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Study on the pyrolysis of phenol-formaldehyde (PF) resin and modified PF resin

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ABSTRACT

The pyrolysis of pure phenol-formaldehyde (PF) resin and boron carbide (B_4C) modified PF resin was investigated by using thermogravimetry (TG) and pyrolysis gas-chromatography–mass-spectrometry (PY-GC/MS). Scanning electron microscope (SEM) and Fourier transform infrared (FT-IR) spectroscopy were also employed to investigate the micro-structural evolution. It was shown from the TG analysis that the char residues of pure PF resin were 62.9 and 60.5% after being pyrolyzed at 700 and 1000 °C, respectively. The degradation and failure of the resin matrix were mainly resulted from the release of volatiles. The phenol and its methyl derivates took a large proportion in the amount of volatiles. In comparison with the pure PF resin, the char residues of B_4C modified PF resin were obviously higher, with the values of 71.9 and 68.4% at 700 and 1000 °C, respectively. Due to the oxidation–reduction reactions between B_4C additive and oxygen-containing volatiles including CO and H_2O, partial carbon and oxygen elements in the volatiles remained in the resin matrix in the forms of amorphous carbon and B_2O_3, respectively. The results of SEM and FT-IR characterization demonstrated the occurrence of the modification, and the amorphous carbon existed in the form of reticular substance. In addition, the amount of the released phenol and its methyl derivates was also decreased drastically due to the formation of borate.

1. Introduction

With the rapid advancement of high technologies such as aerospace, metallurgy, chemical engineering, military industry and so on, more and more materials have been applied in the rigorous environments including high speed, high temperature, high pressure, high corrosion, etc. Consequently, more strict properties are required for the materials and workpieces. Organic polymer materials including synthetic resins are widely used in many fields. However, their applications in high-temperature fields are limited due to the poor heat resistance. Whereas, the carbon residue derived from the pyrolysis of organic resins possesses outstanding thermophysical property. In the past decades, some synthetic resins including phenol-formaldehyde (PF) resin, epoxy resin, furan resin, pitch and so on, were successfully employed as the matrix of thermal ablation materials in the rocket, the impregnant of carbon/carbon composite, the binder of refractory brick, and the matrix of high-temperature adhesive [1–6].

Phenolic resin is the first thermosetting resin synthesized in 1907. It has been proved to possess many good properties including the resistances of heat, corrosion, wear, the excellent mechanics adhesive capacity, etc. However, similar to other polymeric materials, the application of PF resin at high temperatures was also restricted due to the thermal degradation and failure. It is well known that the drastic pyrolysis leads to the disintegration of polymeric structures [7], and subsequently resulting in the failure of resin matrix and its composites [2,3]. In order to meet the application requirement in high-temperature fields, many attempts aiming to promote the thermal stability of polymeric structure and property of the PF resin were carried out [8–14]. By the incorporation of some heat-resistant chemical bond such as B–O in the polymeric system [9–11], or the synthesis of copolymer [12–14], the thermal stability and application temperatures of PF resin can be progressed to some extent.

The thermal ablation materials, carbon/carbon composite, refractory materials and so on are usually applied in the temperatures ranging from 1000 to 3000 °C [1–6]. So, it is predictable that all non-carbon species will be eliminated and a char of coalesced carbon rings will be produced at the mentioned temperatures owing to the inevitable pyrolysis [7]. And the maintenance or promotion of thermal stability of polymeric structure cannot ultimately solve the problem of thermal stability of organic resins and their composite at high temperatures. Since all non-carbon species are eliminated at high temperatures, as well as the PF resin is virtually used as carbon precursor, the elevation of the value of carbonaceous residue is of great importance. If the volatile products can be converted

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and remained in the interior of resins matrix and its composites, the integrity and stability of the residue and the composite will be ameliorated effectively.

To the best of our knowledge, the research concerning this subject has not been reported yet. In our previous work, boron carbide (B_4C) was selected as modification additive for PF resin [15]. The high-temperature adhesives with satisfactory property were successfully prepared using the above-mentioned B_4C modified PF resin [16–18]. In this paper, the pyrolysis of pure PF resin and B_4C modified PF resin were investigated and compared using thermogravimetry (TG) and pyrolysis gas-chromatography–mass-spectrometry (PY-GC/MS).

2. Experimental

2.1. Raw materials

The resol type PF resin was provided by Tianjin Daying Resin Company, and its trade was $213^{\#}$. The viscosity of the resin was 0.8–1.53 Pa s, which was determined by rotary viscosimeter at 20 °C. The content of free phenol was less than 21%. And the solid content was 80 ± 3%. As the modification additive, B_4C powder had the size of 2.5–3.5 μm and purity of 85%. The B_4C modified PF resin was made by directly mixing the PF resin and B_4C with a mass proportion of 19:1. For convenience, the B_4C modified PF resin will be abbreviated as B_4C-PF.

2.2. Testing and analysis

In order to test the modification effect of B_4C, the char residues of pure PF resin and B_4C-PF resin were measured by using thermogravimetry apparatus with the type of SDT Q600 (TA Inc., USA). The TG characterization was carried out under the protection of nitrogen gas at temperatures of 90–1000 °C at a constant heating velocity of 10 °C/min. Before the thermogravimetry analysis, both the pure PF resin and B_4C-PF were previously pregelled at 93 °C. During the experimental research, no curing agent such as methenamine is used.

Pyrolysis gas-chromatography–mass-spectrometry (PY-GC/MS) system was employed to separate and identify the pyrolysis volatiles. For this purpose, a PY-2020S (Frontier, Japan) typed pyrolyzer joining with the injector of gas-chromatograph coupling with GCMS-QP2010 (Shimadzu Co., Japan) typed mass spectrometer was used. In the characterization process, two pyrolysis temperatures of 650 and 750 °C were used, and the interface temperature was fixed at 280 °C. The temperature of pyrolysis chamber before heating and during the separation of the volatiles was maintained at 200 °C. The separation of the volatile products was performed in a 30 m capillary quartz column. Before the chromatograph separation, the temperature of the chromatographic column was progressively increased as follows: (i) 40 °C for 3 min; (ii) from 40 to 260 °C at a rate of 10 °C/min; (iii) the capillary column was maintained at 260 °C for 10 min. Helium gas was used as the carrier gas. The mass range used for the mass selective detector was 19–500 m/z. The decomposition products were identified by means of the comparison between the experimental mass spectrum and the mass spectrum library attached to the PY-GC/MS apparatus. The identification of each volatile products can be confirmed if the qualification percentage reaches 85% and even higher.

A scanning electron microscope (SEM) with the type of SIRION (FEI Co., Netherlands) was employed to investigate the structural morphologies of the pyrolyzed specimens. The element constituents and its relative contents were identified by energy spectrum analysis using GENESIS 60S typed energy dispersive X-ray microanalysis (EDAX) (EDAX Inc., USA) attaching to the SEM apparatus. The Nicolet-Magna 750 typed Fourier transform infrared (FT-IR) spectroscopy (Nicolet Co., USA) was also applied to investigate the structural evolution of the specimens.

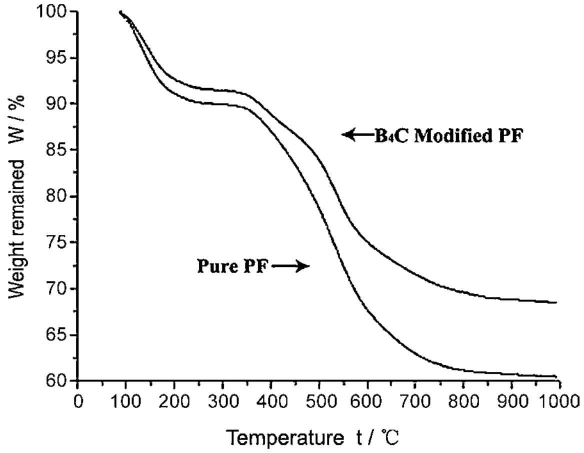

Fig. 1. TG curves of pure PF resin and B_4C-PF resin pyrolyzed in nitrogen atmosphere.

3. Results and discussion

3.1. The TG analysis results

Although the pure PF and B_4C-PF are pregelled at 93 °C, some condensation water and un-reacted oligomers will be released out in the following thermocuring process. As shown in Fig. 1 a slight weight loss can be found at the beginning for both the pure PF resin and B_4C-PF. Such phenomenon is similar to other experimental results reported elsewhere [19,20]. With the elevation of the pyrolysis temperatures, especially above 350 °C, the polymeric system is disintegrated gradually, resulting in the continuous weight loss due to the elimination of various volatiles [3,7,19,20]. Fig. 1 also shows that the char residues of B_4C-PF resin are 71.9 and 68.4% after being pyrolyzed at 700 and 1000 °C, respectively. These values are obviously higher than those of the pure PF resin (62.9 and 60.5%). In our previous work, the elevation of the char residue was regarded as the modification effects of oxidation–reduction reactions between B_4C additive and oxygen-containing volatiles.

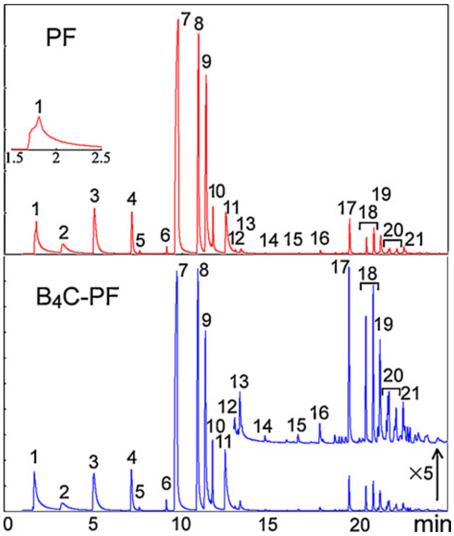

Fig. 2. Pyrograms of pure PF resin and B_4C-PF pyrolyzed at 650 °C.

It is well known that the thermal degradation of PF resin leads to the release of many volatiles including H_2O, CO_2, CO, CH_4, C_2H_6, H_2, phenol and its methyl derivatives, as well as some condensed nuclear hydrocarbons [7,21], and consequently resulting in the failure of resin matrix and its composites [2,3]. The oxygen-containing molecules including CO and H_2O take a large proportion in the amount of volatiles [7]. They provide an oxidation atmosphere for B_4C [22]. Because of the oxidation–reduction reactions between B_4C and oxygen-containing volatiles above 560–600 °C [15,23,24], the carbon and oxygen elements remained in the resin matrix in the forms of amorphous carbon and B_2O_3, respectively [15,25], which should be responsible for the elevation of char residue (Fig. 1). The main modification reactions can be expressed as follows:

$$B_4C + 6CO = 2B_2O_3 + 7C[25]$$

$$B_4C + (8-x)H_2O = 2B_2O_3 + xCO + (1-x)CO_2 + (8-x)H_2[26]$$

$$2B_2O_3 + 2H_2O = 4HBO_2[26]$$

3.2. The comparison and analysis of PY-GC/MS results

3.2.1. The analysis of pyrograms of resins pyrolyzed at 650 °C

The pyrograms of pure PF resin and B_4C-PF pyrolyzed at 650 °C are shown in Fig. 2. The constituent identification of each peak is listed in Table 1. As shown in Fig. 2, strong peaks of phenol and its methyl derivatives such as cresol and dimethylphenol are the main characteristic peaks for both the pure PF resin and B_4C-PF. Many researches on the thermal degradation of phenol-formaldehyde resin could be found elsewhere [7,21,22,27]. According to their opinions, the formation of phenol and its methyl derivatives were the results of the scission of the linkages between the terminal benzene rings (Fig. 3) [27]. Because of the degradation of organic polymeric structure and the subsequent decrease of resin's properties, PF resin and its composites cannot be single-handedly applied in high-temperature fields. For example, the joints bonded by pure PF resin fail quickly at elevated temperatures [16,17].

Table 1
List of volatiles identified using mass spectrum.

No.	Volatiles species	Molecular mass
1	Carbon dioxide, carbon monoxide, nitrogen, methanol	44, 28, 32
2	Benzene	78
3	Toluene	92
4	*o*-Xylene	106
5	*p*-Xylene	106
6	Mesitylene	120
7	Phenol	94
8	*o*-Cresol	108
9	*p*-Cresol	108
10	2,6-Dimethylphenol	122
11	2,4-Dimethylphenol	122
12	Naphthalene	128
13	2,4,6-Trimethyphenol	136
14	2-Methylnaphthalene	142
15	Diphenylmethane	168
16	Dibenzofuran	168
17	9H-xanthene	182
18	Methyl-9H-xanthene	196
19	Anthracene	178
20	Dimethyl-9H-xanthene	210
21	Trimethyl-9H-xanthene	224

In Ref. [21], the separated CO peak and CO_2 peak were also not shown in the pyrogram. In our work, by means of the identification using mass spectrum (Fig. 4), the constituents of peak 1 can be attributed to the mixture of CO, CO_2, N_2, and CH_3OH. Although argon is used as the carrier gas, the peak at $m/z = 28$ cannot be singly attributed to the CO due to the entrapped nitrogen with the same response at $m/z = 28$. The abundance relationship among the peaks at $m/z = 32$, 31, 30 and 29 is quite similar to that of pure methanol mass spectrum provided by the mass spectrum library attached to the apparatus. Although the oxygen also has the same response at $m/z = 32$, it is predictable that the entrapped oxygen will be consumed in the pyrolysis of organic polymeric system. So, the peak shown at $m/z = 32$ is the characteristic peak of methanol, and the peaks at $m/z = 31$, 30, and 29 are those of methanol's frag-

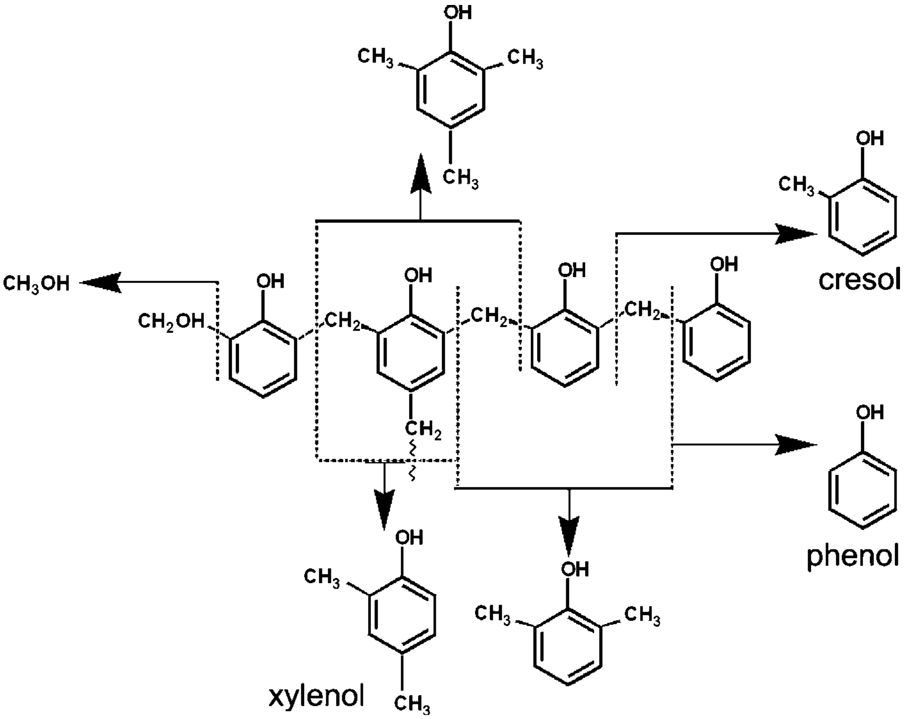

Fig. 3. Formation of phenol and its methyl derivatives (based on Ref. [25]).

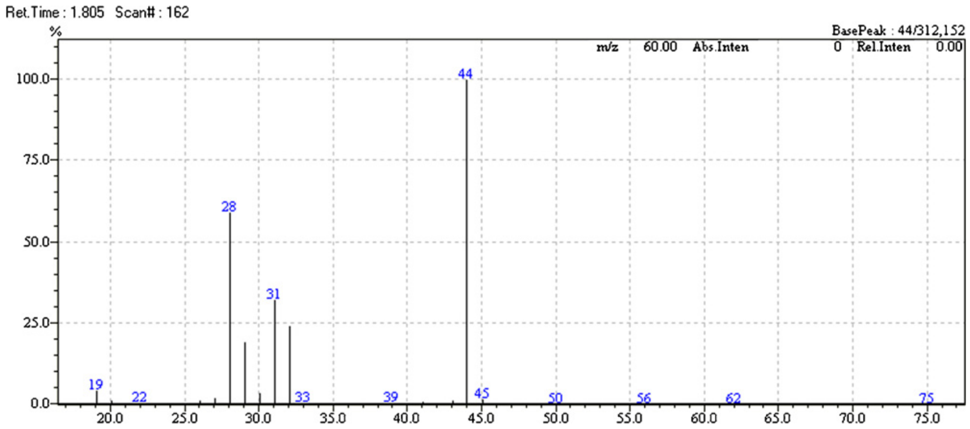

Fig. 4. The identification of the constituents of peak 1 shown in the pyrogram of pure PF resin pyrolyzed at 650 °C using mass spectrum.

ments. As mentioned above, owing to the oxidation–reduction reactions between B_4C and oxygen-containing volatiles [25,26], partial volatiles were converted and remained in the resin matrix [15,18], resulting in the improvement of char residue (Fig. 1).

B_2O_3, the product of the modification reactions, can react with the resin matrix. Consequently, the phenol borate and/or benzyl borate [9–11] with high thermal stability are formed (Fig. 5). But the reaction activity of B_4C at 650 °C is not very high and little B_2O_3 is produced [24]. As a result, the thermal stability of organic polymeric system cannot be progressed rapidly, and the release of the volatiles of B_4C-PF is similar to that of pure PF resin. So, as far as these specimens pyrolyzed at 650 °C are concerned, no obvious difference between the pyrograms of pure PF resin and B_4C-PF is observed (Fig. 2). Besides, because the melting point of B_2O_3 is high up to 450 °C and the temperature of chromatographic column is only 260 °C, the peaks of B_2O_3 cannot be found on the pyrogram.

3.2.2. The analysis of pyrograms of resins pyrolyzed at 750 °C

It is worth noting that, for the pyrogram achieved at 750 °C, distinct differences between the pure PF resin and B_4C-PF resin are exhibited (Fig. 6). As to the pyrogram of pure PF resin, the release of volatiles is similar to that of pure resin pyrolyzed at 650 °C, and also similar to the experimental result of Ref. [21]. In contrast, in the case of B_4C modified PF resin, the amount of phenol and its methyl derivatives drastically decrease, especially for the *o*-Cresol and *p*-Cresol (Fig. 6). And the condensed nuclear hydrocarbons including naphthalene, methylnaphthalene, biphenyl, dibenzofuran, fluorene, phenanthrene, and anthracene are detected at trace levels. In addition, the first peak of B_4C-PF specimen divides into three peaks. By means of the constituent identification of these peaks using mass spectrum attaching to the chromatograph apparatus (Fig. 7), one can find that these peaks still should be attributed to the mixture of CO, CO_2 and the entrapped N_2, though there are some difference in the relative content. In comparison with the program of pure PF resin, CO_2 and CO released from the B_4C-PF specimen become the main volatiles because of the decrease of organic volatiles.

Such change might be interpreted by the introduction of B–O bond in the polymeric system. Some researches have already demonstrated that the thermal stability of organic structure could be progressed effectively by the formation of phenol borate and/or benzyl borate (Fig. 5) [9–11]. The weakening of the peaks of phenol and its methyl derivates indicate that boron oxides (B_2O_3), the product of oxidation–reduction reaction, react with the phenol hydroxyl and benzyl hydroxyl in the residual products. And the elimination of methanol in the pyrogram and mass spectrum of B_4C-PF specimen also might be interpreted by the formation of methyl borate. Consequently, the thermal stability of residue is progressed due to the formation of phenol borate and benzyl borate. Such changes are also responsible for the elevation of the char residue (Fig. 1).

3.3. The morphology analysis of B_4C modified PF resin

In our work, the average sizes of the used B_4C additives are in the range of 2.5–3.5 μm. As shown in Fig. 8(a) that the B_4C grain with distinct crystal configuration insert in the resin matrix after being cured, and the size of the B_4C grain is somewhat larger than 2 μm. While for the specimen treated at 700 °C, white spherical par-

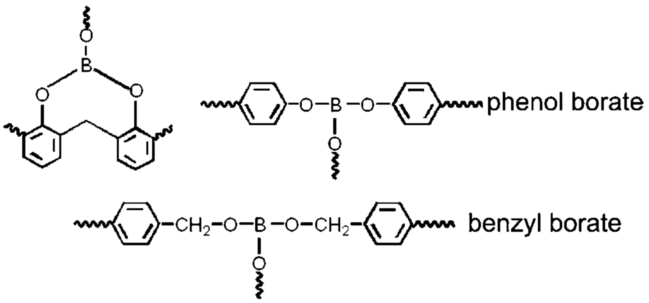

Fig. 5. Formation of phenol borate and benzyl borate.

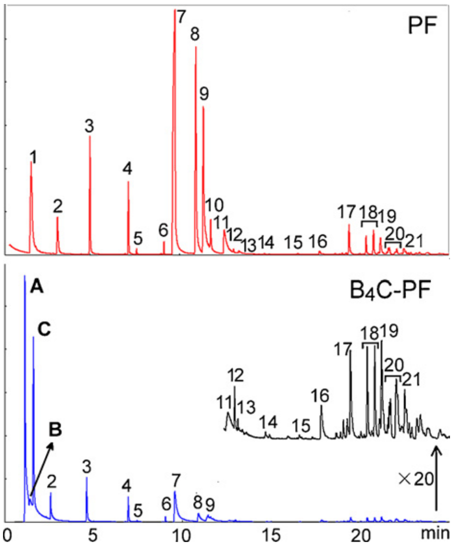

Fig. 6. Pyrograms of pure PF resin and B_4C-PF pyrolyzed at 750 °C.

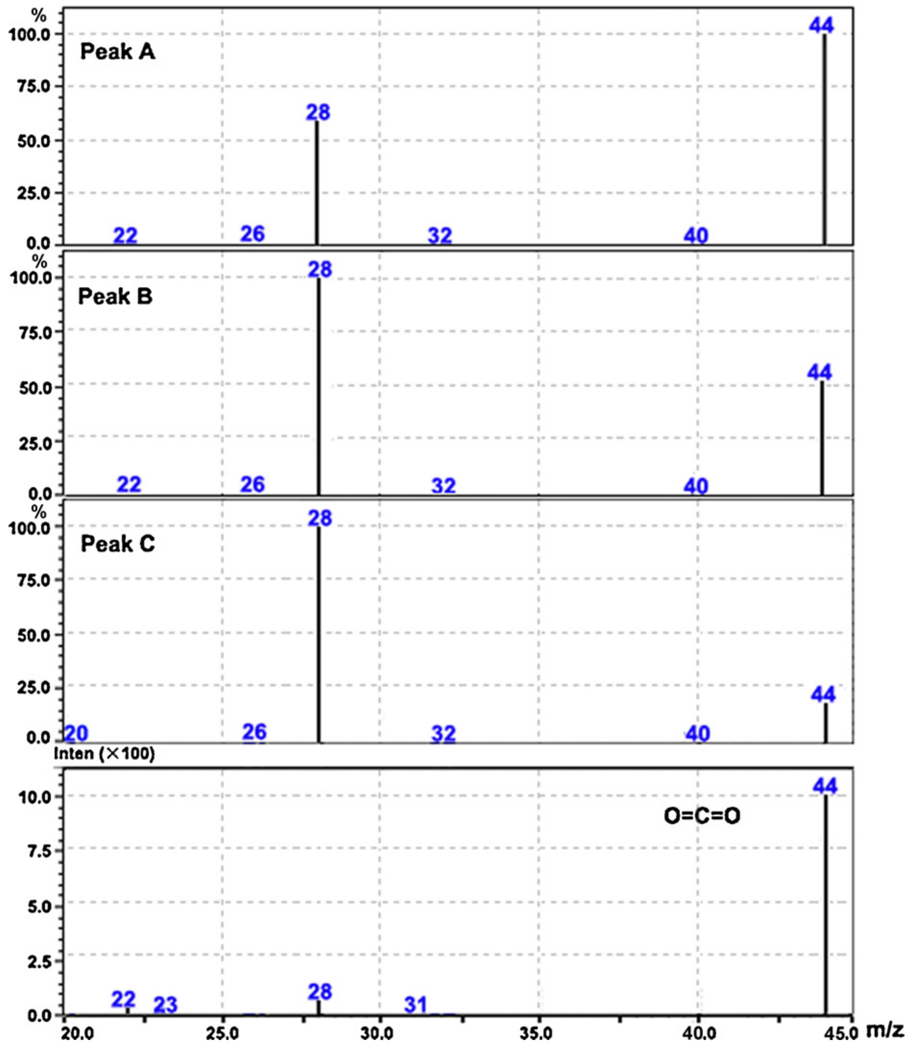

Fig. 7. The mass spectrum of the chromatograph peaks A–C of the B_4C-PF specimen and the standard spectrum of CO_2 extracted from the mass spectrum library.

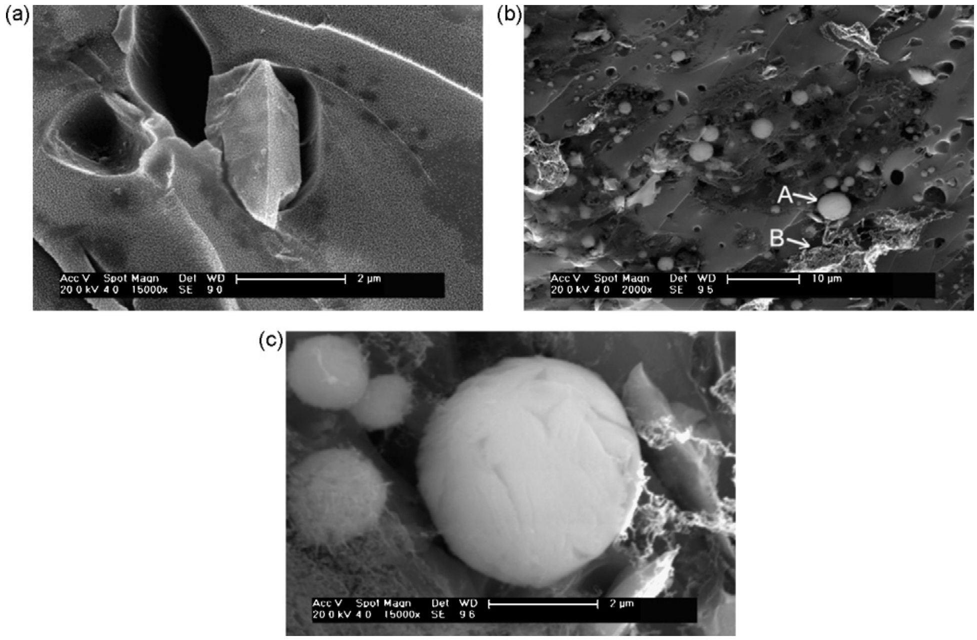

Fig. 8. The morphology comparison of B_4C-PF treated at different temperatures. (a) The morphology of B_4C grain inserted in the resin matrix at 400 °C (15,000×). (b) The morphology of oxidized ceramic particles at 700 °C (2000×). (c) The enlarged morphology of ceramic particle at 700 °C (15,000×).

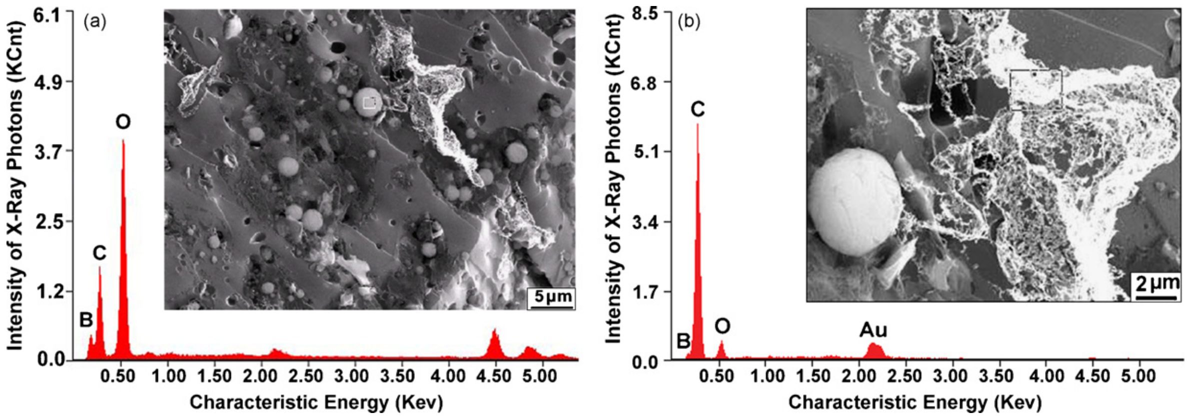

Fig. 9. The EDS analysis of B_4C-PF pyrolyzed at 700 °C. (a) The EDS spectrum of spherical particle. (b) The EDS spectrum of reticular substance.

ticles are clearly shown in the resin matrix (the spherical particle signed by arrow A in Fig. 8(b) and (c)). The volume of some spherical particles is also larger than that of B_4C grains obviously. By means of the energy spectrum analysis using EDAX attached to the SEM apparatus, the white spherical particles can be attributed to the oxidized boron carbide. As shown in Fig. 9(a) and Table 2, the oxygen with high concentration is existing in the spherical particles, which indicates the oxidation of B_4C grains. B_2O_3, the oxidation product, melts and converts into glass phase when the treatment temperatures are higher than 450 °C. The shape of additives consequently changes into sphere due to the surface tension. As reported in Ref. [28], 250% volume expansion occurs during the transformation from B_4C to B_2O_3. So, the volume difference between the initial grains and the oxidized particles is another result of the modification reactions. The volume expansion and excellent wettability of B_2O_3 benefit in the mending of micro-structural defects such as voids and cracks. In our previous study, the joints bonded by the B_4C modified PF resin adhesive exhibited satisfactory bond strength after being treated at high temperatures [16,17], due to the restrain of volume shrinkage and the adhesive properties of B_2O_3 [18].

Besides, it is worthy to be noticed that, some reticular substances are also shown on the resin matrix (the reticular substance signed by arrow B in Fig. 8(b) and (c)). There are significant differences between the morphologies of these reticular substances and those of resin matrix. The distribution of the reticular substances is also very interesting. One can find that these reticular substances disperse in the aggregation zones of spherical particles. Such phenomena suggest the correlation between the products of these reticular substances and oxidized additives. By means of the energy spectrum analysis (Fig. 9(b) and Table 2), these reticular substances can be attributed to the amorphous carbon, another product of the oxidation–reduction reaction, as expressed in Section 3.1.

3.4. The FT-IR analysis of B_4C-PF at different temperatures

The FT-IR spectrums of B_4C-PF treated at 400 and 700 °C are displayed in Fig. 10. As was shown in the literature [3,7], the carbonization of PF resin began at around 350 °C. For the specimen treated at 400 °C, one can find that lots of organic structures still remained. The characteristic peaks at 3102, 2916, 2862, 1470 and 820 cm^{-1} are the vibration of C–H bond existing on benzene rings and methylene linkages, respectively. The peaks at 1608, 756 cm^{-1} are owing to the vibration of benzene ring. The peaks at 1142 and 1211 cm^{-1} are the symmetrical or asymmetrical deformation vibration of ether link (C–O–C bond). Besides, the peaks at 1092, 708 and 428 cm^{-1} are the characteristic peaks of B_4C additives. But the above peaks of the B_4C are not the main peaks because of the intense absorption of organic structures.

In the case of the spectrum of B_4C-PF pyrolyzed at 700 °C, nearly all the peaks of the organic structure eliminated, the main characteristic peaks belong to B_4C ceramic additives. At high temperatures, through pyrolysis, the polymeric system decomposes gradually, and the PF resin tends to eliminate all non-carbon species and produce a char of coalesced carbon rings in the end [7]. At 700 °C, the components of the specimens are char residue and ceramic additives. As to carbon rings, the main substance of the residue, derived from the pyrolysis of resin, the spectral signature are infrared inactive but Raman active because of the symmetry of carbon rings. So the peaks of B_4C become the main peaks on the IR spectrum, especially for the strong peak centered at 1088 cm^{-1}. It is worthy to be noticed that some new peaks are shown on the IR curves. The peaks appeared at 1551 and 876 cm^{-1} can be attributed to the vibration of B–O bond and again demonstrated the occurrence of the modification reaction between B_4C and oxygen-containing volatiles. Besides, a weak peak at 1387 cm^{-1} peak was likely to be due to the phenol borate vibration. The characteristic band of the stretching vibration of B–O bond usually appears in the zone centered at 1350 cm^{-1} [29]. If the phenol borate was

Table 2
The element contribution of spherical particles and reticular substance produced in the interior B_4C-PF at 700 °C.

Element	Spherical particles		Reticular substance	
	wt%	at%	wt%	at%
Boron	33.19	38.09	14.85	16.44
Carbon	39.14	40.44	80.01	79.72
Oxygen	27.67	21.47	05.14	03.84

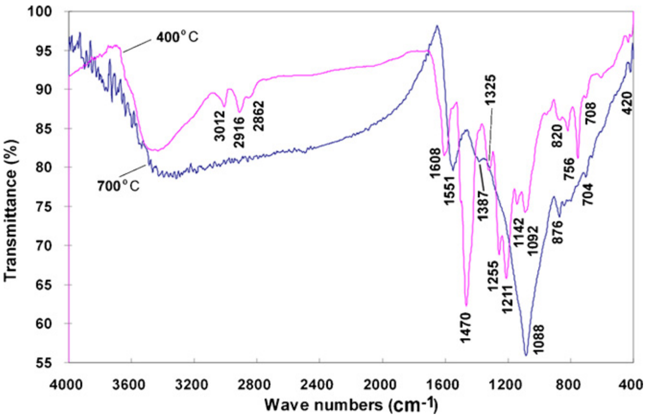

Fig. 10. The FT-IR spectrum of B_4C-PF treated at 400 and 700 °C.

formed, partial share electron cloud of benzene ring might deflect to B–O bond due to the electronegativity of oxygen and the electron-deficient property of boron. As a result, the electron density of the B–O bond increased to some extent, and consequently resulting in a blue-shift of IR characteristic peak. The formation of borate should be another reason for the improvement of char residue.

4. Conclusion

The pyrolysis reactions and disintegration of polymeric structure result in the decrease of char residue of organic resin. For the phenol-formaldehyde (PF) resin, many species of volatiles were released at high temperatures, and the volatilization of phenol and its methyl derivatives took a large proportion in the amount of volatiles.

Boron carbide (B_4C) is an efficient modification additive for the elevation of char residue of PF resin. The char residues of B_4C modified PF resin were 71.9 and 68.4% after being pyrolyzed at 700 and 1000 °C, respectively, which are obviously higher than those of the pure PF resin of 62.9 and 60.5%. Some changes were responsible for the amelioration and were expressed as follows:

(i) Partial carbon and oxygen elements in the volatiles were converted and remained in the resin matrix in the forms of amorphous carbon and B_2O_3 owing to the oxidation–reduction reaction occurring between B_4C additive and oxygen-containing volatiles.

(ii) The amorphous carbon derived from the modification reactions existed in the resin matrix in the form of reticular substance.

(iii) Boron oxides (B_2O_3), the oxidation product, reacted with the polymeric system and its volatiles. This behavior resulted in the formation of phenol borate and benzyl borate with higher thermal stability. As a result, the thermal integrality and stability of the pyrolysis residue was progressed, which also benefits in the elevation of char residue.

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