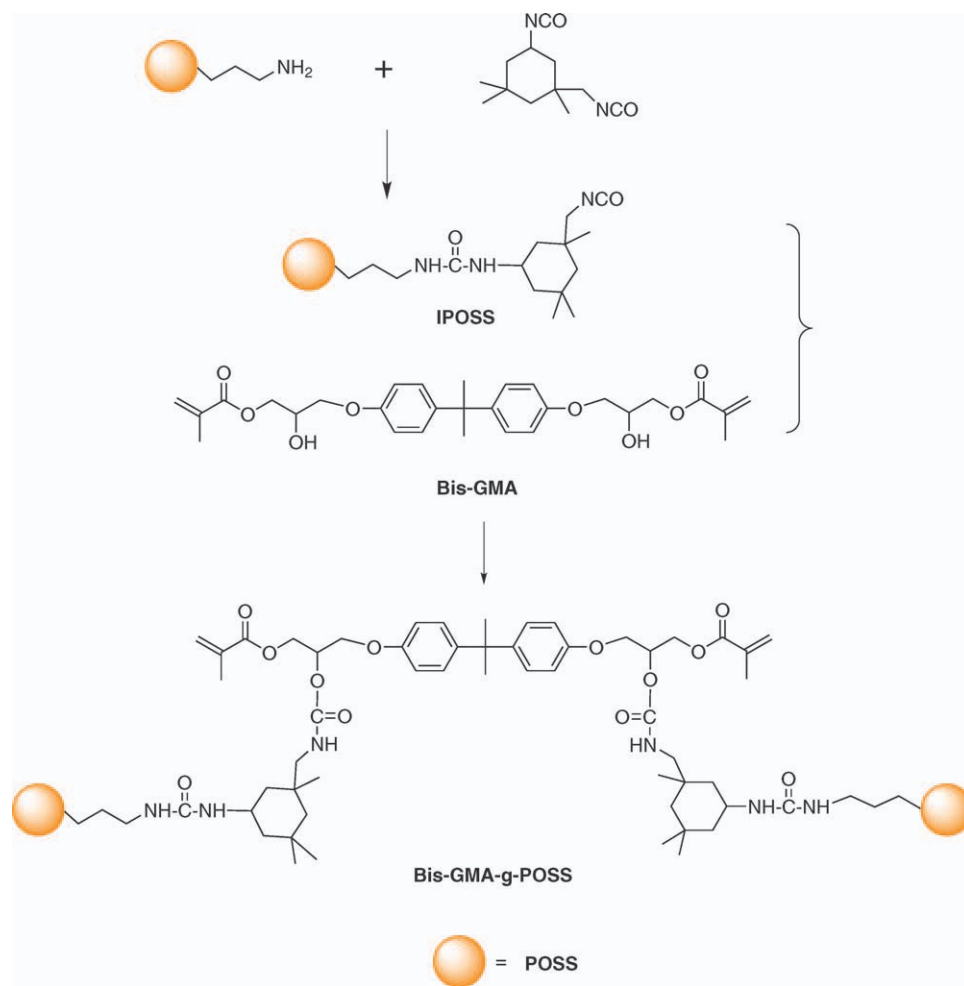
Synthesis of Bis-GMA-*graft*-POSS

A three-necked round flask, fitted with nitrogen inters adaptor, thermometer, and condenser, was charged with 2.22 g (10 mmol) IPDI and 10 mL dried THF. The reaction temperature was raised to 60°C, followed by addition of 8.74 g (10 mmol) POSS dissolved in 15 mL dried THF. The POSS solution was added dropwise under nitrogen flow. After the addition was completely charged, the reaction temperature was slowly increased to 75°C and maintained at this temperature for another 1 h, resulting in isocyante-functionalized POSS (IPOSS).

Then THF solution of Bis-GMA was added to the IPOSS, then DBTDL (0.1 wt %) was injected into the reaction flask as a catalyst. Reaction mixture was kept at 40°C for 4 h. Disappearance of the characteristic –NCO peak at 2270 cm^{-1} in the FT-IR spectrum confirmed that the reaction was completed. The homogenous solution was then transferred to rotary evaporator and concentrated to syrupy consistency. The concentrate was combined with 100 parts of hexane, whereupon the polymer precipitated as s fine white solid. The precipitate was collected by filtration, washed with, and dried in vacuum to obtain Bis-GMA-*graft*-POSS. A representation synthesis route for Bis-GMA-*graft*-POSS is shown in Scheme 2.

Preparation of Bis-GMA/TEGDMA/POSS composites

The mixture of monomers as shown in Table I and initiator system (0.3 wt % CQ/0.2 wt % EDMAB)

Scheme 2 Synthesis of Bis-GMA-*graft*-POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was placed in a mold made from glass slides with 15 ± 1 mm (diameter) × 1.2 ± 0.1 mm (thickness) and irradiated for 200 s for each side by a visible light source (Spectrum 800 Curing Light, Dentsply). Photopolymerization was carried out at room temperature. Five specimens were prepared for each resin. Finally, a series of transparent POSS-modified Bis-GMA/TEGDMA composites (Bis-GMA/TEGDMA/POSS) were obtained and named BP0, BP1, BP3, BP5, and BP10, where the arabic number represents the POSS content (wt %).

Characterization

FT-IR spectra were obtained by using a Bruker tensor 27 instruments operating at room temperature to determinate the structure of the as-prepared precursor in this study. The sample were mixed with the powder of KBr and then pressed into small flakes. The scan range was from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. X-ray diffraction (XRD) measurements were performed on a Rigaku 2500VB2+PC diffractormeter (Cu Kα radiation; 2θ: 3–50°, step time: 2 s). Contact angle measurements

TABLE I
The Compositions of Bis-GMA/TEGDMA/POSS Composites

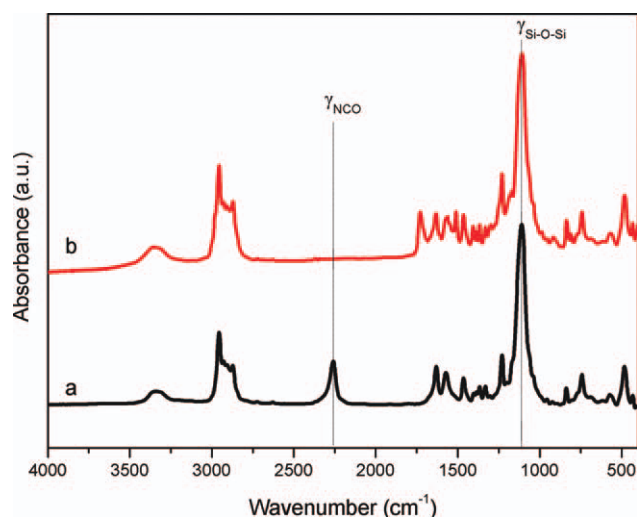| Sample	Bis-GMA (wt %)	Bis-GMA-*graft*-POSS (wt %)	TEGDMA (wt %)	POSS (wt %)
BP0	60.00	0	40.00	0
BP1	58.45	1.55	40.00	1
BP3	55.36	4.64	40.00	3
BP5	52.26	7.74	40.00	5
BP10	44.53	15.47	40.00	10

Figure 1 FT-IR spectra of (a) IPOSS and (b) Bis-GMA-*graft*-POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were performed using an OCA contact angle system with an input power of 55 W. X-ray photoelectron spectroscopy (XPS) were recorded on ESCALAB 250 spectrometer (Thermo Electron Corp.) in the fixed analyzer transmission mode with the Mg Kα X-ray source and a magnetic lens system that yields high spatial resolution and high sensitivity. The pressure in the analysis chamber was maintained at 2×10^{-10} mbar during measurement.

Water absorption specimens were placed in a desiccator and transferred in preconditioning oven at 37°C. After 2 days, each specimen was weighed to an accuracy of ± 0.0001 g on METTLER AL204 electronic balance. This cycle was repeated until a constant weight (m_1) was obtained. And then the samples were placed into 100 mL of distilled water at 37°C. At fixed time intervals (2 h, 6 h, 24 h, 2 d, 4 d, 8 d, 10 d), they were removed, blotted to remove excess water, weighed, and returned to the water until a constant weight (m_2) was obtained. The equilibrium water sorption value W_{sp} (%) was calculated using the following formula (1):

$$W_{SP}(\%) = 100 \left(\frac{m_2 - m_1}{m_1} \right) \qquad (1)$$

Statistical method

The experimental data were analyzed and compared by one-way ANOVA and Tukey test at the significance level of 0.05. The mean and standard derivation was calculated for each materials group including five samples.

RESULTS AND DISCUSSION

Preparation and characterization of Bis-GMA-*graft*-POSS

Here, POSS was grafted onto the Bis-GMA via nucleophilic addition reaction between amino group of POSS and the hydroxyl group of Bis-GMA in two steps as shown in Scheme 2. In the first step, the amino group of POSS was reacted with IPDI to obtain isocyanate-functionalized POSS, which can be easily grafted onto the backbone of Bis-GMA via the nucleophilic addition reaction in the second step. To determine the chemical structure of Bis-GMA-*graft*-POSS, FT-IR, and ^{1}H-NMR analysis were performed and the results were shown in Figure 1 and 2, respectively. It can be clearly seen that the stretching vibration absorption peak of –N=C=O at 2270 cm^{-1} appeared in the FT-IR spectra of IPOSS, indicating that the POSS was successfully functionalized with isocyanate group. Moreover, at the final resultant of IPOSS and Bis-GMA, the stretching vibration band of Si–O–Si at 1170 cm^{-1} appeared while the characteristic peak of –NCO disappeared, suggesting that the POSS was successfully grafted onto the backbone of the Bis-GMA, resulting in the POSS-modified organic–inorganic dimethacrylate prepolymer (Bis-GMA-*graft*-POSS) for dental materials. Although there are many kinds of hydrogen atom that are located in different chemical environments due to the complex structure of the Bis-GMA, it is clearly seen from Figure 2 that the newly formed bond –NH–CO–NH shown in the 8.02 ppm confirms that the POSS was grafted onto the backbone of Bis-GMA. In addition, the chemical shift located in 6.43 ppm is corresponding to the H–C=C of acrylate
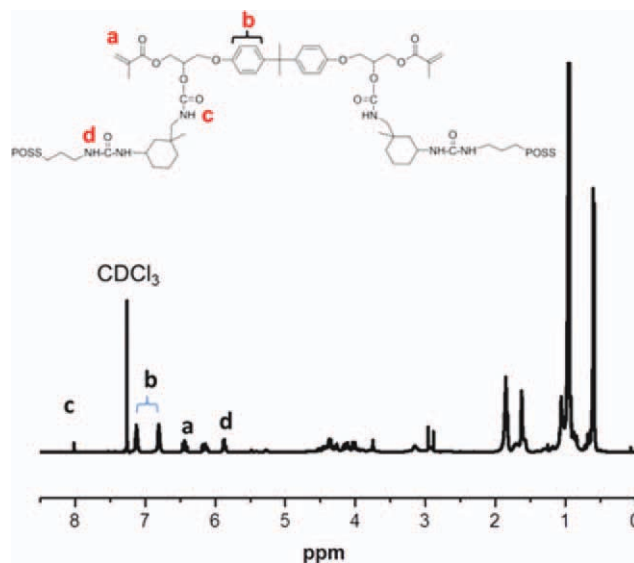

Figure 2 ^{1}H-NMR of Bis-GMA-*graft*-POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
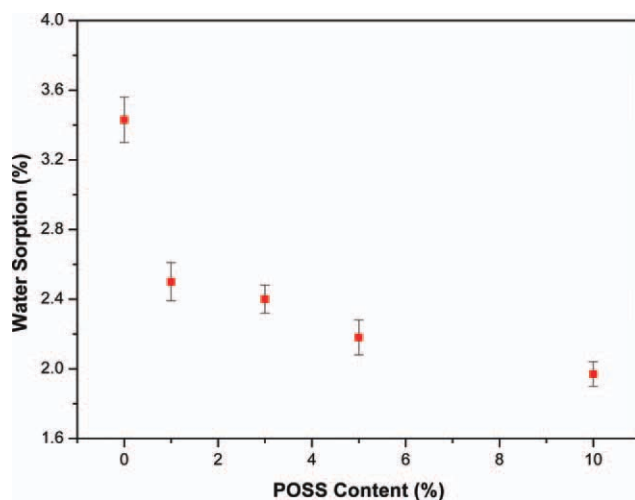
Figure 3 Effect of POSS on water sorption of Bis-GMA/TEGDMA/POSS composites. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

function group, which can be cured via photo-initiation.

Water sorption

Figure 3 shows the water sorption of the Bis-GMA/TEGDMA composites containing different content POSS. It can be seen that all the samples showed water sorption behavior. Moreover, water sorption varied significantly with the increasing of POSS content. Corresponding to the Bis-GMA/TEGDMA, all the POSS-modified Bis-GMA composites show lower water sorption. The water sorption quickly reduced to 2.50% with only 1.0 wt % POSS. And when the POSS content increased to 10 wt %, the water sorption reached 1.97 wt %, which is about half than that of Bis-GMA/TEMDMA. High water sorption of Bis-GMA-based composites is due to the polar hydroxyl group in its structure, which is reported in previous studies.[32–35] It is interesting to note that the incorporation of POSS into Bis-GMA-based resin can significantly reduce the water uptake. Various factors related to the chemistry and structure of the polymer network influence the water sorption of the light-cured composites. The interface between filler and matrix is an important factor which can affect the water uptake. When the filler is added to the polymer resin, the poor miscibility between the inorganic filler and polymer matrix will result in a number of microvoids. Some water molecules can accumulate at the filler–matrix interface or in the microvoids. This occurrence could cause the formation of water clusters.[36] In this study, we grafted POSS onto the Bis-GMA, rather than simply blending them. Because of the strong interaction of POSS and Bis-GMA through covalent bond, there would

be little microvoids in the matrix. Moreover, at the interface, the hydrophobic of POSS repel the existence of water molecules in great quantity. So, the water uptake can be significantly reduced by incorporation of POSS through grafting method.

Surface property

The surface–liquid–air contact angle measurements were surface-sensitive and possibly responded to the outermost monolayer of the surface.[37] To evaluate the effect of POSS on the surface properties of Bis-GMA/TEGDMA, contact angle test was performed, and the results are shown in Figure 4. Unmodified specimen showed a contact angle of 61.6°. However, with only 1 wt % POSS addition, the contact angle increases to 70.5°. Furthermore, with the POSS content is 10 wt %, the contact angle is increased gradually to 92.6°, which is 31° higher than that of pure Bis-GMA/TEGDMA. The surface of the modified composites gradually becomes more hydrophobic and has lower surface polarity, while the surface of neat Bis-GMA/TEGDMA is hydrophilic due to the hydroxyl group. The surface exposed to air would achieve the minimization of interfacial energy by low-energy chemical group's migration to the polymer–air interface,[37,38] and the POSS possesses surface activity, so it could be thought that in the modified composites, the POSS would migrate to the surface of the films, resulting in the decrease of interface energy and the increase in the contact angles.

To further confirm POSS tend to migrate to the surface to modified composites, here the surface elemental composition was measured by X-ray photoelectron spectroscopy (XPS). XPS is sensitive to chemical composition in the surface region including
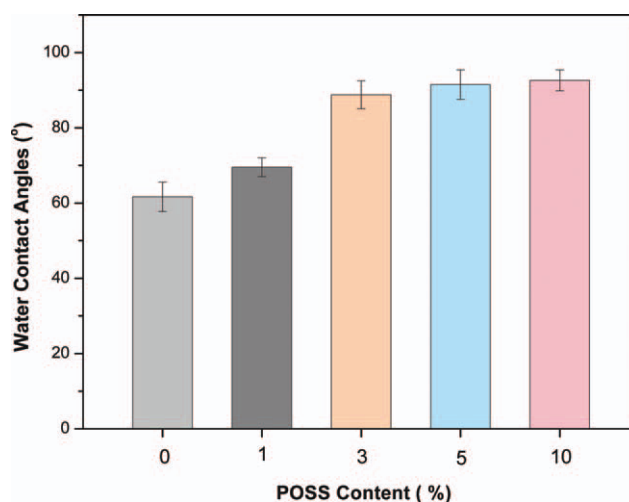

Figure 4 Water contact angles of Bis-GMA/TEGDMA/POSS composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
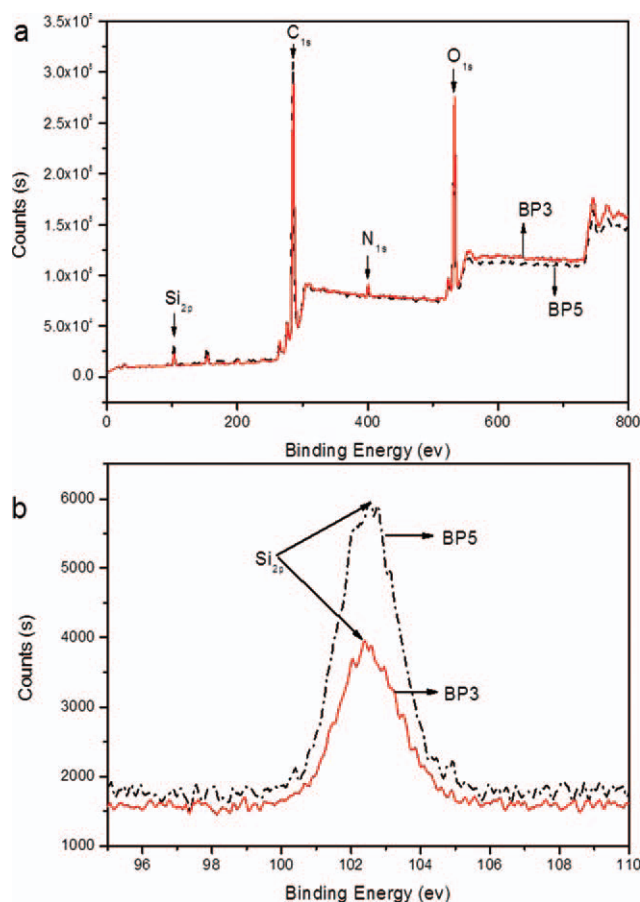
Figure 5 X-ray photoelectron microscopy and characteristic spectroscopy of Si element of sample BP3 and BP5 [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

several monolayers below the actual surface. Figure 5 shows the XPS spectra of BP3 and BP5 and the element composition was summarized in the Table II. It can be clearly seen that the bonding energy peak at about 100 ev is ascribed to the silicon element. It is interesting to note that the silicon contents of BP3 and BP5 from the XPS result are 4.79 and 6.44 wt %, respectively, which are higher than the theoretical values, namely 0.51 and 0.86 wt %. So, there is an enrichment of nonpolar POSS units on the surface of the hybrid materials. The same results was also confirmed by Ni and Zheng for a POSS-modified epoxy resin using X-ray photoelectron spectroscopy.[39]

TABLE II
Element Composition Data of the Surface of BP3 and BP5

Sample	C (%)	O (%)	N (%)	Si (%)	Si (%)[a]
BP3	73.61	19.54	2.06	4.79	0.51
BP5	75.71	16.59	1.26	6.44	0.86

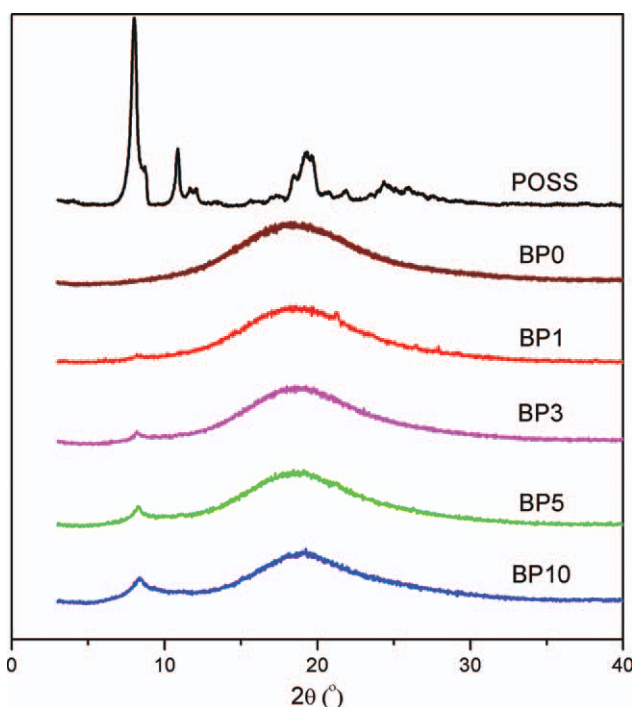[a] Si: theoretically calculated value.

Figure 6 X-ray diffraction profiles of Bis-GMA/TEGDMA/POSS composites. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

X-ray diffraction analysis

The cured film sample is transparent to visible light. This indicates a uniform distribution of the inorganic phase within the polymeric network on a scale smaller than 400 nm. Figure 6 shows the XRD results of pure POSS and Bis-GMA/TEGDMA hybrids containing different content of POSS. Wide-angle X-ray diffraction analyses show the neat POSS with sharp peak located at 7.99°, 10.85°, 19.26°, and 21.98°. These peaks correspond to the strongest reflection of the crystalline of POSS. For all the Bis-GMA/TEGDMA/POSS composites, no significant peaks could be identified, indicating that all the POSS are amorphous. When POSS was grafted onto the Bis-GMA chain, the movements of POSS unties were restrained, resulting in noncrystallization of the POSS and a good distribution in the cured matrix. POSS thus has a good miscibility with the Bis-GMA matrix through the grafting method. The reduced water sorption of the composites implies the good compatibility of POSS with Bis-GMA. This method is different from the results reported by Liu.[40] In their studies, silicon rubber was modified by POSS via directly blending method, part POSS tend to aggregate and form crystal.

CONCLUSIONS

In this study, a new type of dimethacrylate monomer Bis-GMA-*graft*-POSS is successfully synthesized and

characterized. Then a series of Bis-GMA/TEGDMA/POSS were prepared by incorporating Bis-GMA-*graft*-POSS into Bis-GMA/TEGDMA matrix to reduce the water uptake. The results show that the water uptake can be significantly reduced with the increase of POSS content due to its hydrophobic properties. It is also observed that POSS tend to migrate to the surface of modified composites, resulting in a higher contact angle.

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