

DOI <https://doi.org/10.1007/s11595-018-1833-8>

Fluxing Agents on Ceramification of Composites of MgO-Al₂O₃-SiO₂/Boron Phenolic Resin

SHI Minxian¹, CHEN Xia¹, FAN Shanshan¹, SHEN Shirley², LIU Tianxiang¹, HUANG Zhixiong^{1*}

(1.School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China; 2.CSIRO Manufacturing, Gate 5, Normanby Road, Clayton, VIC 3168, Australia)

Abstract: Fluxing agents of zinc borate, antimony oxide, galss frit A and glass frit B, with different melting or softening point temperatures, were added into MgO-Al₂O₃-SiO₂/boron phenol formaldehyde resin (MAS/BPF) composites to lower the formation temperature of eutectic liquid phase and promote the ceramification of ceramifiable composites. The effects of fluxing agents on the thermogravimetric properties, phase evolution, and microstructure evolution of MAS / BPF composites were characterized by TG-DSC, XRD and SEM analyses. The results reveal that the addition of a fluxing agent highly reduces the decomposition rate of MAS / BPF composites. Fluxing agents lower the formation temperatures of liquid phases of ceramifiable MAS / BPF composites obviously, and then promote the ceramification and densification process. The final residues of composites are ceramic surrounded by large amount of glass phases.

Key words: ceramification; boron phenolic resin; ceramifiable polymer composite; fluxing agent

1 Introduction

Ceramifiable polymer-ceramic composites possessing desirable performance of the polymer at room temperature as well as that of a ceramic at elevated temperatures are useful in many applications, such as fire barrier, thermal protection and so on. Ceramification process is widely described and characterized in literatures by the formation of ceramic from polymer composite highly filled with inorganic particles during heat treatment. The created structure can block the propagation of flames and decrease the rate of flammable, caloric fuel production, created during thermo oxidative degradation of polymer matrix, by preventing the burning material from deeper penetration of oxygen^[1].

Imiela *et al* considered that one way of creation of the ceramic structure is the formation of a continuous and porous structure involving amorphous fluxing agent, which softens at elevated temperature and binds mineral particles together^[1]. The addition of certain inorganic materials to the ceramifiable composite could

produce a liquid phase at lower temperatures to facilitate the formation of a strong ceramic^[2]. Glass frit is helpful to decrease the sintering temperature of a ceramifiable composite^[3]. In addition, zinc oxide, ferric oxide, and zinc borate are commonly used to improve the ceramification of the residue resulting from fire burning of silicone-mica composites and other polymer-ceramic composites.

Boron oxide, B₂O₃, is characterized by melting point temperature (T_m) of 450 °C. Low T_m value of B₂O₃ makes it an effective fluxing agent. 15 phr boron oxide was used in montmorillonite-modified silicone rubber-based ceramifiable composites to create glassy phase for adhesion of fillers^[4]. Zinc borate is another fluxing agent of boron compound. Al-Hassany Z^[5] used zinc borate as a low temperature fluxing component in a fire-retardant and fire-barrier poly(vinyl acetate) composites for sealant application, by the function of binding filler particles and inhibiting oxygen mass transfer to the polymer fuel system and retarding further oxidation of the char. Results also showed that the presence of zinc borate was important in the composites as it acted as a synergistic agent when it was introduced with Mg(OH)₂ to form a protective MgO-ceramic by acting as a binder (formation of B₂O₃-ZnO glass). This MgO-ceramic residue combined with the degraded polymeric material led to a protective surface layer during decomposition.

© Wuhan University of Technology and Springer-Verlag GmbH Germany, Part of Springer Nature 2018

(Received: Feb. 25, 2017; Accepted: Apr. 25, 2017)

SHI Minxian(石敏先): Assoc.Prof.;E-mail:minxianshi@whut.edu.cn

*Corresponding author: HUANG Zhixiong(黄志雄): Prof.; E-mail: zhixiong@whut.edu.cn

Mansouri Jaleh *et al*^[6] added glass frits into silicone-based composites, which could be used for an electric cable, to improve low temperature ceramification at elevated temperatures. The results showed that glass frits reacted with mica and silica via an eutectic reaction, but electrical conductivity measurements at elevated temperatures showed a decline in volume resistivity with glass frit addition. Anyway, the addition of glass frits is an useful technique for lowering the temperatures at which mechanical strength is developed in pyrolysed compositions. These glass frits melt at temperatures below the mica-silica eutectic temperature and combine with the inorganic fillers and pyrolysis products of silicone rubber to assist the formation of a ceramic. Imiela *et al*^[11] used glassy oxide frit (Glass frit FR-2050, containing large amount of Na₂O and having a softening point temperature at 515 °C) as a fluxing agent in ceramizable composite, which created strong adhesion between the mica and silica particles. Li YM *et al*^[7] prepared a mica-based ceramifiable ethylene-vinyl acetate composites and suggested that the essential reason for the formation of mica-based ceramic was that glass powder melted firstly, adhered tightly to inorganic stuffing mica powder with high melting point, leading to the formation of an eutectic mixture. The use of glass frit made the ceramizable silicone composite much stronger and securer than that without glass frit^[8].

Softening of solid glass frit and formation of liquid phase usually cause shrinkage. To make sure the gradual formation of liquid phase in a ceramifiable silicone rubber composite^[9], frit blends with different softening point temperatures (3:3:4 of Frit A: Frit B: Frit C, and the softening point temperature of Frit A, B and C is 400, 650, and 850 °C, respectively) were used. The frits play a main role of physical binding to other fillers and keep the integrity of residue in the pyrolysis process at 650 °C and assist the formation of ceramic at 950 °C.

As to polymer-ceramic silicon composites, the strength can be improved by increasing the pyrolysis temperature, but it can be more effectively improved with the addition of certain inorganic fillers. Zbigniew Pędzich^[10] stated that fluxing agent of glass frit acted very effectively and joined together wollastonite particles and ultrafine silica particles produced by silicone rubber decomposition effect. The reaction between the inorganic fillers and the silica from the decomposed polymer matrix forms a eutectic liquid phase at the edge of fillers, which penetrate into the matrix region with increasing temperature and exposure time^[11].

The addition of a fluxing agent really plays an important role in the pyrolysis and ceramification of ceramifiable polymer composites by softening, binding and reacting with particles, lowering ceramic formation temperature and assisting ceramic formation eventually.

As to present, silicon based ceramifiable composites have earned much attention for fire resistant and thermal protection. Reports of phenolic resin based ceramifiable composites are however still limited. Since phenolic resin and composites have been widely reported as thermal protection systems, ultra-temperature adhesives and high temperature coating^[12-15], phenolic resin based ceramifiable composite may be a promising material in thermal protection. Chen Yaxi^[16] fabricated carbon-phenolic (C-Ph) composites to meet the requirements of thermal protection system by introducing ZrB₂ particles, which notably improved the ablation resistance and insulation performance of C-Ph composites mainly owing to the formation of ZrO₂ and B₂O₃. We have been attempting to develop a phenolic resin based ceramifiable composite for high temperature barriers. Ding Jie^[17] reported the improvement of ablation resistance of carbon-phenolic composites by introducing zirconium silicide particles, with the formation of ZrO₂ and SiO₂ during the oxygen-acetylene ablation process.

The preparation and ceramification of MAS / BPF composite have been reported in our previous work^[18]. New phases of ceramic and amorphous glass phase formed at higher than 1 000 °C by melting and ceramification of MAS fillers. It is anticipated to possess satisfactory barrier characteristics with the formation of tough and very dense ceramic at low temperatures. In this work, to facilitate the ceramification of MAS / BPF composite, fluxing agents with different softening point temperatures were added to MAS / BPF composite. The effects of fluxing agent on thermogravimetric properties, phase evolution, and microstructure evolution of MAS / BPF composites will be discussed in details. Fluxing agents lower the forming temperatures of liquid phases of ceramifiable composites directly, and then promote the ceramification and densification process of residues.

2 Experimental

2.1 Materials

Boron phenolic resin (BPF), THC-400 (Shanxi Taihang Impedefire Polymer Limited Company) was used as the matrix. Anhydrous ethanol (Sinopharm Chemical Reagent Co. Ltd.) was used as a solvent.

Magnesia, alumina and silica were used as the fillers. Magnesia and alumina with the particle size of 30nm were from Shanghai Chaowei Nanotechnology Ltd. Aerosil 200 fumed silica and Zinc Borate ($2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$, the melting point of $980\text{ }^\circ\text{C}$) were supplied by Aladdin Industrial (Shanghai) Corporation. Antimony oxide (Sb_2O_3 , the melting point of $656\text{ }^\circ\text{C}$) was supplied by Sinopharm Group Chemical Reagent Co., Ltd. Glass frit A (the softening temperature range of $360\text{--}620\text{ }^\circ\text{C}$ and the main compositions of 74.07% Bi_2O_3 , 12.76% ZnO , 2.23% Na_2O , 1.52% Al_2O_3 , 1.39% SiO_2 , 1.02% CaO , 0.1% P_2O_5 , and 0.12% SnO_2) and glass frit B (the softening temperature range of $550\text{--}830\text{ }^\circ\text{C}$ and the main compositions of 70.8% SiO_2 , 14.05% Na_2O , 8.72% CaO , 3.86% MgO , 0.92% Al_2O_3 , and 0.4% K_2O) were purchased from GuiZhou Wylton Jinglin Electronic Material Co., Ltd. Zinc borate, antimony oxide, glass frit A and glass frit B were used as the fluxing agents.

2.2 Sample preparation

BPF was ground into micro-size powders, and then dissolved in ethanol. Nano fillers of magnesia, alumina, silica and fluxing agents were added to BPF ethanol solution by mechanical stirring at $80\text{ }^\circ\text{C}$ until a homogeneous batch. The obtained homogeneous batch was pre-cured in an oven with an air blower at $80\text{ }^\circ\text{C}$ for 4 h, and was molded and cured through a hot compression molding technique with the cure procedure of $80\text{ }^\circ\text{C}$ for 1 h, $100\text{ }^\circ\text{C}$ for 1 h, $120\text{ }^\circ\text{C}$ for 2 h, $160\text{ }^\circ\text{C}$ for 3 h, and $180\text{ }^\circ\text{C}$ for 2 h under 10 MPa pressure. The control sample without fluxing agent was also prepared by the same process. The formulas of the composites are shown in Table 1.

Table 1 Formula of MAS / BPF with fluxing agents

Sample	^a Content (phr)					
	BPF	^b MAS	Zinc borate	Antimony oxide	Glass frit A	Glass frit B
BPF-0(control)	100	40	0	0	0	0
BPF-1	100	40	5	0	0	0
BPF-2	100	40	0	5	0	0
BPF-3	100	40	0	0	5	0
BPF-4	100	40	0	0	0	5

^a Content per hundred content of BPF (phr)

^b the mass ratio of 2:2:6 of $\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2$ in MAS

Heat treatment of samples was performed in air using a muffle furnace. Samples were heated from room temperature to 600, 800, 1 000 and 1 200 $^\circ\text{C}$, respectively, at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, and held for another 2 h, and then naturally cooled down to room

temperature in the muffle furnace.

2.3 Characterization of composites

The crystal phases of the residues after pyrolysis were characterized with a RU-200B/D/MAX-RB RU-200B Rotation Anode High Power X-ray Diffractometer (Rigaku Corporation, Japan). XRD data were obtained from 5° to 70° (2θ) at a step of $5^\circ/\text{min}$.

The morphology of the residues after pyrolysis was identified by a scanning electron microscope (SEM, JSM-IT300, JEOL, Japan). Samples were sputter-coated with gold before observation.

Thermogravimetric analysis was performed on a thermogravimetric analyzer (STA449c/3/G, NETZSCH, Germany) at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ (air atmosphere). Samples were analyzed from room temperature to 1 200 $^\circ\text{C}$.

3 Results and discussion

3.1 Thermogravimetric analysis

The thermogravimetry, derivative thermogravimetry curves and thermal characteristics of composite samples of BPF-0, BPF-1, BPF-2, BPF-3, and BPF-4 are shown in Fig. 1 and Table 2.

Table 2 Thermal characteristics of decomposition of MAS / BPF composites

Samples	^a $T_5/^\circ\text{C}$	^b $T_{10}/^\circ\text{C}$	^c $T_{\text{max}}/^\circ\text{C}$	^d DW(%/ $^\circ\text{C}$)	^e $R_{\text{end}}/\%$
BPF-0(control)	401	508	530	0.237	53.4
BPF-1	306	452	532	0.165	44.4
BPF-2	342	460	533	0.09	47.2
BPF-3	337	448	530	0.174	44.5
BPF-4	417	513	529	0.173	48.3

^a Thermal decomposition temperature at 5% weight loss;

^b Thermal decomposition temperature at 10% weight loss;

^c The temperature of the maximum degradation rate;

^d Derivative weight at T_{max} ;

^e Residue weight percentage at 1 200 $^\circ\text{C}$.

All samples show small mass loss at temperature under 200 $^\circ\text{C}$. The thermal decomposition temperatures T_5 and T_{10} are defined as the temperature with 5% and 10% weight loss, respectively. The T_{10} of pure boron phenolic resin is 320 $^\circ\text{C}$ in nitrogen atmosphere^[22]. The T_{10} of composite samples of BPF-0, BPF-1, BPF-2, BPF-3, and BPF-4 in air is 508, 452, 460, 448, and 513 $^\circ\text{C}$, respectively. It is obvious that the addition of MAS fillers and fluxing agent leads to a remarkable increase of thermal stability of ceramifiable composites. The sample BPF-1 shows the lowest decomposition temperature of T_5 . Three reasons may be responsible

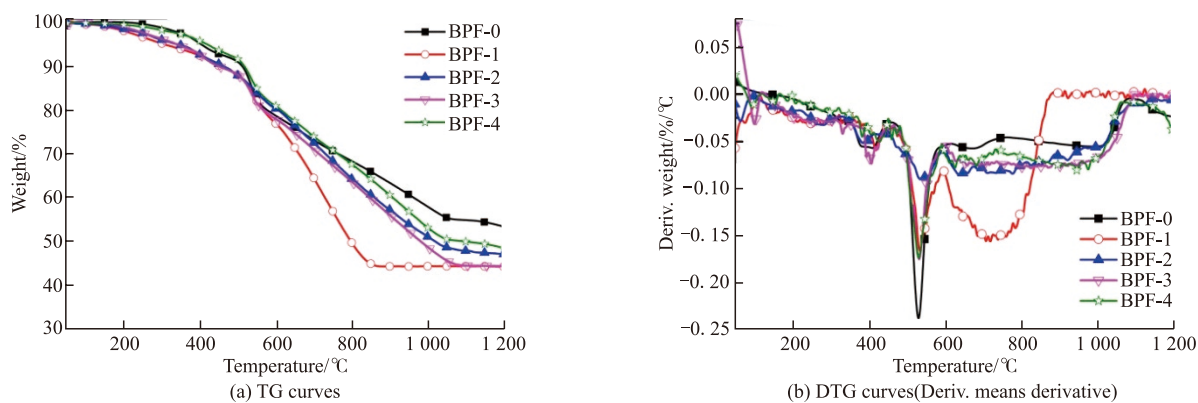


Fig.1 TG and DTG curves of MAS/BPF samples

for it. Firstly, zinc borate ($2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$) decomposes and dehydrates at its early stage at about 300°C ^[5], which results in quick weight loss^[19]. Water-releasing fillers depress the thermogravimetric stability of composite^[20]. Secondly, the dehydration stage is an endothermic process and it decreases the onset of decomposition. Lastly, the water released from zinc borate also decreases the sample temperature^[21].

T_{10} of samples BPF-0 and BPF-4 is similar and higher over 500°C . T_{10} of samples of BPF-1, BPF-2, and BPF-3 is similar, however it is about 50°C lower than that of samples of BPF-0 and BPF-4.

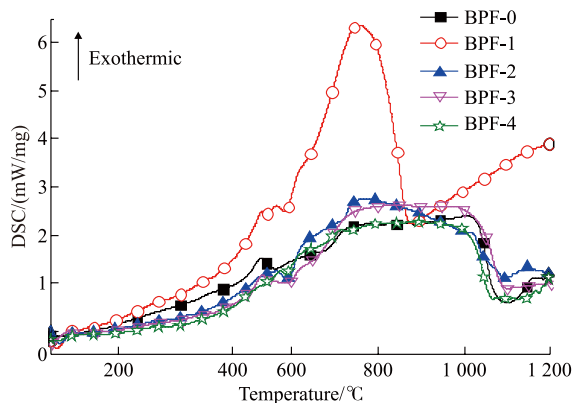
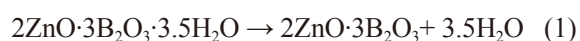


Fig.2 DSC curves of samples

The maximum weight loss rate of all samples appears at about 530°C , which is attributed to the fast decomposition of boron phenolic resin. It is consistent with the previous report^[22]. However, the fillers retard the decomposition rate of boron phenolic resin of composite, and the DW is a lot lower than that of pure boron phenolic resin of about 4^[22]. The derivative weight of sample BPF-0 at T_{\max} is 0.237, and it is the highest in all samples. It is worth noting that the derivative weight at T_{\max} of sample BPF-2 is the lowest in all samples, lower than half of that of sample BPF-0. Furthermore, the derivative weight of sample BPF-2 in the whole temperature range from room temperature to 1200°C

changes gently. It indicates that the addition of fluxing agents reduces the decomposition rate of composites.

As shown in Fig.1, sample BPF-1 has another wide weight loss peak at temperature of about $550\text{--}900^\circ\text{C}$. It results from the dehydration of zinc borate and further oxidation and decomposition of carbon char formed by pyrolysis of boron phenolic resin matrix. The dehydration of zinc borate can be described by equation (1) for a creation of an amorphous structure with boric oxide, which is beneficial for the purpose of improving the char properties^[5]. However, the new amorphous structure of boric oxide is not melted at temperature of $550\text{--}900^\circ\text{C}$ and there is no eutectic liquid phase formed to avoid further oxidation and decomposition of the carbon char. So the R_{end} of BPF-1 is the lowest of all samples. Correspondingly, the DSC curve of BPF-1 shows a higher exothermic peak in this temperature range, as shown in Fig.2.



3.2 Phase evolution of composites during ceramification

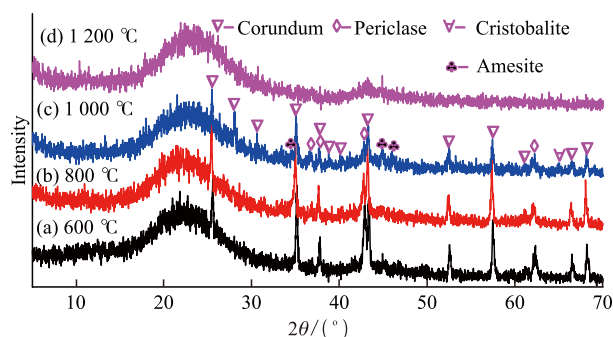


Fig.3 XRD patterns of sample BPF-0 at different calcine temperatures

Fig.3 shows the XRD patterns of sample BPF-0 calcined from room temperature to 600 , 800 , 1000 , and 1200°C , respectively, and held at the target temperature for another 2 h. Sample BPF-0 has no obvious

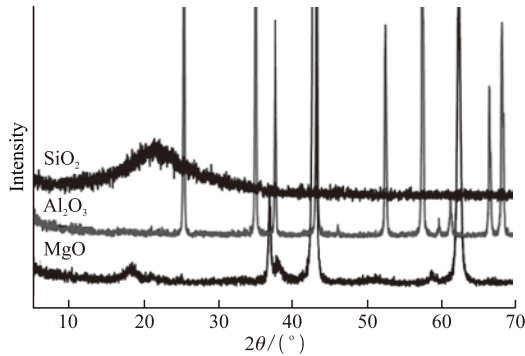


Fig.4 XRD patterns of MgO, Al₂O₃, and SiO₂ at room temperature phase evolution when calcined at 600 °C and 800 °C, and the main peaks overlap with the characteristic peaks of raw materials of MgO, Al₂O₃, and SiO₂, as shown in Fig.4. Corundum, periclase, cristobalite, and amesite are formed when calcined at 1 000 °C. When sample BPF-0 was calcined at 1 200 °C, the crystal phase of ceramic can not be distinguished. The ceramic phase formed at 1 000 °C may not be stable. There is much amorphous phase, which may be caused by the

classification of MAS and carbon residues of boron phenolic resin.

Fig.5 shows the XRD patterns of composite samples at different calcine temperatures. As shown in Fig.5 (a), the XRD patterns of sample BPF-1 calcined at 600 °C only show peaks of MAS and zinc borate. Corundum and periclase are formed at 800 °C, however much phase transformation appears at 1 000 °C. Corundum, mulite, amesite, periclase, cassiterite, and cordierite are formed at 1 000 °C. However, the XRD pattern of sample BPF-1 indicates large amount of amorphous phase at 1 200 °C, partly because of the melting of zinc borate, which is capable of forming an amorphous phase by softening and a fluxing capability. Ceramic phase formed at 1 000 °C is unstable to be ceramic at 1200 °C. It can be concluded that the ceramifiable temperature is not lowered obviously by the addition of zinc borate because the melting point of zinc borate is near the ceramifiable temperature of the MAS/BPF composites.

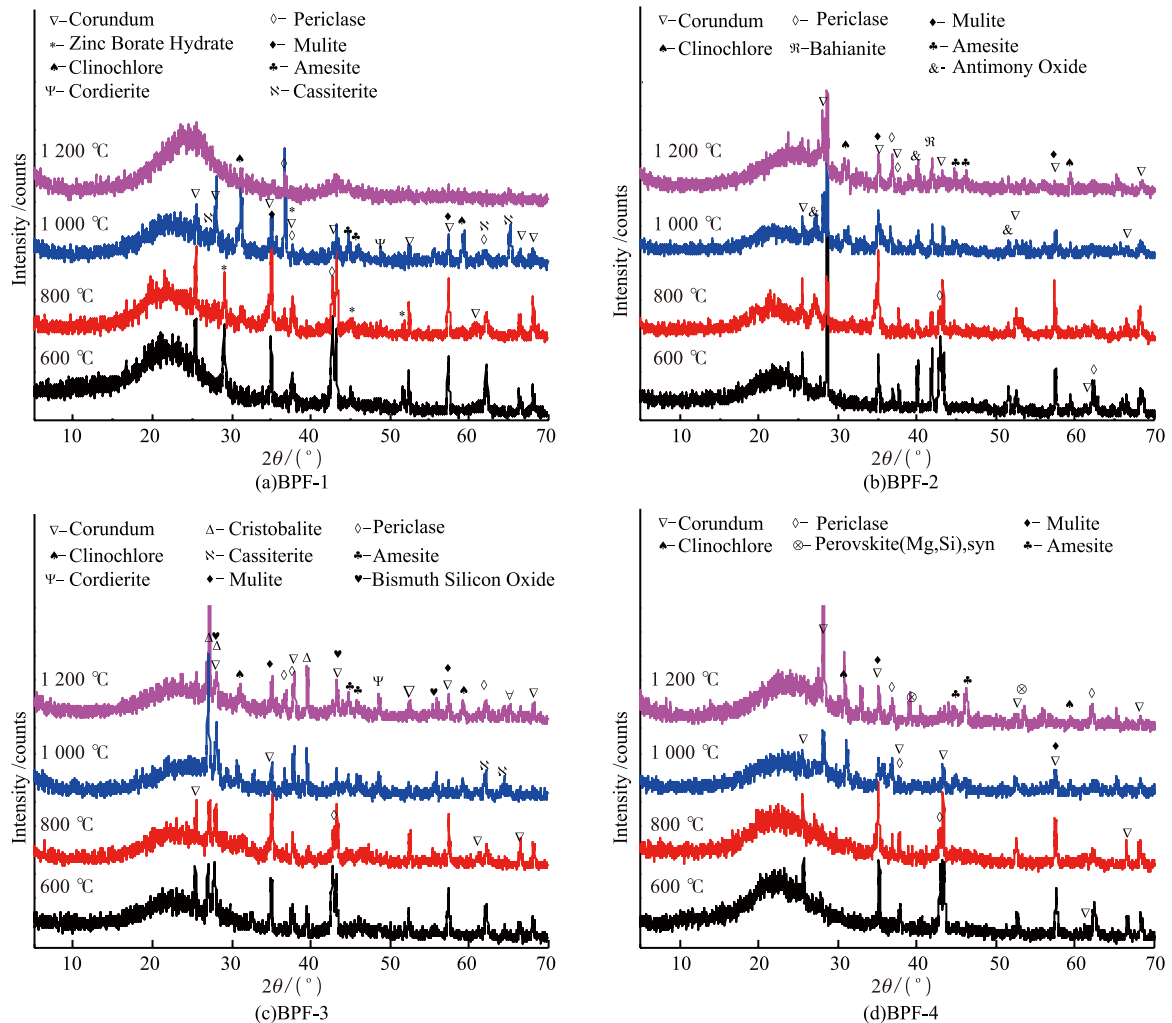


Fig.5 XRD patterns of (a) BPF-1, (b) BPF-2, (c) BPF-3, and (d) BPF-4 at different calcine temperatures

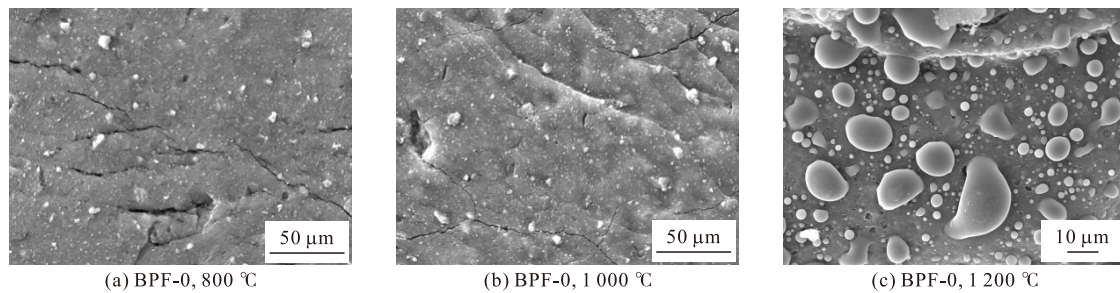


Fig.6 SEM images of sample BPF-0 in cross section calcined from room temperature to different target temperatures and held for another 2 h

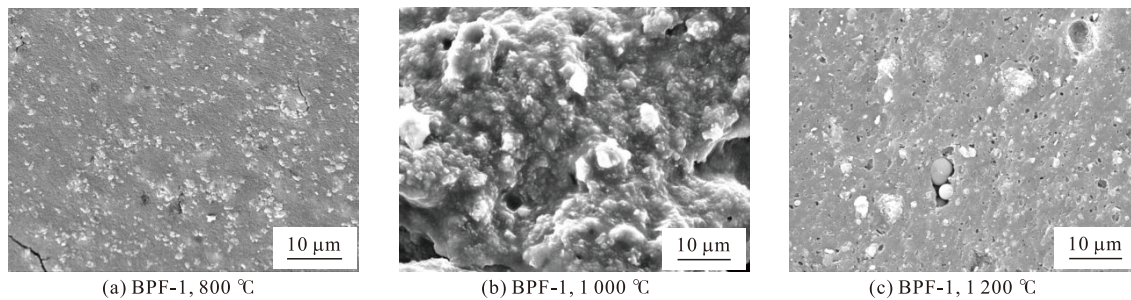


Fig.7 Cross section SEM images of sample BPF-1 calcined from room temperature to different target temperatures and held for another 2 h

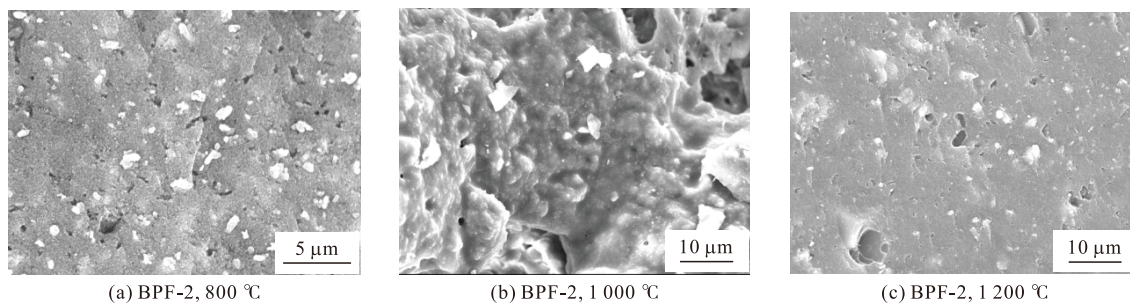


Fig.8 Cross section SEM images of sample BPF-2 calcined from room temperature to different target temperatures and held for another 2 h

As shown in Figs.5(b)-5(d), ceramic phases stabilize in all samples of BPF-2, BPF-3, and BPF-4 at 1 200 °C. The XRD patterns show the fluxing agents of antimony oxide, glass frit A and glass frit B interacted with MAS. The fluxing agents of antimony oxide, glass frit A and glass frit B, with low melting or softening point temperatures, lower the ceramifiable temperature of MAS /BPF composites. In addition, the melting of fluxing agents at a low temperature and formation of an eutectic liquid phase could affect the ceramification of MAS /BPF composites. It will be further discussed in the next part of SEM analysis.

3.3 Microstructure evolution of composites during ceramification

Fig.6 shows the microstructures of cross section of sample BPF-0 calcined from room temperature to target temperatures and held for another 2 h. There are many cracks in sample residue calcined at 800 °C and 1 000 °C, which results from the decomposition of boron phenolic resin. As shown in Fig.6(c), there is no obvious cracks in residue because of the appearance of liquid phase, and penetration of liquid phase into the cracks.

It can be seen from Fig.7(a) that the residue of sample BPF-1 has cracks calcined at 800 °C. Compared to sample BPF-0, liquid phase has been formed in sample BPF-1 at 1 000 °C and encapsulated the ceramic particles, as shown in Fig.7(b). The formation of liquid phase is attributed to the melting of zinc borate in sample BPF-1. The addition of fluxing agent facilitates ceramification at a lower temperature^[23]. Meanwhile, flocculent structures of residue of sample BPF-1 at 1 000 °C transform into densified structures with glass phases and cavities at 1 200 °C.

As shown in Fig.8(a), obvious liquid phase can be observed at 800 °C in sample BPF-2, resulted from the melting of the fluxing agent of antimony oxide. Cracks and cavities exist in residues of sample BPF-2 calcined at 800 °C. However, the residue shows less cracks and cavities at 1 000 °C, and further densification at 1 200 °C because of penetration of liquid phase and further ceramification of residue.

Fig.9 shows the effects of glass frits with low softening point temperatures on the microstructures of residues of samples BPF-3 and BPF-4. Liquid phases have

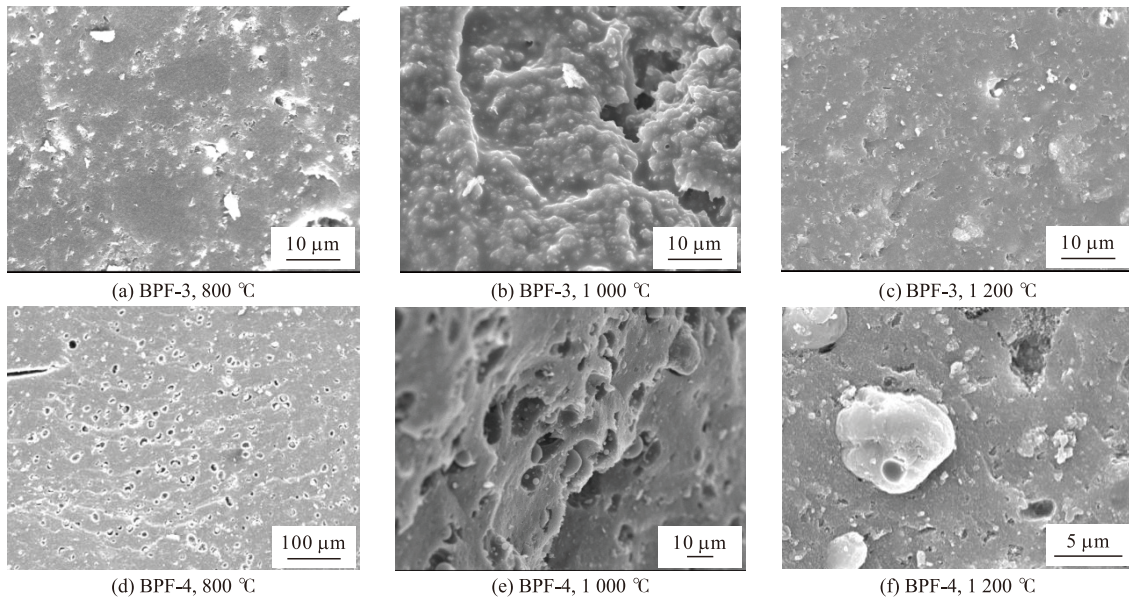


Fig.9 Cross section SEM photos of sample BPF-3 and BPF-4 calcined from room temperature to different target temperatures and held for another 2 h

been formed in samples BPF-3 and BPF-4 calcined at 800 °C. Furthermore, densification can be observed at 800 °C, as shown in Figs.9(a) and 9(d), which is caused by the softening of glass frit A (the softening point temperature range of 360 °C-620 °C) and glass frit B (the softening point temperature range of 550 °C-830 °C). When the calcine temperatures are up to 1 000 °C and 1 200 °C, respectively, the ceramification and densification of residues of sample BPF-3 and BPF-4 are further processed, as shown in Figs.9(b)-9(f), and eventually ceramic phase formed. The final residues of composites are ceramic surrounded by large amount of glass liquid phases. The microstructure of sample BPF-3 is more smooth and densified than that of BPF-4, which indicates that glass frit A is more effective to the ceramification of MAS/BPF composite than glass frit B.

It can be concluded from microstructural analysis that fluxing agents lower the forming temperatures of liquid phases directly, and then promote the ceramification and densification of residues. The softening point temperature range of fluxing agent should be considered for the target ceramification temperature of ceramifiable composites, and it should be lower than the target ceramification temperatures of composites. Glass frit A may be a better one than the other three fluxing agents for ceramifiable MAS / BPF composites to lower the ceramifiable temperature.

4 Conclusions

The thermal properties, the phase evolution and the microstructures of the MAS / BPF composites

with different fluxing agents calcined at different temperatures have been investigated. The fillers retard the decomposition rate of boron phenolic resin, and the derivative weight of the composites at the temperature of the maximum degradation rate is highly lower than that of pure boron phenolic resin. Furthermore, the addition of fluxing agents reduces the decomposition rate of MAS / BPF composites. Only 5 phr of fluxing agents lower the formation temperatures of liquid phases of ceramifiable composites obviously, and then promote the ceramification and densification of residues. The best choice of fluxing agent for MAS / BPF composite is glass frit A, which transforms into liquid phase at about 800 °C and results in further ceramification and densification at temperature about 1 000 °C. Fluxing agent modified MAS / BPF composite is expected to be a thermal retardant material with its low decomposition rate and ceramifiable performance.

References

- [1] Imiela M Anyszka R, Bielin'ski DM, *et al.* Effect of Carbon Fibers on Thermal Properties and Mechanical Strength of Ceramizable Composites Based on Silicone Rubber[J]. *Journal of Thermal Analysis & Calorimetry*, 2016, 124 (1): 197-203
- [2] Mansouri J, Burford RP, Cheng YB. Pyrolysis Behaviour of Silicone-based Ceramifying Composites[J]. *Mater. Sci. Eng. A*, 2006, 425: 7-14
- [3] Marosi G, Márton A, Anna P, *et al.* Ceramic Precursor in Flame Retardant Systems[J]. *Polymer Degradation and Stability*, 2002, 77: 259-265
- [4] Anyszka R, Bielin'ski DM, Pe,dzich Z, *et al.* Influence of Surface-modified Montmorillonites on Properties of Silicone Rub-

- ber-based Ceramizable Composites[J]. *Journal of Thermal Analysis & Calorimetry*, 2015, 119: 111-121
- [5] Al-Hassany Z, Genovese A, Shanks RA. Fire-retardant and Fire-barrier poly(vinyl acetate) Composites for Sealant Application[J]. *Express Polymer Letters*, 2010, 4(2): 79-93
- [6] Mansouri J, Wood CA, Roberts K, et al. Investigation of the Ceramifying Process of Modified Silicone-silicate Compositions[J]. *J. Mater. Sci.*, 2007, 42: 6 046-6 055
- [7] Li YM, Deng C, Wang YZ. A Novel High-temperature-resistant polymeric Material for Cables and Insulated Wires Via the Ceramization of Mica-based Ceramifiable EVA Composites[J]. *Composites Science and Technology*, 2016, 132: 116-122
- [8] Anyszka R, Bielin'ski DM, Pedzich Z, et al. Effect of Mineral Fillers on Properties of Silicone Rubber-based Ceramizable Composites. Part 1. Kinetics of Vulcanization and Mechanical Properties of Composites[J]. *Przem. Chem.*, 2014, 93: 1 291-1 295
- [9] Wang J, Ji C, Yan Y, et al. Mechanical and Ceramifiable Properties of Silicone Rubber Filled with Different Inorganic Fillers[J]. *Polymer Degradation and Stability*, 2015, 121: 149-156
- [10] Pędzich Z, Anyszka R, Bieliński DM, et al. Silicon-Basing Ceramizable Composites Containing Long Fibers[J]. *Journal of Materials Science and Chemical Engineering*, 2013, 1: 43-48
- [11] Hanua LG, Simon GP, Mansouri J, et al. Development of Polymer-ceramic Composites for Improved Fire Resistance[J]. *Journal of Materials Processing Technology*, 2004, 153-154: 401-407
- [12] Zhang Y, Shen S, Liu Y. The Effect of Titanium Incorporation on the Thermal Stability of Phenol-formaldehyde Resin and Its Carbonization Microstructure[J]. *Polymer Degradation & Stability*, 2013, 98(2): 514-518
- [13] Tate JS, Gaikwad S, Theodoropoulou N, et al. Carbon/Phenolic Nanocomposites as Advanced Thermal Protection Material in Aerospace Applications[J]. *Journal of Composites*, 2013, 2013: 1-9
- [14] Wang ZJ, Kwon DJ, Gu GY, et al. Ablative and Mechanical Evaluation of CNT/Phenolic Composites by Thermal and Microstructural Analyses[J]. *Composites Part B Engineering*, 2014, 60(2): 597-602
- [15] Srikanth I, Daniel A, Kumar S, et al. Nano Silica Modified Carbon-phenolic Composites for Enhanced Ablation Resistance[J]. *Scripta Materialia*, 2010, 63(2): 200-203
- [16] Chen Y, Chen P, Hong C, et al. Improved Ablation Resistance of Carbon-phenolic Composites by Introducing Zirconium Diboride Particles[J]. *Composites Part B Engineering*, 2013, 47: 320-325
- [17] Ding J, Huang ZX, Luo H, et al. The Role of Microcrystalline Muscovite to Enhance Thermal Stability of Boron-modified Phenolic Resin, Structural and Elemental Studies in Boron-modified Phenolic Resin/Microcrystalline Muscovite Composite[J]. *Materials Research Innovations*, 2015, 19, SUPPL 8: S8-605
- [18] Shi MX, Fan SS, Luo W, et al. Pyrolysis Behaviour of Boron Phenolic Resin-based Ceramicable Composites by Introducing of MAS[J]. *Advanced Materials Research*, 2017, 1142: 138-145
- [19] Guo SY, Wang ZQ, Li SZ, et al. Effect of Zinc Borate on Mechanical Properties and Flame-Retardancy of PVC[J]. *Polymeric Materials Science and Engineering*, 1997, 13: 100-105
- [20] Hamdani-Devarenes S, Pommier A, Longuet C, et al. Calcium and Aluminium-based Fillers as Flame-retardant Additives in Silicone Matrices II. Analyses on Composite Residues from an Industrial-based Pyrolysis Test[J]. *Polymer Degradation and Stability*, 2011, 96: 1 562-1 572
- [21] Wei Z, Li W. The Synergism Effect of the Zinc Borate on Fire Retardancy of Low Density Polyethylene[J]. *Plast. Sci. & Technol*, 2006, 34: 40-43
- [22] Dai J, Peng C, Wang FZ, et al. Effects of Functionalized Graphene Nanoplatelets on the Morphology and Properties of Phenolic Resins[J]. *High Performance Polymers*, 2016, 28 (5): 1-7
- [23] Qin Y, Rao ZL, Huang ZX, et al. Preparation and Performance of Ceramizable Heat-resistant Organic Adhesive for Joining Al₂O₃ Ceramics[J]. *International Journal of Adhesion & Adhesives*, 2014, 55: 132-138