Bionic boron/silicon-modified phenolic resin system with multifunctional groups: synthesis, thermal properties and ablation mechanism

Fengyi Wang1,2,3, Zhixiong Huang1, Zhiguang Guo2,3

1School of Material Science and Engineering, Wuhan University of Technology, Luoshi Road No.122, 430070 Wuhan, People’s Republic of China
2Hubei Collaborative Innovation Centre for Advanced Organic Chemical Materials and Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, People’s Republic of China
3State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People’s Republic of China
✉ E-mail: zguo@lcp.cas.cn

Abstract: A kind of silicon-and-boron-modified phenolic–formaldehyde resin (SBPF) with excellent thermal stability was fabricated via a simple two-step method and used for the matrix of ablation materials. The structure and thermal stability of the modified phenolic–formaldehyde resin (PFs) were characterised. The results showed that boron and silicon elements have been incorporated into SBPF in the form of a chemical bond. Meanwhile, the cured products showed an increase in graphite structure and a decrease in disordered structure due to the incorporation of boron and silicon. Compared with the ordinary phenolic resin, the initial thermal degradation temperature and charring yield at 800°C of SBPF increased by 73°C and 15 wt%, respectively. Further, the modified PFs, nano-Al2O3 powders, glass powders and vitreous silica fibres were used to obtain a novel ceramicizable phenolic moulding composite. The morphology, chemical composition and ablative characteristics of the composites were explored. The results showed that a compact and homogeneous SiO$_2$–Al$_2$O$_3$ layer formed on the ablated surface and protected the carbonised matrix and fibres from further oxidation. Compared with the ordinary PF composites, the SBPF composites showed a highly decreased linear/mass ablation rates, indicating the synergistic effect of boron and silicon modification on the enhanced ablation property.

1 Introduction

As the most commonly used polymer, phenol–formaldehyde resins (PFs) are widely employed as adhesives, structural materials and matrix for ablative materials owing to their outstanding mechanical properties and heat resistance [1–3]. However, their applications, especially in the field of ablation composites, are impeded by the low decomposition temperature, low charring yield and poor mechanical stability at high temperature. For this reason, an increasing demand for phenolic-based ablative materials has attracted extensive research to improve their mechanical, ablation or multifunctional properties. Incorporating various functional elements or groups into the structure of phenolic resin was considered to be an effective and convenient way to obtain modified PFs with multifunctional properties, such as boron, organic silicon, maleimide, phosphorus compounds and phenyl-phenol and so on [4–10]. Gao et al. [11, 12] did some significant work on the synthesis of boron modified phenolic resin (BPF). As is reported in the literature, it is proved that the formation of borate linkage showed very high bond energy and meanwhile decreased the probability of forming ether or ester linkage, which leads to the excellent thermal resistance of the BPF [13, 14]. Organic silicon is another attractive modifier for phenolic resin due to its excellent thermal stability [15, 16], flame retardancy [17], toughness [18] and moisture resistance [19]. It is very meaningful to incorporate silicone into organic polymers [20–24] to impart superior properties to the mixture. Some reports proved that the incorporation of silicone into organic polymers is an effective way to improve the oxidation resistance of polymers [16, 21, 24, 25]. Haraguchi et al. [25, 26] prepared phenolic/silica hybrid by using silicon alkoxide as silicon resource and mechanical and thermal properties have been improved. However, the main problem is the incompatibility of silicone and phenolic resin, and phase separation would always happen, which result in an unstable hybrid system [16, 27, 28]. The mechanical and thermal properties of the hybrids could be affected by the phase structure (including dispersion state [29], particle size [18, 30] and interface of the phases [25]) to a great extent. It is generally believed that introducing of boron or phosphorous compounds [24–28] or inorganic modifiers [29, 30] into the backbone of phenolic resin could make a dramatical structural modification. Li et al. [31] synthesised boron and silicon modified phenolic resin by adding boric acid (BA) and hexamethylenetetramine (HMTA) into the silicon phenolic resin (SN) as the curing agent, finding that the formation of the stable chemical bonds (B–O, Si–O) and oxide compounds of boron and silicon during thermal degradation contributed to the higher thermal stability.

Although BA and organic silicon have been well established as multifunctional building blocks in polymer synthetic chemistry, very few attempts have been made to combine both BA and silicone with PFs [31] to our knowledge, which may provide novel composite materials with multifunctional properties. In addition, researches on the synergistic effect of boron and silicon on the thermal properties and phase structure of PF need to be studied deeply. To this end, the aim of this paper intends to introduce boron and silicon structure into PFs by a simple method and obtain a modified resin with a novel structure which has high cross-link density and high char yield under high temperature. In this study, a thermal-resistant silicon-and-boron-modified phenolic–formaldehyde resin (SBPF) was prepared a simple two-step method and used for the matrix of ablation materials. The structure of PF, silicon modified PF (SPF) and SBPF was characterised by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) and Raman spectroscopy, respectively.
Thermal stability of the investigated composites was estimated by thermogravimetric analysis (TGA) and derivative thermal gravimetric analysis (DTG), respectively. Further, a novel phenolic resin composite was prepared by compression moulding using SBPF as the matrix, nano-Al\(_2\)O\(_3\) powder as the filler, glass powder with a low melting point as the forming additive and vitreous silica as the reinforced materials. The ablation properties of the composites were determined by oxyacetylene torch environment. The microscopic structure of the resulted residues was studied using scanning electron microscopy (SEM). The constituents of the residues were investigated using energy dispersive spectroscopy (EDS). In addition, the effect of the matrix on thermal stability, microstructure and ablation properties of the fibre reinforced composites was also investigated. This research provides a significant way to design ablation resistant phenolic resin composites.

2 Experimental

2.1 Materials

Phenol, paraformaldehyde (PFA), BA, hydrochloric acid (HCl), NaOH, acetone and ethanol were all of the analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. Phenyltriethoxysilane (PTES) and hexamethylenetetramine were purchased from Aladdin Chemicals Co., Ltd. All the above chemicals were used as received. Vitreous silica fibre was purchased from Jintaidaheng Glass Fiber Cloth Weaving Factory, China. Nano-Al\(_2\)O\(_3\) ceramics powder (particle size of 20–80 nm) was purchased from Nabo New Material Technology Co., Ltd, China. Glass powder (325 meshes, the softening temperature from 600 to 800°C) was purchased from Yuyang Minerals Sales Departments, China.

The composition of glass powder: SiO\(_2\) (70.8 wt%), Al\(_2\)O\(_3\) (0.92 wt%), ZrO\(_2\) (8.72 wt%), CaO (3.86 wt%), K\(_2\)O (0.4 wt%), Na\(_2\)O (14.05 wt%), and Fe\(_2\)O\(_3\) (0.25 wt%).

2.2 Preparation of SBPF

The synthesis route of SBPF was designed as shown in Fig. 1. A series of repeated trials, the molar ratio of phenol: formaldehyde: boric acid: PTES was calculated to be 1: 1.2: 0.2: 0.1. All the details of formula are listed in Table 1. In the first step, phenol, paraformaldehyde and NaOH as a catalyst were added into a three-necked flask. Then the mixture was mechanical stirred strongly and held the temperature at 70°C for 1.5 h and followed by a vacuum dehydration process. Then salicyl alcohol (SA) was acquired according to our previous work [32]. In the second step, a mixed solution (pH ∼7) containing PTES, HCl and ethanol was stirred strongly for 10 min and added into the acquired SA slowly and then reaction continued at refluxing temperature (∼105°C) for 30 min. Then BA dissolved in ethanol was added into the mixture drop by drop and reacted for another 2 h. Finally, after a water-removing process, the product SBPF was acquired. The pristine PF and SPF were also prepared with the same process for comparison.

To remove the disturbance of residual reactants on the test results, the purification of all modified PFs was conducted. The modified PFs were immersed into a sodium hydroxide solution for several minutes and then washed with deionised water for several times. Then, the purified products were obtained by a centrifugalisation and drying process. Finally, the modified PFs after purification were cured in an oven. The cured modified PFs were used as the sample for the following tests. The resins were cured following the scheme: 120°C for 2 h, 180°C for 4 h and 200°C for 2 h.

2.3 Fabrication of nano-Al\(_2\)O\(_3\)/vitreous silica fibre/phenolic composite

The nano-Al\(_2\)O\(_3\), glass powders and ethyl alcohol were added to the PF, SPF and SBPF, respectively, by mechanical stirring for 1 h with a post-ultrasonic treatment for 30 min. Then, a uniform glue adhesion agent was obtained. The mixture solution contained phenolic, nano-Al\(_2\)O\(_3\) and glass powder particles at the mass ration...
of 10:5:1. The fabrication of composite was arranged in layers of plain weave vitreous silica fibre cloth, including the manual impregnation (hand layup method) with glue adhesion agent. The impregnated fabrics were left in the prepregging rack at ambient temperature for 24 h to evaporate the solvent inside for better impregnation of the resin into fabrics. The ceramizable composite was prepared in the platen press by compression moulding. The as-produced composites were designated as V-PF, V-SPF and V-SBPF. The obtained composite was 40 × 40 mm² in size and 4 mm in thickness. Then, the composites were cut into specimens under the required size for experimental purpose.

2.4 Testing and characterisation

FT-IR spectra were obtained using a Nicolet 6700 infrared spectrometer. TGA was measured on a NETZSCH STA449F3 instrument at a heating rate of 10°C/min. The crystal structure of cured products was characterised by XRD using a D8 Advance X-ray diffractometer with CuKα radiation (λ = 0.154 nm) at 2θ ranging from 10° to 80°. The degree of structural order information was characterised by Raman spectra using a Renishaw inVia Reflex system at an excitation wavelength of 514.5 nm. The morphology of sample surfaces was exhibited on a field-emission scanning electron microscope (FESEM, JEOL JSM-6701F) with Au-sputtered specimens. The element distribution maps of the samples were obtained by EDS (EDS, Kevex).

The ablation test was performed using an oxyacetylene flame torch and the characteristic values were calculated based on ASTM E285-80. K-tape thermocouple was firmly attached with the composites at the centre of back faces of a specimen to record temperature changes as a function of time during the test. The external body of the thermocouple was protected with the help of aluminium tape. The distance and the angle between the specimen surface and the torch tip were 20 mm and 90°, respectively. The flame temperature in the present ablation testing system was estimated to be ∼2200°C and the heat flux was about 80 kW/m². Plate test specimens were of 40 × 40 mm² in size and 10 mm in thickness. Temperature enhancement with time was recorded and displayed during the flame exposure on the surface of the composite for the duration of 100 s. Both the linear and mass ablation rates were calculated by dividing the specimen thickness or the weight change before and after the test for each specimen.

3 Results and discussion

3.1 IR analysis of cured modified phenolic resins

The chemical bonds of cured PF, SPF and SBPF are characterised by FT-IR spectra as shown in Fig. 2 and Table 2. The absorption peaks at 3410, 2924, 1384 and 1225 cm⁻¹ of SBPF can be assigned to C–OH, C–H, B–O and CH2–O–CH2, respectively. In addition, the absorption peaks assigned to C=C and C–H groups in the benzene ring could be found obviously in the FT-IR curves of all three samples, indicated that ring opening reaction did not happen during the reaction process. It is notable that peaks at 887, 814 and 754 cm⁻¹ which assigned to C–H flexural vibration of benzene rings decreased by the incorporation of boron and silicon, suggesting that substitution reaction took place on the benzene rings while boronates and silicates were formed by the reaction of B–OH and Si–O–C with phenolic hydroxyl and methylol groups of PF. Compared with the curve of PF, the phenol hydroxyl stretch at 1225 cm⁻¹ of the cured SBPF almost disappeared, and the new absorption peaks at 1384 and 651 cm⁻¹ assigned to B–O and B–C stretch vibrations begin to appear [33]. Moreover, the bands at 1056 and 973 cm⁻¹ were assigned to Si–O–Si and Si–O–ph [21]. As the disturbance of residual impurities has been eliminated, the appearance of the new absorptions peak was caused by the boron and silicon incorporation. According to the above analysis, it is suggested that boric and silicon elements have been incorporated into the modified phenolic resin.
3.2 Thermal properties of cured modified phenolic resins

TGA and DTG curves of cured PF, SPF and SBPF are presented in Figs. 3 and 4, respectively. The characteristic thermal decomposition data, such as temperature at 5% weight loss ($T_{5\%}$), temperature at maximum weight loss rate ($T_{\text{max}}$) and char yields at 800°C are listed in Table 3. As can be seen from Fig. 3, the initial thermal degradation temperature ($T_{5\%}$) for BSPF and SPF was 463 and 402°C, respectively, which was higher than that of the PF (390°C). The pyrolysis processes of cured PF, SPF and SBPF are similar in all of which three major reaction regions exist. In the first region of 0–300°C, very little mass loss was observed due to the evolution of unreacted oligomers and crosslinked by-products [34]. In the range of 300–600°C, the main mass changes were observed owing to the decomposition reactions. When the temperature was increasing to the range of 600–800°C, the mass loss rates was trending to zero (Fig. 4). The mass loss changes observed were attributed to the breakage of C–O and O–H bonds and redistribution reactions of B–O and Si–O bonds. The incorporation of BA and PTES improved the thermal stability, and the charring yield at 800°C of the sample after pyrolysis were 62.0, 68.2 and 77.0%, respectively, indicating the synergistic effect of boron and silicon modification on the thermal stability of phenolic resin. As is shown in Fig. 4 and Table 3, it can be seen that sample SBPF showed a higher decomposition peak temperature ($T_{\text{max}}$) and a lower decomposition rate compared with PF and SPF, suggesting that boron and silane modification on phenolic could effectively enhance thermal performance. In addition to the thermal decomposition temperature and char yield, cross-link density also has an important implication on the pyrolysates structures of cured PF. The average number of methylene bridges connected to phenolic nuclei increases with the elevation of cross-link density by introducing boron and silicon, which can prevent the release of phenol and its derivatives. And the fracture of the chemical bonds for the cured SBPF occurs at higher temperatures, increasing the thermal decomposition temperature of the cured resins. The cured SBPF showed a three-dimensional network structure with a high degree of branching, suggesting that the PF thermosets with multiple heat-resistant functional groups were more thermal stable than neat phenolic resin.

3.3 Microstructure of cured modified phenolic resin

Raman spectroscopy has been widely used to acquire information on microstructural changes in carbonaceous polymer materials, particularly the degree of structurally order information. The D-band nearly 1358 cm$^{-1}$ is mainly associated with amorphous carbon and the G-band nearly 1580 cm$^{-1}$ is derived from the C–C stretching mode [35]. The relationship between the D band and the
G band intensities has been widely used in the literature in different forms, such as $I_D/I_G$, to illustrate the degree of structural order about carbonaceous materials [36]. And the microcrystalline size ($L_a$), which corresponds to the in-plane dimension of the single microcrystalline domain in carbonised products, can be determined from the integrated intensity ratio $I_D/I_G$ as follows [2]:

$$L_a = 4.4(I_D/I_G)^{-1} \quad (1)$$

Fig. 5 shows the Raman spectra measured for cured PF, SPF and SBPF. According to formula (1), the crystal size $L_a$ of SPF and SBPF is calculated to be 3.08 and 3.29 nm, respectively, much larger than that of PF (1.65 nm). The obvious changes about the degree of structural order of cured PFs demonstrate that the boron and silicon incorporation has made a rearrangement of crystalline structure which results in an increase of graphite structure and a decrease of the disordered structure. The results suggested that the incorporation of boron or silicon in the phenolic resin structure not only did benefit to the formation of the graphene sheet but also promoted the graphitisation of phenolic resin. The increased thermal stabilities of hybrids may also be ascribed to the formation of orderly carbon structure [37].

XRD pattern is also a useful tool to investigate the graphene structure of carbonaceous materials. Fig. 6 shows the XRD patterns of the cured PF, SPF and SBPF. The large and wide peak appeared around $2\theta = 20^\circ$ was typical of amorphous diffraction peaks confirming the presence of an amorphous phase in the cured products, and was shifted by the introduction of boron and silicon.

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**Fig. 6** XRD patterns of cured PF, SPF and SBPF samples

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**Fig. 7** Ablated surface morphologies of composites

a, b V-PF,
c, d V-SPF and
e, f V-SBPF
towards the 002 reflection of turbostratic carbon structure, which is around 25°. Another weaker and broadband was around 42°, which may correspond to a second order of the main amorphous peak. At the same time, the small peak appeared around 2θ = 27.9° was a crystalline diffraction peak from B2O3, indicated that a small part of B2O3 did not react with a hydroxyl group in the phenol. In addition, according to the fact that there is not any peak related to PF in the diffraction pattern of SPF and SBPF, it can be concluded that there is not any stacked form of graphene layers in SPF and SBPF different from PF stacking. As calculated from Bragg’s law, the interlayer spacing (d-spacing) of the cured PR is larger than that of cured SPF and SBPF. The decrease of the d-spacing may be due to the crystalline improvement resulting from the addition of boron and silicon, and the lowering in electron density due to the boron and silicon substitution. In summary, an almost thorough polycondensation reaction among the reactants has taken place in the synthesis and curing process of SBPF according to the XRD and FT-IR analyses.

3.4 Structure and surface morphology of char layers

In order to investigate the ablative properties of modified PFs based composites, the morphologies of all the composites after ablation were explored via the oxyacetylene torch tests, which shows a diversity of char layers formed in the ablation. Fig. 7 designates the morphology of the ablated surface of V-PF, V-SPF and V-SBPF specimens after ablation.

The morphology of composite V-PF after ablation (Figs. 7a and b) shows an obvious destruction of vitreous fibres which exposed to air entirely. It also shows that not only the phenolic matrix was decomposed completely, but also the nanoparticles were blown off by the scouring action of the jet stream, resulting in a serious damage on the surface. The glass powder and nano-Al2O3 melt and distribute in the space between fibres and do not tend to adhere to the fibre surface, which was due to the rapid degradation of phenolic matrix and formation of released gas such as H2O, CO and CO2. The SEM images of V-SPF and V-SBPF experienced ablation (Figs. 7c–f) show completely different surface morphologies of the modified composites from that of composite V-PF. The ablated surface of V-SPF shows a homogeneous and compact structure which was covered by a molten layer. And the V-SBPF after ablation also shows a compact surface with a thermal protective layer covered by lots of melt spheres. The lower porosity and little destruction of fibres on the surface of V-SBPF indicated that the interaction between the matrix and fibres became strengthened and harder to be stripped out with an increase of boron and silicon content. Introduction of a small quantity of boric acid and siloxane segment could remarkably improve the

| Sample | Ablation properties |
|--------|---------------------|
|        | Linear ablation rate, mm/s | Mass ablation rate, g/s |
| V-PF   | 0.079               | 0.053              |
| V-SPF  | 0.072               | 0.038              |
| V-SBPF | 0.063               | 0.029              |

Fig. 8 SEM and EDS images of the molten layer mixed with pores for the ablated V-SBPF surface

a SEM image
b, c EDS images

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composites' mechanical properties in ablation, obviously. This dramatic phenomenon might be accumulated to the possibility that the flexibility of boric acid and siloxane segment promotes molecular movement of matrix, strengthening interaction between the resin matrix and fibres while avoiding reducing crosslink density excessively. Besides, the B–O and Si–O segment lowered internal stress and defects in matrix, and strengthened their bonding strength. The nano-Al₂O₃ acted as a heat dissipater and provided a much better network for heat transfer in a random direction, reducing the temperature concentration in the composites. After an extremely high temperature ablation, the nano-Al₂O₃ turned to be a highly viscous melt with strong adhesion strength and was left on the surface of the composite, which partially seals the pores and avoids phenolic matrix and vitreous silica fibres from more ablation. In the outer region, next to the ablated centre, nano-Al₂O₃ can react with SiO₂ to produce mullite (Al₆Si₂O₁₃) where there is lower temperature, flow rate and pressure relative to the centre region [38]. Therefore, nano-Al₂O₃ and the produced SiO₂ are sintered together to form a dense layer that block the conducted heat and resist the ultra-high temperature scouring of oxyacetylene flame.

The ablation properties of the composites are measured by calculating the linear and mass ablation rates and presented in Table 4. The linear and mass ablation rates of the V-PF are 0.079 mm/s and 0.053 g/s, respectively. With SBPF substitution for ordinary PF as the matrix in the composite, the linear ablation rate and mass ablation rate of the composite V-SBPF decreased evidently (0.063 mm/s and 0.029 g/s). Compared with unmodified composite V-PF, the V-SBPF composite showed highly improved ablation resistance.

### 3.5 Elemental analysis of char layer of composite V-SBPF

To study the mechanism of the ablation process of V-SBPF, the ablated surface of composite V-SBPF has been investigated by SEM and EDS analyses. As shown in Figs. 8 and 9, two morphological characteristics in the SEM image can be observed during the ablation process: (i) a compact layer mixed with small pores; and (ii) vitreous silica fibres adhere to lots of spherules.

The SEM morphology and EDS results of the compact layer mixed with small pores are shown in Fig. 8 and Table 5. Notably, it is found that a number of white spots embedded in the interior of the grey layer. According to the results of EDS, the main elements in white spots show different contents compared with those in the grey layer. As shown in Figs. 8b and c, the majority elements of O, Al and Si were found. Some minority elements of Zr and Ca were found as well, which were derived from the minor part of the glass powder. As shown in Fig. 8b and Table 3, the molar ratio of O to Al to Si detected in white spots was close to 6:2:1, which meant that the white spots were made of SiO₂ and Al₂O₃. In addition, the main chemical constituents of the grey layer are O, Al and Si, among which the content of Al is relatively lower. The molar ratio of oxygen and silicon in the grey layer is approximately equal to 1.8. These results imply that the thin film

![SEM and EDS images of the fibres for the ablated V-SBPF surface](image_url)
on the surface of V-SBPF composites was made of SiO2. Liquid SiO2 aggregates together with the increase of temperature and forms a layer embedded in solid Al2O3 accumulations. The SiO2–Al2O3 layer protects the matrix and fibres from more ablation and binds the vitreous silica fibres firmly during the ablation process.

Due to the exfoliation of high speed fire stream, part of the ablated surface showed a kind of morphology which was uncovered with SiO2–Al2O3 layer while adhering to lots of spherules. Fig. 9 shows the SEM morphology and EDS results of this area. However, vitreous silica fibres on the ablated surface of V-SBPF composites are not completely exposed to oxidative atmosphere owing to the protection of spherules. As shown in Fig. 9c, the major elements of C, Al, Si detected on surface of the vitreous silica fibre surface, confirming the presence of SiO2–Al2O3 layer and carbonised matrix. Moreover, large amounts of spheres containing O, Si and Al are also shown on the surface of the vitreous silica fibre (Figs. 9a and b), and the oxygen contents of spheres were relatively high. According to Table 5, EDS data show that the molar ratio of O to Al to Si in the sphere is approximately equal to 8:1:1.5, which meant that the white EDS data show that the molar ratio of O to Al to Si in the sphere is approximately equal to 8:1:1.5, which meant that the white

| Sample | C     | wt% | Si     | wt% | Al     | wt% | Zr     | wt% | Ca     | wt% | Na     | wt% |
|--------|-------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|
| Fibres | A     | 53.83 | 67.14 | 28.79 | 21.48 | 14.92 | 10.69 | 2.5  | 0.55   | 0.23 | 0.12   |     |
|        | B     | 48.34 | 63.15 | 0.63  | 0.49  | 47.87 | 35.63 | 2.79 | 0.84   |     |        |     |

4 Conclusion

A kind of SBPF with excellent thermal stability was fabricated via a simple two-step method and used for the matrix of ablation materials. The structure of the modified PFs was characterised by FT-IR, XRD and Raman spectroscopy. The results showed that boron and silicon elements have been incorporated into SBPF in the form of a chemical bond. Meanwhile, the cured products showed an increase in graphite structure and a decrease in disordered structure due to the incorporation of boron and silicon. Thermal behaviour of the products was investigated by TGA and DTG. Compared with the ordinary phenolic resin, the initial thermal degradation temperature and char yield at 800°C of SBPF increased by 73°C and 15 wt%, respectively. In addition, the modified PFs, nano-Al2O3 powders, glass powders and vitreous silica fibres were used to obtain a novel ceramizable phenolic moulding composite. The composite V-SBPF after ablation also shows a compact surface with a thermal protective layer covered by lots of melt spheres, which confirmed the good adhesion between SBPF and fibre at high temperature. The decreased linear and mass ablation rates for V-SBPF (0.063 mm/s and 0.029 g/s) indicated that the V-SBPF possessed highly improved ablation resistance due to silicon and boron modification. In summary, this work provides a significant way to obtain a modified phenolic resin with excellent thermal stability, and it would be an innovative way for the design of the phenolic-based ablative materials.

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6 References

[1] Gao, J.A., Li, X., Wu, W.H., et al.: ‘Octa(aminophenyl) polyhedral oligomeric silsesquioxane-boron-containing phenol-formaldehyde resin nanocomposites: synthesis, cured, and thermal properties’, Polym. Compos., 2011, 32, (5), pp. 829–836
[2] Chang, Y., Shen, S.H., Liu, Y.J.: ‘The effect of titanium incorporation on the thermal stability of phenol-formaldehyde resin and its carbonization microstructure’, Polym. Degrad. Stab., 2013, 98, (2), pp. 514–518
[3] Islam, S.A., Balsbaugh, M.A., Xu, P.J.: ‘High temperature ablation of kaolinite layered silicate/phenolic resin/asbestos cloth nanocomposite’, J. Hazard Mater., 2008, 150, (1), pp. 136–145
[4] Abdalla, M.O., Ludwig, A., Mitchell, T.: ‘Boron-modified phenolic resins for high performance applications’, Polymer, 2003, 44, (24), pp. 7353–7359
[5] Inamurana, M., Matsu, K., Takeda, S., et al.: ‘A new role for phosphorus in graphitization of phenolic resin’, Carbon, 1999, 37, (2), pp. 261–267
[6] Rahaman, A.R., Kok, M., Farsalil, M.N., et al.: ‘High temperature ablation of kaolinite layered silicate/phenolic resin/asbestos cloth nanocomposite’, Macromol. Mater. Eng., 2004, 289, (2), pp. 208–212
[7] Hasegawa, I., Fukuda, Y., Kajiwara, M.: ‘An improved procedure for fabricating SiO2–TiO2–phenolic resin hybrid fibers as precursors for long SiC fibers by sol–gel processing’, J. Eur. Ceram. Soc., 1997, 17, (12), pp. 1467–1473
[8] Liu, Y.H., Jie, T.L.: ‘Pyrolysis and structure of hyperbranched polyborate modified phenolic resin’, Carbon, 2007, 45, (10), pp. 1965–1971
[9] Kawamoto, A.M., Pardini, L.C., Diniz, M.F., et al.: ‘Synthesis of a boron modified phenolic resin’, J. Aerosp. Technol. Manage., 2010, 2, (2), pp. 169–182
[10] Gao, J.G., Jiang, C.J., Su, X.H.: ‘Synthesis and thermal properties of boron-nitrogen containing phenol formaldehyde resin/MMT nanocomposites’, Int. J. Polym. Mater., 2010, 59, (8), pp. 544–552
[11] Gao, J.G., Liu, Y.F., Yang, L.T.: ‘Thermal stability of boron-containing phenol formaldehyde resin’, Polym. Degrad. Stab., 1999, 63, (1), pp. 19–22
[12] Xu, P.J., Jie, T.L.: ‘Pyrolysis of hyperbranched polyborate modified phenolic resin’, Polym. Eng. Sci., 2010, 50, (7), pp. 1382–1388
[13] Zhang, W.F., Liu, C.L., Ying, Y.G., et al.: ‘The preparation and characterization of boron-containing phenolic fibers’, Mater. Chem. Phys., 2010, 121, (1-2), pp. 89–94
[14] Zhang, C.L., Ma, C.C.M.: ‘Synthesis, characterization, thermal properties and flame retardance of novel phenolic resins/silica nanocomposites’, Polym. Degrad. Stab., 2004, 83, (2), pp. 207–214
[15] Zhang, Y., Lee, S., Younens, M., et al.: ‘Phenolic resin-trisilanophenyl polyhedral oligomeric silsesquioxane (POSS) hybrid nanocomposites: structure and properties’, Polymer, 2006, 47, (9), pp. 2984–2996
[16] Zhao, D.X., Ou, A.J., Liang, G.Z., et al.: ‘Flame retardancy materials based on a novel fully end-capped hyperbranched polysiloxane and biomimetic diallyl/2-phenylsilanolphenol a resin with simultaneously improved integrated performance’, J. Mater. Chem., 2011, 21, (18), pp. 6584–6594
[17] Zhang, Y., Shang, C.Y., Yang, X., et al.: ‘Morphology and properties of TGDDM/DDS epoxy systems toughened by amino-bearing phenyl silicone resins’, J. Mater. Sci., 2012, 47, (10), pp. 4415–4427
[18] Santiago, A., Martin, L., Iruin, J.J., et al.: ‘Microphase separation and hydrophobicity of uranium siloxane copolymers with low siloxane content’, Prog. Org. Coat., 2014, 77, (4), pp. 798–802
[19] Ni, Y., Zhang, S.X., Nie, K.M.: ‘Morphology and thermal properties of inorganic–organic hybrids involving epoxy resin and polyhedral oligomeric silsesquioxane’, Polymer, 2004, 45, (16), pp. 5557–5568

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methane polydimethylsiloxane-modified hybrid materials composed of phenolic resin and silica prepared by in situ polymerization, *Biosurf. Biotribol.* 2018, Vol. 4, Iss. 3, pp. 85–1101

[20] Ren, Q.Y., Zou, H.W., Liang, M.: ‘The preparation and properties study of methoxy functionalized silicone-modified epoxy resin’, *J. Appl. Polym. Sci.*, 2014, 131, (9)

[21] Ren, Q.Y., et al.: ‘Effect of La2O3/CeO2 particle size on high-temperature oxidation resistance of electrodeposited Ni-La2O3/CeO2 composites’, *Trans. Nonferrous Met. Soc.*, 2014, 24, (11), pp. 3571–3577

[22] Li, S., Chen, F.H., Zhang, B.X., et al.: ‘Structure and improved thermal stability of phenolic resin containing silicon and boron elements’, *Polymer Degrad. Stab.*, 2016, 133, pp. 321–329

[23] Wang, F.Y., Huang, Z.X., Liu, Y., et al.: ‘Novel cardanol-containing boron-modified phenolic resin composites: non-isothermal curing kinetics, thermal properties, and ablation mechanism’, *High Perform. Polym.*, 2017, 29, (3), pp. 279–288

[24] Gao, J.G., Xia, L.Y., Liu, Y.F.: ‘Structure of a boron-containing bisphenol-F formaldehyde resin and kinetics of its thermal degradation’, *Polymer Degrad. Stab.*, 2004, 83, (1), pp. 71–77

[25] Costa, L., diMontelera, L.R., Camino, G., et al.: ‘Structure-choating relationship in phenol-formaldehyde type resins’, *Polymer Degrad. Stab.*, 1997, 56, (1), pp. 23–35

[26] Cuesta, A., Ohana, I., Dresselhaus, M.S., Endo, M.: ‘Raman and X-ray study of As5F7-vapor-grown graphite fibers’, *Carbon*, 1989, 27, (3), pp. 417–421

[27] Si, J.J., Li, J., Wang, S.J., et al.: ‘Enhanced thermal resistance of phenolic resin composites at low loading of graphene oxide’, *Compos. A. Appl. Sci. Manuf.*, 2013, 54, pp. 166–172

[28] Wang, F.Y., Huang, Z.X., Qin, Y., et al.: ‘Thermal behavior of phenolic-based ceramizable composites modified by nano-aluminum oxide’, *High Perform. Polym.*, 2016, 28, (9), pp. 1096–1101

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