

Allylated Novolac/4,4'-Bismaleimidodiphenylmethane Resin Containing Polyhedral Oligomeric Silsesquioxane: Preparation, Morphology and Thermal Stability

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ABSTRACT: Allylated novolac/4,4'-bismaleimidodiphenylmethane resin (AN/BDM) had been modified with well-defined inorganic building blocks-polyhedral oligomeric silsesquioxane (POSS). Octamaleimidophenyl polyhedral silsesquioxane (OMPS) was used as the cocuring reagent of the AN/BDM resin to prepare POSS-modified AN/BDM resin, and POSS content was between 0 and 17.8 wt %. The curing reaction of the POSS-modified AN/BDM resin was monitored by means of Fourier transform infrared spectroscopy (FTIR), and the results revealed that maleimide groups on OMPS molecule could undergo the curing reaction between allyl groups and maleimide groups. Therefore, the crosslinked network containing

POSS was formed. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to study the morphology of the cured POSS-modified AN/BDM resins. The homogeneous dispersion of POSS cages in AN/BDM matrices was evidenced. Thermogravimetric analysis (TGA) indicated that incorporation of POSS into AN/BDM crosslinked network led to enhanced thermal stability. The improved thermal stability could be ascribed to higher crosslink density and inorganic nature of POSS. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3903–3908, 2007

Key words: allylated novolac; polyhedral oligomeric silsesquioxane; morphology; thermal properties

INTRODUCTION

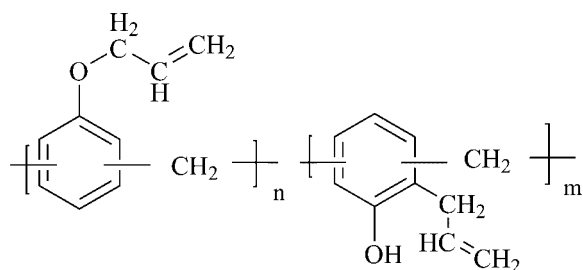
Organic-inorganic hybrid polymers have received considerable attention because of their enhanced properties compared with the mother homogenous polymers.^{1–4} The organic-inorganic hybrid polymers with a predetermined molecular architecture can be obtained by using well-defined inorganic clusters.⁵ Polyhedral oligomeric silsesquioxane (POSS) are of nanosized cage structure with a silica-like core surrounded by eight organic vertex groups.⁶ The organic groups of POSS compounds allow for their incorporation into organic polymers through physical blending or copolymerization.^{7–11} Because of its stable silica-like structure and controllable functionality, POSS compounds have been regarded as a new class of precursors to prepare organic-inorganic hybrid materials.⁵ Incorporation of the compact nanometer-sized POSS molecule into organic polymers results in an improvement of many properties, such as increased glass transition temperature, decomposition temperature and modulus, reduced flammability, and increased gas permeability.^{3,4,12–14}

Allylated novolac/4,4'-bismaleimidodiphenylmethane (AN/BDM) resins are a class of addition-cure phenolic resin, which are suitable for advanced processing technology (such as resin-transfer molding, i.e., RTM).¹⁵ The resin system possess excellent processing properties, such as low viscosity and long pot life at injection temperature and no volatile releasing upon curing.¹⁵ The cured resins display high thermal decomposition temperature, good mechanical properties.¹⁵ Therefore, AN/BDM resins are ideal candidates as matrices for high-temperature-resistance composite.

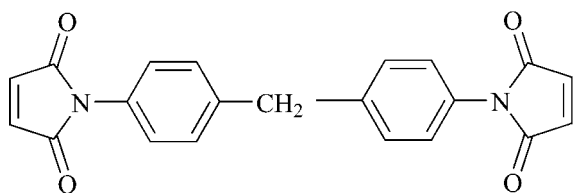
However, as high performance material, the thermal stability especially the ceramic yield at 900°C of the AN/BDM resins needs further improving. To improve the thermal stability and oxidative resistance of organic material, organic-inorganic hybrid polymers have attracted great interest. Furthermore, to the best of our knowledge, the AN/BDM resin containing POSS cages has not been reported yet.

In this work, we reported the preparation and characterization of the POSS-modified AN/BDM resins. Octamaleimidophenyl polyhedral silsesquioxane (OMPS) was used as the cocuring reagent of the AN/BDM resin, and POSS cages acted as the additional nanostructure crosslink sites. The curing reaction of the POSS-modified AN/BDM resin was confirmed by Fourier transform infrared spectroscopy

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Allylated novolac resin (AN)



4,4'-Bismaleimidodiphenylmethane (BDM)

Figure 1 Structures of allylated novolac resin (AN) and 4,4'-bismaleimidodiphenylmethane (BDM).

(FTIR). The morphology of the cured POSS-modified AN/BDM resins was examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The thermal stability of the cured POSS-modified AN/BDM resins was studied by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Allylated novolac (AN) resin was synthesized in our laboratory, and the allylation degree was 103% (O-allylation = 100% and C-allylation = 3%), which was calculated from $^1\text{H-NMR}$. 4,4'-Bismaleimidodiphenylmethane (BDM) was purchased from Fengguang Chemical Factory. The structures of AN resin and BDM were depicted in Figure 1. Phenyl trichlorosilane and benzyl trimethyl ammonium hydroxide (40% in methanol) were procured from J and K Chemical Corp. Maleic anhydride, 10% palladium in charcoal (Pd/C), fuming nitric acid and *p*-toluenesulfonic acid were purchased from Beijing Chemical Factory. Benzene, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), hexane, ethyl acetate, toluene and triethyl amine were received from Beijing Chemical Reagent Corp. All other chemicals were used as received, except for THF and triethyl amine, which were treated with calcium hydride for 12 h and then distilled before being used.

Synthesis of OMPS

OMPS had been synthesized by following the literature method with some modification and the synthesis procedure was depicted in Figure 2.^{5,6,16–19}

According to the method reported in the literature, octaphenyl polyhedral silsesquioxane (OPS) was obtained by hydrolysis and condensation of phenyl trichlorosilane in benzene, and the as-prepared product rearranged in the presence of trimethyl ammonium hydroxide (40% in methanol) as catalyst.¹⁶ The resulted OPS could undergo nitration reaction by using fuming nitric acid as solvent at lower reaction temperature. Under the present reaction condition, it had been proposed that only one hydrogen atom on each aromatic ring of POSS was substituted by nitril group.^{5,17} Therefore, octanitrophenyl polyhedral silsesquioxane (ONPS) was obtained. The nitril groups could be reduced to amino groups with Pd/C as catalyst; and octaaminophenyl polyhedral silsesquioxane (OAPS) was synthesized.^{17,18} OMPS could be synthesized via the imidization reaction between OAPS and maleic anhydride. The synthetic method of OMPS used in this work was different from that reported in literatures. In the reported method, the

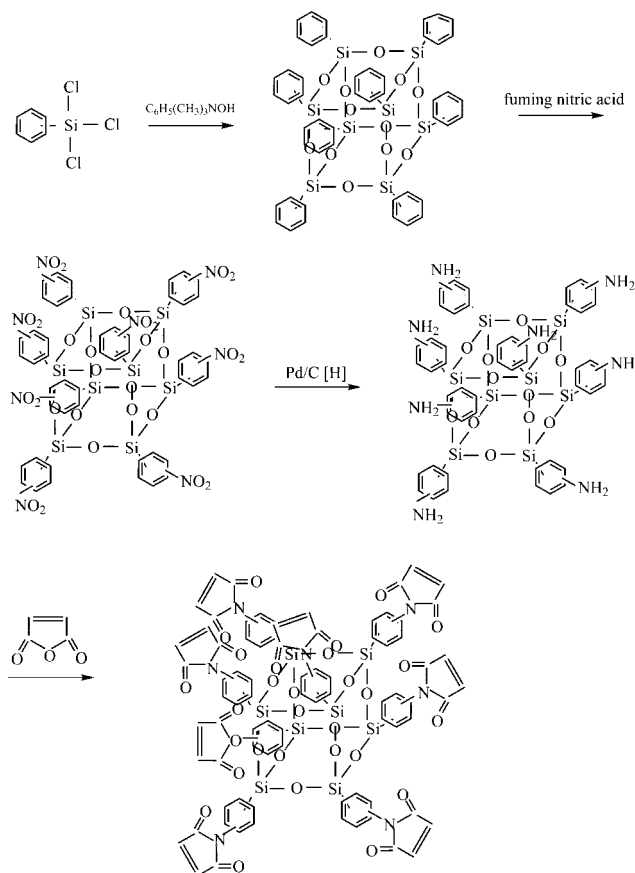


Figure 2 Synthesis of octamaleimidophenyl polyhedral silsesquioxane (OMPS).

imidization reaction was catalyzed by using weak base as catalyst.^{18,19} Here, *p*-toluenesulfonic acid was used as catalyst to facilitate the imidization reaction. A typical procedure was described as follows.

OAPS (2.11 g, 0.0018 mol), DMF (33.67 g), and toluene (16.88 g) were charged into a three-neck flask, to which maleic anhydride (2.16 g, 0.020 mol) was added in installments at 25°C. The mixture was magnetically stirred for 2 h at 25°C. Then, *p*-toluenesulfonic (0.21 g) was added and mixed well. The mixture was heated to 130°C and kept for 8 h at this temperature. The mixture was cooled and was poured into ca. 1500 mL of water. The resulted solid was filtered and washed with deionized water for several times. Finally, the solid was dried in vacuum at 30°C for 5 h to yield OMPS as a yellowish solid.

¹H-NMR (DMSO-*d*₆), ppm: 7.1 (protons in C=C of maleimide groups), 7.2–7.5 (aromatic protons).

²⁹Si-NMR (DMSO-*d*₆) ppm: –82 ppm.

FTIR (KBr powder) cm⁻¹: 1776 (C=O, out of phase), 1716 (C=O, in phase), 1482 (aromatic ring), 1381(C–N), 1131(Si–O–Si).

Preparation of the POSS-modified AN/BDM resin

In this work, the molar ratio for allyl groups of AN resin and maleimide groups of BDM monomer was 1 : 0.3. A typical procedure was described as follows.

In a 100 mL three-necked flask equipped with a magnetic stirrer, condenser, and thermometer, AN resin (6.54 g) was charged. OMPS (1.32 g) was dissolved with the smallest amount of DMF, and the solution was added drop wise under stirring to afford a homogeneous solution. Then, the temperature was slowly increased to 130°C and maintained 1 h at this temperature. BDM (2.51 g) was added and the mixture was stirred another 1 h at 130°C. The mixture was poured into mold and the majority of solvent was evaporated at 60°C. To remove the residue solvent, the samples were dried in vacuum at 120°C for 4 h. The samples were cured at 170°C for 4 h, 200°C for 4 h, and 250°C for 6 h to access a complete curing reaction. The content of OMPS fed to the AN/BDM resin was controlled to be 6.7, 12.7, and 17.8 wt %, respectively.

To confirm the reaction between OMPS and AN resin, the AN resin containing 12.7 wt % OMPS was also prepared by using the similar method, and the prepared AN resin containing 12.7 wt % OMPS was treated by heating in the same manner as mentioned above.

Measurement and techniques

FTIR

The FTIR measurements were conducted on a Tensor 27 Fourier transform infrared spectrometer at

room temperature (25°C). The samples were cast on KBr plate. In all cases, 32 scans at a resolution of 2 cm⁻¹ were used to record the spectra.

SEM

To investigate the morphology of the POSS-modified AN/BDM resin, the samples were fractured under cryogenic condition with liquid nitrogen. The obtained fractured surfaces were examined with XL30-FEG SEM. The fractured surfaces were coated with a thin layer of gold prior to investigation.

XRD

The XRD measurements were carried out at room temperature (25°C) on a D/max 2500 X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm). Specimens were scanned from 3 to 80° with a scan speed of 0.2° min⁻¹.

TGA

A Netsch STA409PC thermal gravimetric analyzer was used to investigate the thermal stability of the POSS-modified AN/BDM resins. All the thermal analysis was conducted in nitrogen atmosphere from 25 to 900°C at a heating rate of 10°C min⁻¹. The thermal degradation temperature was taken as the onset temperature at which 5 wt % of weight loss occurred.

RESULTS AND DISCUSSION

Thermal curing reaction of the POSS-modified AN/BDM resins

The blend of AN resin and BDM monomer could undergo curing reaction at elevated temperatures. It has been proposed that the predominant curing reaction is "Ene" reaction and Diels–Alder reaction between allyl groups and maleimide groups.^{20,21} To prepare the POSS-modified AN/BDM resins, OMPS was employed as the cocuring reagent of the AN/BDM resin. Therefore, the AN/BDM networks containing POSS cages structure could be obtained via the *in situ* curing reaction between allyl groups of AN resin and maleimide groups of BDM monomer and OMPS.

FTIR could provide some information about the change tendency of functional groups involved in the curing process. First, FTIR spectroscopy was carried out to investigate the curing reaction between AN resin and OMPS to confirm the reaction between AN resin and OMPS. Shown in Figure 3 was the FTIR spectra of the AN resin containing 12.7 wt %

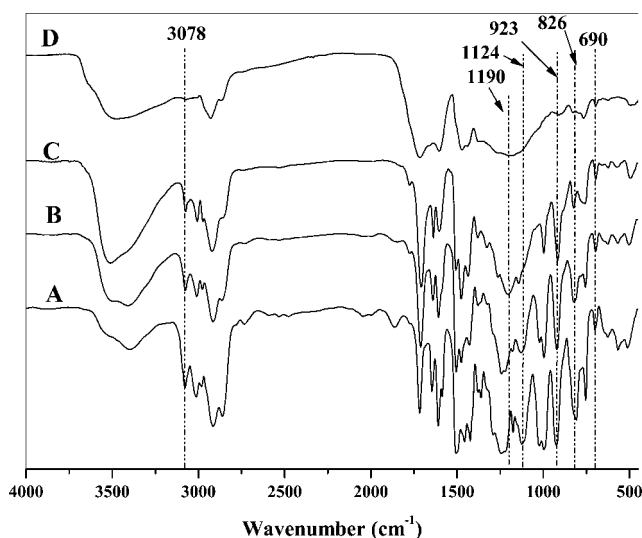


Figure 3 FTIR spectra of the AN resin containing 12.7 wt % OMPS at different curing stage: (A) uncured resin (B) 170°C 4 h (C) 200°C 4 h (D) 250°C 6 h.

OMPS at different curing stages. The characteristic bands at 3078 cm^{-1} , 826 cm^{-1} , and 690 cm^{-1} were attributed to maleimide groups, and the characteristic band at 923 cm^{-1} was assigned to allyl groups.^{20,22} With the proceeding of the curing reaction, the intensity of the above-mentioned bands decreased. At the same time, a new band formed at 1190 cm^{-1} , which was attributed to succinimide groups formed in the curing reaction.^{20,22} These results indicated that the curing reaction between allyl groups and maleimide groups had occurred. Thus, OMPS could be used as cocuring reagent to prepare the POSS-modified AN/BDM resins.

Shown in Figure 4 was the FTIR spectra of the AN/BDM resin containing 12.7 wt % POSS at different thermal curing stages. It could be seen that the characteristic bands of maleimide groups and allyl groups decreased to a considerable extent, and the band attributed to succinimide groups appeared. At the same time, the absorption band at ca. 1130 cm^{-1} assigned to symmetric Si—O—Si stretching absorption of POSS cages was presented during all the curing cycles, and this indicated the existence of the silsesquioxane cages structure.

The FTIR spectra demonstrated that the AN/BDM networks containing POSS had formed. However, it should be noted that the characteristic bands of maleimide groups and allyl groups were still discernible, implying an incomplete to the curing reaction. The same phenomenon was also reported in other cured POSS-containing system.^{3,19,23} The incomplete curing reaction might be ascribed to the combination of the high crosslink density of the systems and the immobility of the POSS cages structure.

Morphology of the POSS-modified AN/BDM resins

In this work, the morphology of the AN/BDM networks containing POSS was examined by SEM and XRD.

Shown in Figure 5 were SEM images of the fracture morphology for (A) cured 12.7 wt % POSS-modified AN/BDM resin and (B) cured AN/BDM resin. The cured 12.7 wt % POSS-modified AN/BDM resin exhibited the featureless morphology and no discernable phase separation was observed, which was similar to that of the neat AN/BDM resin. The SEM images suggested that maleimide groups of OMPS cages had taken part in the formation of the crosslinked network.

The morphology of the AN/BDM network containing POSS was further investigated by means of XRD. Figure 6 showed XRD profiles of OMPS and the POSS-modified AN/BDM resins with different POSS content as well as the parent AN/BDM resin. For XRD profile of OMPS, there were two distinct diffraction peaks at $2\theta = 5.64^\circ$ and 19.44° , corresponding to a d -spacing of 1.57 nm and 0.46 nm, respectively. The peak corresponding to a d -spacing of 1.57 nm was caused by the size of the OMPS molecules.^{16,18} And the broad peak at $2\theta = 19.44^\circ$ was due to the different isomers of the OMPS molecules.¹⁸ In contrast to the case of the neat OMPS, the AN/BDM networks containing POSS showed an absence of the peak at $2\theta = 5.64^\circ$. The results of XRD analysis indicated that the aggregation of the POSS cages was avoided in the cured POSS-modified AN/BDM resins.

It has been suggested that the aggregation degree of POSS cages in organic polymers could be gradually diminished with the increase in the functionality

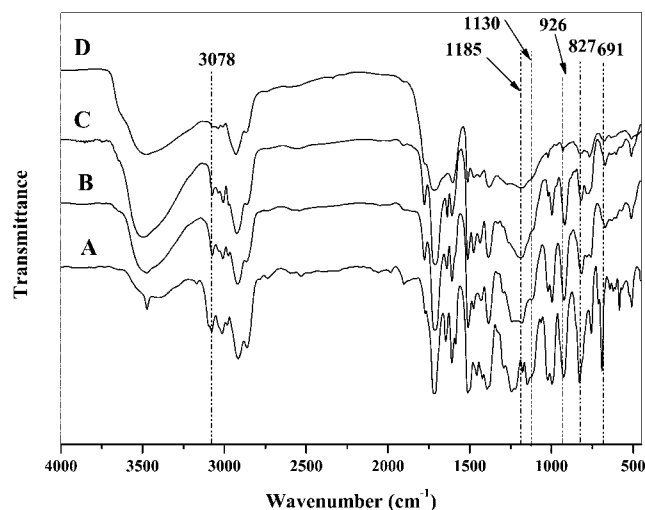
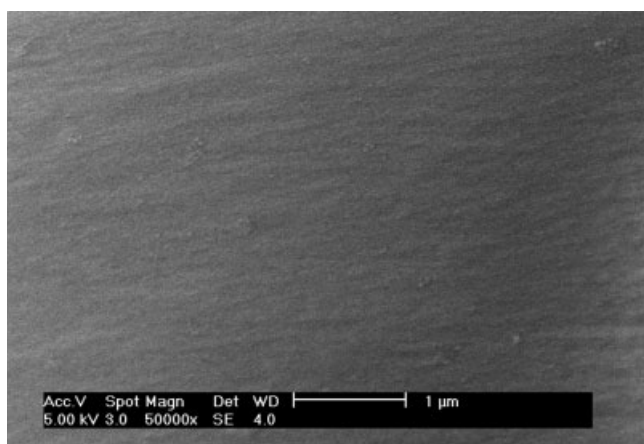
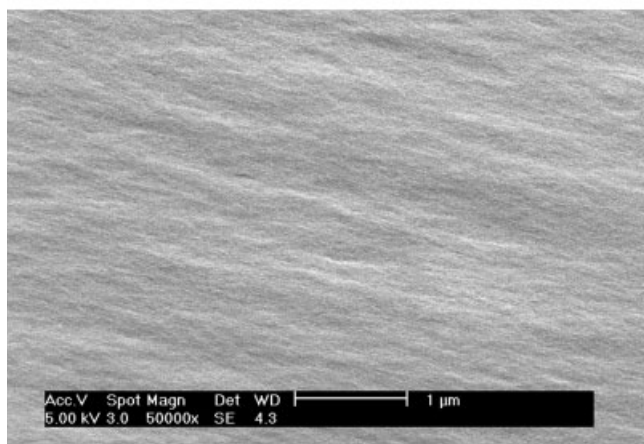


Figure 4 FTIR spectra of the AN/BDM resin containing 12.7 wt % OMPS at different curing stage: (A) uncured resin (B) 170°C 4 h (C) 200°C 4 h (D) 250°C 6 h.



(A)



(B)

Figure 5 SEM images of (A) the 12.7 wt % POSS-modified AN/BDM resin and (B) the parent AN/BDM network.

of POSS molecule.² Polyfunctional POSS monomers could be used to prepare thermosetting networks containing POSS cages. In this case, the single-phase polymer networks with POSS molecularly dispersed might be formed.²³ In this work, there were eight maleimide functional groups on one OMPS molecule, and the POSS cages structure could chemically bond to AN resin matrix via the reaction between maleimide groups and allyl groups, which had been evidenced by FTIR spectra. In addition, at the early stage of the curing, "Ene" reaction was predominant, and "Ene" reaction was an extent chain reaction in nature. Because of the rapid increase in the molecular weight, the mobility of the macromolecular chain decreased. Therefore, an aggregation of POSS cages was avoided.

In summary, the results of SEM and XRD provided evidences that POSS cages had been dispersed in the organic AN/BDM matrix on the molecular level through the cocuring reaction.

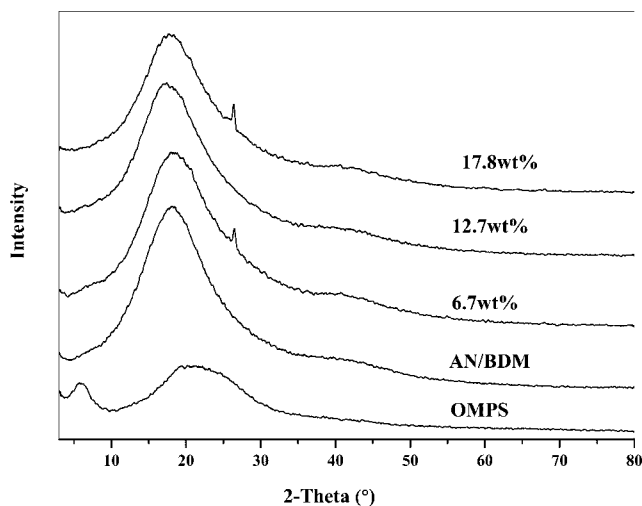


Figure 6 XRD patterns of the POSS-modified AN/BDM resins with different POSS content and OMPS as well as the parent AN/BDM resin.

Thermal stability of the POSS-modified AN/BDM resins

TGA technique was employed to investigate the thermal stability of the POSS-modified AN/BDM resins and the parent AN/BDM resin.

Shown in Figure 7 was the TGA profiles recorded in nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. In all cases, the single-step decomposition was observed. This implied that incorporation of POSS cages into the crosslinked network did not change the decomposition mechanism.

It could be seen from Figure 7 that the thermal stability was enhanced because of incorporation of POSS cages into the AN/BDM crosslinked network.

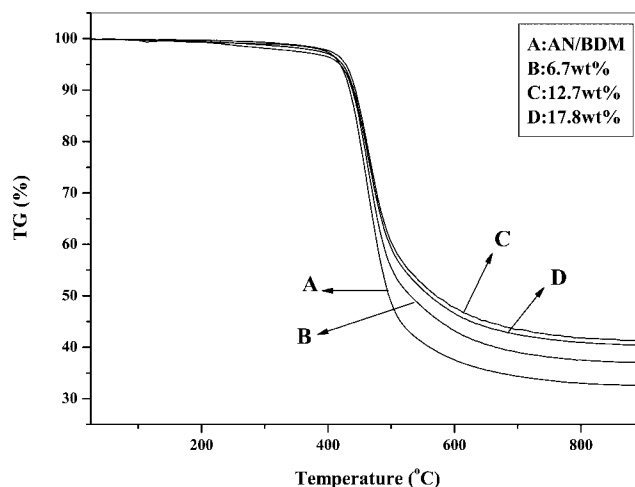


Figure 7 TGA profiles of the POSS-modified AN/BDM resins with different POSS content and the parent AN/BDM network.

For the parent AN/BDM resin, the 5 wt % loss temperature occurred at 414.7°C and the ceramic yield at 900°C was 31.51%. However, the POSS-modified AN/BDM resins displayed an improved thermal stability. For the 12.7 wt % POSS-modified AN/BDM resin, 5 wt % loss temperature reached 426.6°C. At the same time, the rates of the decomposition were decreased and the ceramic yield at 900°C increased to 41.25%.

The improvement of the thermal stability should be ascribed to introduction of POSS cages structure into the crosslinked network. First, the crosslink density of the AN/BDM network containing POSS was higher, because OMPS could provide eight junction sites per cube. Second, the inorganic component could provide additional heat capacity to stabilize the bulk material against thermal decomposition.²⁴ Therefore, the inorganic component and the higher crosslink density might account for the improvement of the thermal stability.

However, it also should be noted that the improvement of the thermal stability was not proportional to POSS content. For example, the 17.8 wt % POSS-modified AN/BDM resin exhibited lower 5 wt % loss temperature than that of the 12.7 wt % POSS-modified AN/BDM resin. This might result from the change of the crosslink density. Incorporation of POSS into the crosslinked network might lead to two effects. On the one hand, the crosslink density of the network could be improved because of the additional crosslinked site provided by the polyfunctional POSS molecule; on the other hand, at higher POSS content, the massive and bulky POSS cages might take up the crosslinking site instead of matrix resin. This effect might be more significant at higher POSS content; therefore, the crosslinked density was lower than that at less POSS content. In addition, in our previous study, it had been evidenced that with the decrease in the crosslinked density, the thermal stability of the AN/BDM resins reduced.²⁵ Therefore, to obtain better properties, the POSS content in the system should be optimized.

CONCLUSIONS

A series of the POSS-modified AN/BDM resins with improved thermal stability were prepared by the curing reaction between OMPS and AN/BDM. The results of FTIR spectra verified that the AN/BDM crosslinked network containing POSS cages could form through the curing reaction. The

results of the SEM and XRD demonstrated that the aggregation of POSS cages was avoided and POSS cages were dispersed in the matrices on the molecular level. The thermal stability of the POSS-modified AN/BDM resins was improved due to incorporation of the inorganic component into the polymeric matrix and the higher crosslink density resulted from the additional junction sites.

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