Research Article

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Polyhedral oligomeric silsesquioxane (POSS)-modified phenolic resin: Synthesis and anti-oxidation properties

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Abstract: In this work, octamercapto polyhedral oligomeric silsesquioxane (POSS-8SH) and octaphenol polyhedral oligomeric silsesquioxane (POSS-8Phenol) were successfully synthesized. POSS-8Phenol was added into the synthesis process of liquid thermoset phenolic resin (PR) to obtain POSS-modified phenolic resin (POSS-PR). Chemical structures of POSS-8SH, POSS-8Phenol, and POSS-PR were confirmed by FTIR and ^1H -NMR. TG and DTG analysis under different atmosphere showed that char yield of POSS-PR at 1,000°C increased from 58.6% to 65.2% in N_2 , which in air increased from 2.3% to 26.9% at 700°C. The maximum pyrolysis temperature in air increased from 543°C to 680°C, which meant better anti-oxidation properties. XRD results confirmed both POSS-8Phenol and POSS-PR-generated crystalline SiO_2 in air, which could explain the improvement of anti-oxidation properties. SEM showed that the POSS-PR had phase separation during curing process. Finally, carbon fiber fabric-reinforced POSS-PR (C-POSS-PR) was prepared to verify the anti-oxidation properties of POSS-PR.

Keywords: phenolic resin, polyhedral oligomeric silsesquioxane, thermal stability, anti-oxidation properties, carbon fiber-reinforced composite

1 Introduction

As an indispensable member of the polymer family, PR has many excellent properties, such as thermal stability,

high hardness, high carbon residue yield, and flame resistance. It has been widely used in coatings, heat-barrier materials, carbon material precursors, and adhesives (1). However, since phenolic groups and methylene groups in PR's crosslinking structure, the PR's high-temperature anti-oxidation properties are always poor, and materials usually have cracks and deformation under the erosion of hot oxygen (2). As the matrix resin of ablation materials or refractory materials for aircraft or space shuttles, it is particularly important to improve the anti-oxidation properties of phenolic resins (3). Previous works to modify phenolic resin could be divided into two parts: one of the methods was to improve the molecular structure of PR, such as Xylok resin prepared through introducing hydrophobic aromatic (4), benzoxazine resin (5) which did not release small molecules in the curing process, and phenol triazine resin prepared through the reaction of PR with trialkylamine and cyanogen halide (6). The other method was to introduce inorganic elements such as boron (7), silicon (8), and zirconium (9). However, these modification methods mainly improved the thermal stability and the char yield of phenolic resin in inert environment and paid less attention to the thermal stability in air.

Many studies reported that silicone was an effective ingredient to improve the antioxidant properties of PR. Li et al. (8) synthesized silicone-modified PR through the esterification reaction between methyltrimethoxysilane and novolac resin; high-temperature oxidation experiments showed that the siloxane improved oxidation resistance of the phenolic resin; the improvement of oxidation resistance was related to the formation of SiO_2 at high temperature in air. Xiao et al. (10) studied the ablation resistance of various silicone coatings and ceramic coatings by oxy-acetylene flames test. That research showed that phenolic resin with silicone coatings had satisfactory anti-overheating property and ablation resistance and was the first choice for ablation-resistant materials. Silicone also played a role in heat insulation materials. Yin et al. (11) mixed novolac resin, methyltrimethoxysilane, and the curing agent, the porogen, to prepare a phenolic/silicone

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composite aerogel. Tests showed that the silicone resulted in a layered micro-mesoporous structure and higher thermal stability than the original PR aerogel. In test, when the surface temperature was about 1,800°C, the back surface temperature was lower than 200°C.

As a kind of silicone material, polyhedral oligomeric silsesquioxane (POSS) had a silicon-oxygen inorganic core and many exteriors, which could be designed as amino, phenyl, vinyl, etc. (12,13) that endowed POSS excellent design flexibility in polymer modification. POSS-modified polymers included vinyl resin (14), epoxy resin (15), male amide (16), polyurethane (17), and phenolic resin (18–20). Raw materials for the preparation of Benzoxazine and Phenol Triazine like aniline and cyanogen halide were toxic (4–6), and the introduction of inorganic elements into the phenolic resin could easily be led to obvious phase separation (7–9). For POSS-modified PR, the trimethoxysilane needed during synthesizing POSS was safe and easy to obtain, and the synthesis method was simple. Especially, the functional group of POSS was easy to be designed, which help solve the incompatibility between POSS and the PR.

In this study, we first synthesized POSS-8SH with octamercapto groups through the condensation reaction of trimethoxysilane (21,22) and then synthesized POSS-8Phenol through the Michael addition reaction (23–25). POSS-8Phenol was introduced into the synthesis process of PR. Experimental route and main chemical structures were showed in Figure 1. Chemical structures of POSS-8SH, POSS-8Phenol, and POSS-PR were confirmed by FTIR and ^1H -NMR. The internal morphology and elements distribution of cured POSS-PR were studied by SEM and EDS. The thermal stability and thermal anti-oxidation properties of POSS-PR under nitrogen and air were compared by TG and DTG. The crosslinking degree of cured resin was analyzed by DMA. The crystal structure of pyrolysis products under different atmosphere was analyzed by XRD. The change of element content before and after pyrolysis was analyzed by XPS. Finally, the anti-oxidation properties of POSS-PR were further confirmed by comparing the flexural strength of carbon fiber-reinforced POSS-PR after high-temperature oxidation test.

2 Experimental

2.1 Materials

Phenol, formaldehyde (37%), sodium hydroxide, concentrated hydrochloric acid, anhydrous MgSO_4 , used solvents

Figure 1: Experimental route and chemical structures of POSS-8SH, POSS-8Phenol, and POSS-PR.

such as methanol, dichloromethane and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd (Wuhan, China). (3-Mercaptopropyl)trimethoxysilane (MPTS) and di-*n*-butylamine (DnBA) were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). 4-Maleimidophenol (4-HPM) was purchased from WengJiang Reagent Co., Ltd (Guangdong, China). Unidirectional carbon fiber cloth was purchased from Weisheng New Material Technology Co., Ltd (Jiangsu, China). All chemical reagents and materials were used directly without further purification.

2.2 Preparation of octamercaptopropyl polyhedral oligomeric silsesquioxane (POSS-8SH) and octaphenol polyhedral oligomeric silsesquioxane (POSS-8Phenol)

The synthesis of POSS-8SH was achieved through condensation between siloxanes. Specific synthesis steps were

similar to literature (22). Briefly, 10 mL MPTS was dissolved in 240 mL methanol, and 20 mL concentrated hydrochloric acid was added. Then the mixed solution was stirred and refluxed at 90°C for 24 h. After standing and cooling, some white precipitate could be observed. The precipitate was washed three times with cold methanol, then washed three times with deionized water after dissolving in dichloromethane. The organic phase was separated and dried with anhydrous MgSO_4 . POSS-8SH was obtained after dichloromethane was removed by vacuum drying.

POSS-8Phenol was prepared by the Michael addition reaction between POSS-8SH and 4-HPM. POSS-8SH (5 g, 4.912 mmol) and DnBA (1 mol% of 4-HPM, 0.051 g, 0.393 mmol) as catalyst were dissolved in 200 mL acetone. 4-HPM (7.355 g, 39.296 mmol) was dissolved in 150 mL acetone and then dripped into previous mixed solution in 1 h; the molar ratio of mercapto group to maleimide group was 1:1. The mixed solution was stirred at room temperature for 4 h. A light-yellow precipitate could be observed after dropping deionized water into the mixed solution. After repeating the process above three times and vacuum drying, POSS-8Phenol was obtained.

2.3 Preparation of POSS-modified phenolic resin (POSS-PR)

In this part, POSS-8Phenol was well-dissolved in hot phenol (94.110 g, 1 mol) with mass percent of 3%, 5%, and 8% and then mixed with 37% formaldehyde solution (121.740 g, 1.5 mol) and 50% NaOH (2.000 g, 0.025 mol). First, the solution was stirred and gradually heated to 60°C and the temperature was kept for 2 h. Then the mixed solution was heated to 95°C in 30 min and the temperature was kept for 1 h. After water and by-products were removed under reduced pressure distillation at 95°C for 50 min, POSS-modified phenolic resin (POSS-PR) was obtained; products were marked as 3% POSS-PR, 5% POSS-PR, and 8% POSS-PR, respectively. Except the POSS-8Phenol, synthesis steps of the neat phenolic resin (PR) were consistent with process above. All samples were cured following next procedure: 80°C (1 h), 95°C (1 h), 120°C (2 h), 150°C (2 h), and 200°C (1 h).

2.4 Preparation of carbon fiber-reinforced POSS-PR composite (C-POSS-PR)

POSS-PR resin was dissolved in alcohol with a mass ratio of 1:1 to prepare the resin solution. The resin solution was

Figure 2: Curing process of C-POSS-PR.

applied to carbon fiber cloth with a brush and allowed to dry for 24 h at room temperature. The infiltrated cloth was cut into small pieces (160 × 140 mm) and layered with the layer number of 22. Then the stacked fabric was placed in a 150 × 100 × 4 mm mold for hot compression molding; the curing process was showed in Figure 2. The cured C-POSS-PR sheet was cut into 80 × 15 × 4 mm specimens to test the flexural strength before and after the oxidation treatment.

2.5 Characterization

Fourier infrared spectroscopy (FT-IR) was used to characterize the chemical structure of POSS-8SH, POSS-8Phenol, and POSS-PR, on KBr pellets from 400 to 4,000 cm^{-1} by a Nicolet Nexus IR Spectra (Madison, WI, USA).

The chemical structures of POSS-8SH and POSS-8Phenol were further confirmed by Proton nuclear magnetic resonance ($^1\text{H-NMR}$) (Bruker Avance III, 500 MHz, Germany). Each sample was dissolved in deuterated chloroform (CDCl_3) and tetramethylsilane (TMS) was selected as the reference.

The internal surface morphology of the fractured cured modified phenolic resin was observed by scanning electron microscope (SEM, s-4800, HITACHI, Japan) at an accelerating voltage of 10 kV. An Energy dispersive X-ray spectroscopy (EDS) attached to the SEM was performed to investigate elements' distribution of Si, O, and C.

The thermal stability of POSS-PR was studied via thermogravimetric (TG) and derivative thermogravimetry (DTG) (STA449F3, NETZSCH, Germany) from ambient temperature to 1,000°C in air or nitrogen, at the heating rate of 10°C/min and the flow rate of 50 mL/min.

The storage modulus and $\tan \delta$ of POSS-PR were determined by dynamic thermomechanical analysis (DMA) (DMA/SDTA 861e METTLER TOLEDO, Switzerland). A dual cantilever beam bending mode was employed. Test samples were approximately 3.5–4.0 mm thick, 8–9 mm wide, and 80 mm long. The temperature was risen from 100°C to 350°C at 5°C/min, and the frequency was 1.0 Hz.

X-ray diffraction analysis (D8 Advance, BRUKER AXS GMBH, Germany) was used to analyze crystal structure of POSS-8Phenol's and POSS-PR's pyrolysis products. XRD data were performed from 5° to 80° at a step of 4°/min.

Element content of Si, C, and O in pyrolysis products of POSS-PR was analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi) (Mg K α X-ray source). All spectra were calibrated with the C 1s peak at 284.8 eV.

The flexural strength of the C-POSS-PR composites was tested by universal mechanical testing machine with a loading rate of 2 mm/min. Each sample was oxidized for 10 min in the muffle furnace.

3 Results and discussion

3.1 Analysis and characterization of POSS-8SH and POSS-8Phenol

3.1.1 FTIR analysis of POSS-8SH and POSS-8Phenol

In the POSS-8SH's FTIR spectrum of Figure 3, the asymmetric stretching vibrations' peak of the Si–O–Si skeletal was appeared at 1,100 cm^{-1} , and peaks at 550 and 480 cm^{-1} were due to the deformation vibrations of the POSS skeletal.

Figure 3: FTIR spectra of POSS-8SH and POSS-8Phenol.

The stretching vibration peak of S–H was located at 2,551 cm^{-1} . Absorption bands at 2,820 and 2,950 cm^{-1} were assigned to alkane $-\text{CH}_2$ groups. Absorption peaks at 1,264 and 690 cm^{-1} were attributed to Si–C asymmetric and symmetric stretching vibrations, respectively (22). Peaks from 1,334 to 1,442 cm^{-1} were due to bending vibrations of $-\text{CH}_2\text{CH}_2\text{CH}_2-$. Results above indicated that MPTS was successfully transformed into caged octamercaptopropyl polyhedral oligomeric silsesquioxane (POSS-8SH) through condensation reaction between trimethoxy-silanes.

The FTIR spectrum of POSS-8Phenol was showed in Figure 3. It could be clearly seen that the S–H stretching vibration absorption peak at 2,551 cm^{-1} disappeared, and the characteristic peak of C=C of 4-HPM could not be observed which usually appeared at 3,100 cm^{-1} (24). Results above indicated that the S–H reacted completely with the electron-deficient C=C in the Michael addition reaction. The peaks at 1,712 and 3,349 cm^{-1} were attributed to the C=O stretching vibration and the O–H stretching vibration, respectively. The stretching vibration peak of the benzene ring appeared at 1,606 and 1,509 cm^{-1} , and the single peak at 834 cm^{-1} was typical single substitution peak in benzene ring. The peak at 1,547 cm^{-1} was attributed to C–N stretching vibration (24). It was worth noting that the stretching vibration peak of C–H had always existed around 2,925 cm^{-1} . All results above indicated that POSS-8Phenol was successfully synthesized.

3.1.2 ^1H -NMR analysis of POSS-8SH and POSS-8Phenol

^1H -NMR spectra of POSS-8Phenol, 4-HPM, and POSS-8SH are showed in Figure 4. Among them, POSS-8SH showed four kinds of proton peak with chemistry shift at 0.78, 1.46, 1.73, and 2.57 ppm, and the integral ratio of 2:1:2:2, which was consistent with proton numbers of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ in POSS-8SH. In addition, there was no $-\text{SiOCH}_3$'s proton peak near 0 ppm from the MPTS, which indicated that the cage octagonal structure of POSS-8SH was completely condensed. After the Michael addition reaction with 4-HPM, it could be clearly observed that the proton peak at 1.46 ppm of $-\text{SH}$ disappeared completely. At the same time, the strong electron-deficient proton peak at 6.92 ppm of C=C in 4-HPM also disappeared. Two new peaks at 2.97 and 3.70 ppm appeared, which were assigned to two kinds of protons in $\text{S}-\text{CH}-\text{SH}_2$ of POSS-8Phenol, respectively (23). These results indicated that the reaction between $-\text{SH}$ and C=C was complete and POSS-SH, POSS-8Phenol were successfully synthesized. It was worth noting that when CDCl_3 was the solvent, the proton peak of the phenol group

Figure 4: ^1H -NMR spectra of POSS-8SH, 4-HPM, and POSS-8Phenol.

was very active to exchange protons with CDCl_3 , so the proton peak of the phenolic hydroxyl group could not be observed (peak h); it would show again when the solvent changed to deuterated acetone.

3.1.3 Thermal stability and pyrolysis analysis of POSS-8Phenol

The thermal stability of POSS-8Phenol was analyzed via TG and DTG under different atmosphere. The weight-temperature curve of POSS-8Phenol is showed in Figure 5a. The residual weight of POSS-8Phenol in N_2 or air at $1,000^\circ\text{C}$ was 42% and 18%, respectively. Figure 5b showed

the derivative weight-temperature curves; it could be basically divided into three stages. The first stage occurred at 180°C ; it might be due to chain break of $-\text{CH}_2\text{CH}_2\text{CH}_2-$ between POSS cage and organic group, which was the most vulnerable part in POSS-8Phenol (26). The second stage from 300°C to 410°C was assigned to the breaking of imide ring, which was the typical pyrolysis temperature of poly-imide (27). The third stage from 450°C to 750°C showed POSS-8Phenol had different behavior in N_2 or air. In N_2 , the pyrolysis process occurred from 450°C to 710°C ; it was due to the breaking of Si-O-Si cage (26). Different from pyrolysis behavior in N_2 , it could be found that POSS-8Phenol had additional behavior in air and the main temperature peak was at 670°C .

Figure 5: TG and DTG curves of POSS-8Phenol in air or N_2 : (a) Weight-temperature curve (TG); (b) Derivative weight-temperature curve (DTG).

Figure 6: XRD patterns of cracking product of POSS-8Phenol.

In order to study POSS-8Phenol's different behavior in air or N_2 , XRD was used to analyze crystal structure of pyrolysis products above. Spectra are showed in Figure 6; some crystal peaks could be found in residual product after pyrolysis in air, but only two amorphous peaks in N_2 . After checking with the XRD database, it could be concluded that crystal peaks when pyrolysis in air were due to the cristobalite, a kind of SiO_2 (PDF39-1425). Two amorphous peaks at 23° and 44° were due to the amorphous carbon pyrolysis products in N_2 , corresponding to (002) and (100) lattice plane for amorphous carbon (PDF26-1079), which was common in XRD analysis of organic pyrolysis products (18).

Combined with thermal analysis and XRD analysis, the pyrolysis behavior of POSS-8Phenol could be summarized as Figure 7. Three temperature stages were corresponded to the chain scission of different part in POSS-Phenol. When the POSS-8Phenol transferred into crystal SiO_2 , hot oxygen would definitely be consumed from $-SiO_{1.5}-$ to SiO_2 . On the other hand, the crystal SiO_2 could play a role as the barrier to resist the erosion of hot oxygen into the material (3). Therefore, POSS-8Phenol had the potential to improve the oxidation resistance of phenolic resin.

Figure 7: Pyrolysis process of POSS-8Phenol in air or N_2 .

3.2 Analysis and characterization of cured POSS-PR

3.2.1 FTIR analysis of the cured POSS-PR

The FTIR spectra of cured POSS-PR resin were used to study the state of POSS in the matrix resin. As showed in Figure 8, the characteristic peak of Si–O–Si at $1,100\text{ cm}^{-1}$ and C=O at $1,712\text{ cm}^{-1}$ still existed after curing. Even though the intensity of them was weak, it could be observed that the intensity increased with the increased POSS content, which indicated that POSS still maintained its unique cage structure during the curing process of POSS-PR. Other absorption peaks were basically the same as before modification; the distribution of characteristic peaks was as follows: the peak of O–H of the phenol group and $-CH_2OH$ at $3,500\text{ cm}^{-1}$ (broad peak); the stretching vibration peak of C–H in $-CH_2-$ from $2,800$ to $2,950\text{ cm}^{-1}$; the stretching vibration peak of the C=C double bond in the benzene ring at $1,610$ and $1,510\text{ cm}^{-1}$; the peak of C–O in phenolic group at $1,270\text{ cm}^{-1}$; the stretching vibration peak of aliphatic C–O at $1,130$ and $1,005\text{ cm}^{-1}$; the ortho-substituted and para-substituted peak of the benzene ring at 760 and 870 cm^{-1} , respectively.

3.2.2 Thermal stability and pyrolysis products analysis of the cured POSS-PR

Figure 9a and b, respectively, show the weight-temperature curve and derivative weight-temperature curve from room temperature to $1,000^\circ\text{C}$ in nitrogen atmosphere. From the TG in Figure 9a, it could be seen that with

Figure 8: FTIR spectra of cured product of PR, 3% POSS-PR, 5% POSS-PR, and 8% POSS-PR.

Figure 9: TG and DTG curves of PR and POSS-PR: (a and c) weight-temperature curve (TG), (b and d) derivative weight-temperature curve (DTG).

POSS-8Phenol content increased, the char yield of POSS-PR increased from 58.6% to 65.2% in N₂, which could be explained from the increase of crosslinking degree of POSS-PR. In phenolic resin, the crosslinking point of a phenol molecule is 3, while that of a POSS-8Phenol molecule is 16. In addition, the bond energy of Si–O–Si (452 kJ/mol) was much higher than that of C–O (336 kJ/mol) or C–C (356 kJ/mol). Figure 9b show the derivative weight-temperature curve of POSS-PR; two main DTG peaks could be found. For neat PR, peak values were 397°C and 515°C, while that increased to 418°C and 535°C with the content of POSS-8Phenol increased. Consistent with the reason for the improvement of char yield, the increase of pyrolysis peak temperature was also due to the increase of crosslinking degree and bond energy.

In order to explore the difference of crosslinking degree between POSS-PR and neat PR, the DMA results of 5% POSS-PR and pure PR are shown in Figure 10. Although there was no obvious peak on $\tan \delta$ -temperature curve, the glass transition temperature of 5% POSS-PR was obviously higher than that of neat PR. Compared with pure PR, 5% POSS-PR had smaller $\tan \delta$ and higher modulus.

Generally, for the same type of polymer, higher glass transition temperature and modulus meant higher crosslinking degree.

Generally speaking, the pyrolysis of polymer in nitrogen was due to the breaking of chemical bonds, while the pyrolysis in air occurs due to additional consideration of oxidation reaction. From Figure 9c, the residual weight of neat PR had dropped to 2.3% at 700°C in air, while that of POSS-PR was 12.7%, 22.7%, and 26.9%. Although all of them were lower than 4% after 800°C, result above indicated POSS-8Phenol had the improvement to slow down the oxidation reaction of PR. The difference between main DTG peaks in Figure 9d also confirmed this conclusion. There were three pyrolysis peaks in each curve. Little difference could be found about the first peak around 390°C, but the temperature of the second peak increased from 486°C to 513°C with the content of POSS-8Phenol increased. This phenomenon was more obvious near the maximum DTG peak. The shape peak at 544°C meant severe oxidative weightlessness in neat PR, but it developed into a plateau in POSS-PR which meant the reduction of oxidation rate. After taking the middle value of the

Figure 10: DMA result of cured PR, 5% POSS-PR.

plateau as the peak value, peak values were 636°C, 652°C, and 680°C, respectively. Those results confirmed that POSS-8Phenol could improve the thermal anti-oxidation properties of PR.

Figure 11 show the XRD patterns of pyrolysis product of 8% POSS-PR. Similar to POSS-8Phenol's pyrolysis result, crystal SiO_2 still could be found when pyrolysed in air, while only amorphous carbon existed in N_2 . Above results confirmed the improvement of the anti-oxidation properties, and the reason for the improvement was bound up with the formation of crystalline SiO_2 .

Figure 12 show the XPS spectra of the cured product and the pyrolysis product of 8% POSS-PR in different atmosphere. When pyrolysed in N_2 , the content of O decreased sharply and that of C increased, which was the result of the dehydration reaction of the phenolic resin in the carbonization process under N_2 . The slight decrease of Si could be attributed to the increase of C caused by carbonization, which led to an increase in the total number. When pyrolysed in air, only a small

Figure 11: XRD patterns for pyrolysis product of 8% POSS-PR.

Figure 12: XPS patterns for pyrolysis product of 8% POSS-PR.

amount of carbon was left, which corresponded to the lower residual weight when pyrolysed in air in Table 1. Main elements in the pyrolysis products under air were Si and O, and the atomic ratio was close to 1:2, which corresponded to the SiO_2 confirmed in the XRD results. From the results above, it could be concluded that the pyrolysis process of POSS-PR in air led to a sharp increase of Si, and the ratio of Si to O was consistent with silicon dioxide.

3.2.3 Micro morphology and element distribution of the cured POSS-PR

The fractured surface of cured POSS-PR was characterized by SEM; relevant images are showed in Figure 13. The fractured surface of PR was homogeneous. After the introduction of the POSS-8Phenol, obvious phase separation occurred regardless of the POSS content from 3% to 8%. In Figure 11b, the phase separation size of 3% POSS-PR was mainly about 2 μm , and some small spherules with a diameter of 500 nm or even smaller could be observed, which indicated that the generation of phase separation was faster than the curing process of POSS-PR and spherules were gradually formed from nanoscale cores. With POSS-8Phenol content increased, the average diameter of the spherules increased from 1.5 to 2 μm , and core structure could not be observed any more. It could be concluded that although the spherules had a certain compatibility with PR, the compatibility gradually got worse as the content of POSS-8Phenol increased.

Elements mapping of Si, C, and O was showed in Figure 14. Figure 14a was a typical SEM image of 8% POSS-PR. First, the mapping of Si element in Figure 14b

Table 1: Main thermal stability data of POSS-PR

Sample	In N ₂			In air			
	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	Char yield (1,000°C)	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	Char yield (700°C)	Char yield (1,000°C)
PR	397	515	58.6	486	544	2.5	1.2
3% POSS-PR	401	524	59.3	507	636	13.3	2.3
5% POSS-PR	410	530	62.2	516	652	21.9	2.6
8% POSS-PR	419	537	65.8	513	680	26.3	3.2

Figure 13: SEM images of the cured product of: (a) PR, (b) 3% POSS-PR, (c) 5% POSS-PR, (d) 8% POSS-PR. **Figure 14:** EDS analysis of 8% POSS-PR. (a) SEM image of 8% POSS-PR; (b) Si mapping of image "a;" (c) C mapping of image "a;" (d) O mapping of image "a."

shows that the Si element was evenly divided into the matrix and the phase separation, and there was no obvious aggregation of Si. But the mapping of C and O in Figure 14c and d show differences; it could be clearly

observed that the mass content of C and O at the area of phase separation was significantly lower than the surrounding matrix area. Therefore, it could be confirmed that a part of POSS-8Phenol was present in the matrix and copolymerized with PR's structure, but the other part occurred was phase separation, and gradually became the spheres dispersed in the modified resin from the nanoscale to the micron level. The different phenomenon between Si with C and O might be due to the fact that the silicon in the material was as low as 1 wt%; it was hard to see the aggregation.

3.3 Antioxidant performance test of C-POSS-PR

Figure 15 showed the flexural strength of C-PR, C-3%POSS-PR, C-5%POSS-PR, and C-8%POSS-PR before and after oxidation, which were marked as S1, S2, S3, and S4, respectively. Compared with the flexural strength of C-PR (590.271 MPa) before oxidation, the addition of POSS led to the overall decrease in flexural strength,

Figure 15: Flexural strength of C-POSS-PR after 500°C oxidation for 10 min.

which could result from the phase separation in POSS-PR. Among them, the flexural strength of C-POSS-PR increased (411.46, 450.904, 470.987 MPa) with the increase of POSS content. This was due to that POSS-8Phenol had more phenolic groups, which increased the crosslinking degree of the resin. Results above indicated that the bending strength of C-POSS-PR was together affected from the degree of POSS-PR crosslinking and phase separation.

Usually, carbon fiber would be rapidly oxidized under air atmosphere above 400°C which might cause complete destruction of the material. In order to verify the oxidation resistance of POSS-PR, C-POSS-PR was subjected to 500°C oxidation treatment. The flexural strength after treatment is showed in Figure 15. It could be clearly seen that the flexural strength of C-PR after oxidation treatment decreased significantly (217.342 MPa), while the flexural strength of C-POSS-PR was higher (223.705, 341.959, 268.194 MPa). When the POSS content was 5%, the flexural strength increased most (57.33%). Combined with the previous thermal analysis results of POSS and POSS-PR, that improvement could be attributed to the form of crystalline SiO₂ when C-POSS-PR oxidized in air, which absorbed and prevented hot oxygen into the material.

4 Conclusion

In order to improve the anti-oxidation properties of phenolic resins, POSS-modified phenolic resins (POSS-PR) were prepared, in which POSS was efficiently prepared by siloxane condensation reaction and Michael addition reaction. Chemical structures of POSS and POSS-PR were successfully characterized. In POSS-PR, some POSS was copolymerized in the resin, but others were aggregated to form phase separation. POSS-PR had higher char yield and pyrolysis temperature in N₂, and the max pyrolysis temperature increased from 543°C to 680°C in air, which approved the effect of POSS to improve anti-oxidation properties of phenolic resins. Through the analysis of the structure of pyrolysis products, that improvement resulted from the generation of SiO₂ when POSS-8Phenol pyrolysis in air. In order to further verify the oxidation resistance of POSS, carbon fiber-reinforced POSS-PR composites were successfully prepared. After high-temperature oxidation test, the flexural strength of composites increased from 217.342 to 341.959 MPa. Results above fully proved that POSS-PR had higher anti-oxidation properties than pure PR resin.

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