

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Intergrowth charring for flame-retardant glass fabric-reinforced epoxy resin composites

Jun Jiang^a, Yanbo Chen^a, Yuan Liu^{*a}, Qi Wang^a, Yueshan He^b, Biwu Wang^b

An interfacial intergrowth charring method is designed and employed in glass fabric-reinforced epoxy resin composites. Unlike the traditional bulk-charring flame resistance mode in which phosphorus flame retardants distributed in a resin matrix catalyze resin to independently form a char layer that does not readily combine with glass fabric, the interfacial method grafts a reactive phosphorus flame retardant on a glass fabric surface, and the grafted glass fabric is then compounded with epoxy resin to obtain interfacial flame-retardant composites. At combustion temperature, the acids from the flame retardants carbonize the interfacial resin and produce an intergrown char layer (the char grows up from the glass fiber surface) that closes the inherent gaps and grids of the glass fabric. In this means, the chemically produced char combines with the glass fabric, i.e., the natural non-combustible physical barrier in the composites, to construct a sealed and compact fire proof shield. This shield, composed of glass fabric frameworks and char fillings, exerts a much greater isolating effect on flammable volatiles, oxygen and combustion heat than independent chemical char layers formed in bulk mode, thus showing significantly improved flame retardance relative to the latter with the same flame retardant content. Additionally, interfacial mode avoids the stress concentration caused by flame-retardant particles directly dispersed in resin and hence can endow the composites with excellent mechanical properties.

1 Introduction

Epoxy resins (EPs) have such desirable properties as solvent resistance, low shrinkage, excellent electrical insulation, good mechanical properties and satisfactory adhesion¹⁻⁴. At present, glass fabric-reinforced EP composites are widely applied in printed circuit boards, insulation devices and various electrical tools⁵. However, with a limiting oxygen index (LOI) of only 19, flammability is an obvious disadvantage of the resin and the flame resistance requirements of the above products are not easily satisfied⁶. Accordingly, flame retardance modification of an EP and its composites is important and significant. Particularly, due to concerns related to the safety of traditional halogen additives, halogen-free flame-retardant materials have recently attracted increasing attention both in academia and industries^{7,8}. In recent years, researchers have used various halogen-free flame retardants containing phosphorus, nitrogen and silicon, elements without environmental issues, in EP-based materials⁹⁻¹⁸. Phosphorus has been shown to be the most efficient in the above systems^{7,19}. Generally, flame-retardant particles are added to an EP prepolymer glue and well mixed, and the resulting mixture is then coated on the glass fabrics layer by layer; finally, the coated glass fabrics are dried, cured and compressed into composite laminates. Once the materials burn, the phosphorus flame retardants distributed in the resin decompose into phosphorus acids that carbonize the polymer. With excess phosphorus in the system, the chemically produced carbide can construct a continuous, dense and strong charring shield layer, thus effectively protecting the internal resin by blocking out the fire^{20,21}.

Based on the charring flame resistance mechanism, most researchers focus on the molecular design and synthesis of new and more efficient phosphorus flame retardants; as well as the synergism of different flame retardants. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives, as reactive phosphorus flame retardants, have been commercially applied in various thermoset resins including EP^{22,23}. Through the reaction between phosphaphenanthrene and epoxy groups, DOPO structure

^a Polymer Research Institute of Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, China; E-mail: liuyuan42001@163.com; Fax: +86-28-85402463; Tel: +86-28-85405133

^bNational Engineering Research Centre of Electronic Circuits Base Materials, Dongguan 523039, China

was introduced to the backbone of EP, thus greatly increasing the stability and dispersion of the flame retardant. However, as a bulk flame resistance mode, some shortcomings are inherent and inevitable. The construction of a continuous shield layer completely from resin carbonates must depend on high-loading phosphorus flame retardants that are not easily dispersed; but that easily deposit in viscous EP glue. In addition, even for the reactive flame retardants with good dispersion like DOPO, the rigid phenanthrene rings introduced in the bulk resin matrix also lead to stress concentration, thus causing serious deterioration of the mechanical properties. Accordingly, low flame retardant loading and maintenance of high performance for flame-retardant thermoset polymers remains a challenge.

In recent years, surface fire-proof methods were employed in some composites. In the research of Kandola, B. K. etc., glass fibre-reinforced polyesters were protected by intumescent mats/fabrics containing silicate fibres, expandable graphite and in some cases borosilicate glass bounded together by an organic matrix to effectively improve the flame retardance of composites²⁴⁻²⁶. This is a novel idea different from conventional bulk flame resistance mode.

During our long-term investigation of flame-retardant polymers, we have determined that except the factors of the used flame retardants themselves, the actual flame retardance of polymer composites is also relevant to the combination form of flame retardants with materials as well as charring growth means decided by the form. In our previous work²⁷, an interfacial flame-resistance mode was designed and successfully applied to glass fiber-reinforced nylon 6 to eliminate the wick effect of the glass fiber. This mode enriched a charring catalyst on the resin-glass fiber interface at which wick action occurs. At the combustion temperature of the nylon, a quickly produced intumescent char layer with an inert and rough surface replaced the original smooth and high-energy surface of raw glass fiber; the adsorption, wetting, spreading and flowing of a polymer melt on the glass fiber surface were retarded, therefore effectively weakening the physicochemical factors causing the wick effect.

Unlike thermo-plastic resins, thermoset polymers such as EP without melt flow behaviour during combustion are lack of wick effect. For its composite, the compounded glass fabric actually constitutes a natural non-combustible physical barrier to protect the inertial resin. Due to the shield effect, the composites possess greater fire resistance than pure EP resin. However, glass fabric is full of inherent gaps between fibers and in the grids (Fig. 1), which make the shield insufficiently compact to provide effective isolation.

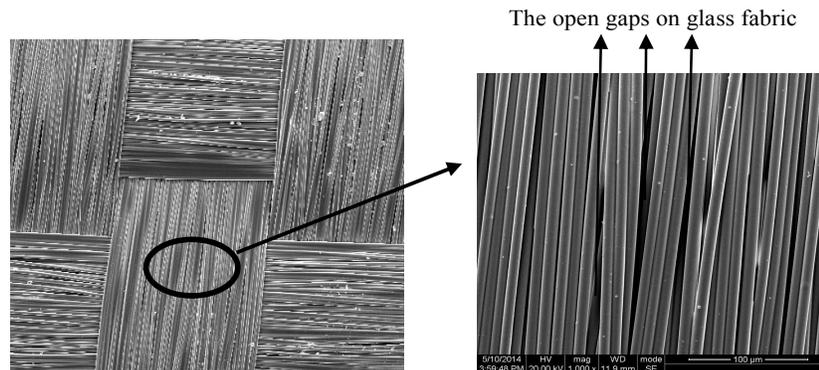
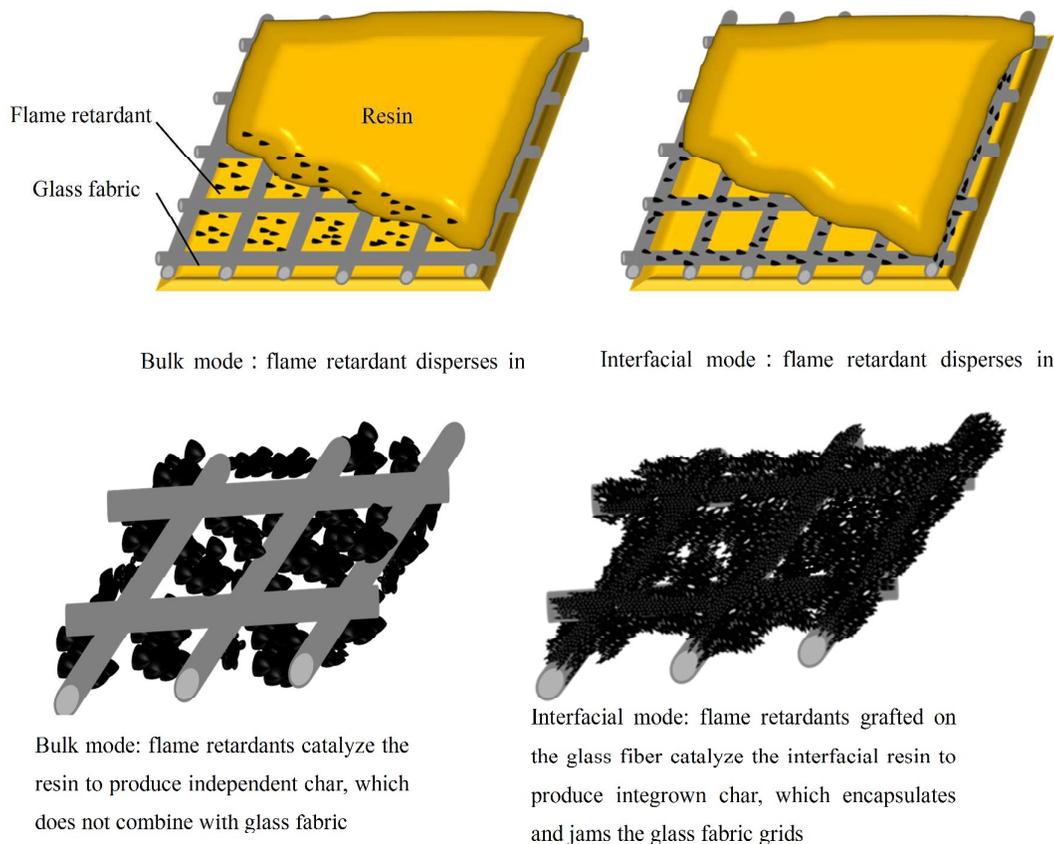


Fig. 1 SEM images of raw glass fabric surface

In this paper, an interfacial intergrowth charring mode is proposed and applied to glass fabric-reinforced EP composite systems. In this mode, the char is designed to intergrow with the glass fiber rather than independently produced from the bulk resin region as in the conventional mode. In this manner, the combination of chemical char and glass fabric can be realized. When the intergrowth char

from adjacent glass fibers grows and merges, the original gaps and grids on the glass fabric are jammed and closed. Hence, a high-quality shield barrier composed of a high-strength framework (glass fabric) and dense fillings (chars) is produced. The above mechanisms are shown in Scheme 1. As a compact composite barrier is more capable of effectively blocking off heat, oxygen and degraded volatiles, these interfacial composites have much greater flame retardance.



Scheme 1 Comparison of bulk and interfacial flame resistance modes

2 Experimental section

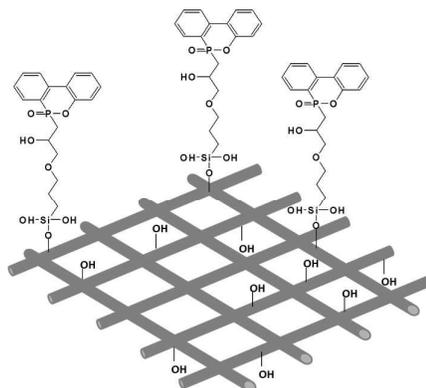
2.1 Materials

EP(diglycidyl ether of bisphenol-A type, epoxy equivalent weight: 489 g/eq) was purchased from Huntsman Advanced Materials Co., Ltd., and phenolic novolac resin hardener (hydroxyl equivalent weight: 105 g/eq) was supplied by Momentive Chemical Co., Ltd. Glass fabrics, 7628#, were purchased from Jushi Group Co., Ltd. DOPO was purchased from Shengshida Tech&Trade Co. Ltd., China. The silane coupling agent, γ -glycidylxypropyltrimethoxysilane (SCA), was purchased from Chengdu Thinkbond Chemical Co. Ltd., China.

2.2 Synthetic procedure

Calculated amounts of DOPO (21.60 g) powder and excessive SCA (28.30 g) at a molar ratio of 1:1.2 were mixed at 120°C. As DOPO was dissolved completely in SCA, the reagents were poured into a three-necked flask equipped with an oil-bath pot, a mechanical stirrer and a reflux condenser. The reaction temperature was maintained at 180°C for 4 h. After cooling to room temperature, the viscous colloidal product was repeatedly washed with 3000 ml deionized water to hydrolyze SCA-DOPO to obtain reactive

hydroxyl group, and meanwhile removed the excessive SCA. The washed white colloid was collected by filtration and dried at 100°C in a vacuum for 24 hours. The final obtained product was 38.30 g (yield: 93.40%). 5.00 g hydrolyzed SCA-DOPO was dissolved in 65.0 ml ethyl alcohol and then a piece of glass fabric (16.0 × 17.0 cm², 6.40 g per piece) was immersed in this mixed solvent for 15 min and dried at 130 °C for 3 h to prepare one piece glass fabric grafted with SCA-DOPO (Scheme 2). Finally, the piece of grafted glass fabric was repeatedly washed with 2000mL ethyl alcohol to remove the unreacted reactants. The average increased weight of every piece of glass fabric was 0.86 g.



Scheme 2 Glass fabric grafted with reactive phosphorus flame retardant

2.3 Preparation of composites

For the Bulk-mode system, the epoxy resin (7.50 g), hardener (phenolic novolac resin, 1.70 g) and flame-retardant DOPO (1.23 g) were mixed in butanone solvent (5.6 mL). The above glue was stirred for 30 min and evenly coated on one piece of raw glass fabrics (RGF), which was then heated in an oven at 155°C for 5 min to remove the solvent. Subsequently, a certain number of glass fabric pieces (the number was adjusted by the thickness of the test samples: 8 pieces for 1.6 ± 0.1 mm and 10 pieces for 2.0 ± 0.1 mm) were laminated and cured in a vulcanizing machine through a heating program at 190°C for 2 h. Finally, the obtained laminates were cut into the bars for the next tests.

For the interfacial-mode system, the procedure was the same, except grafted glass fabrics (GGF) were used instead of RGF, and the coated glue did not contain any flame retardant.

All the samples mentioned were prepared by Shengyi Technology Co., LTD.

2.4 Characterization

Energy dispersive spectrometry (EDS; INCA, Oxford Instrument) and X-ray fluorescence (XRF) from Shimadzu Corporation (XRF-1800) were used to analyze the elemental compositions of RGF and GGF.

The surface morphologies of RGF and the residual glass fabrics in the composite bars after burning were observed on a JEOL JSM-5900LV scanning electronic microscope (SEM; JEOL Ltd., Tokyo, Japan) with conductive gold coating and an acceleration voltage of 10 kV.

The vertical burning test was performed on an HK-HVRA instrument made by Zhuhai Huake Testing Equipment Co. Ltd., with the bars dimension of 125.0 × 13.0 × 1.6 mm³, according to ASTM D 3801-10. The limit oxygen index (LOI) was measured by a Dynisco LOI instrument, with the bars dimension of 140.0 × 3.0 × 1.6 mm³, according to ASTM D2863-97.

The atmosphere permeability of the residual glass fabrics with char was measured with a gas

permeability tester (Labthink, VAC-V1) according to ASTM E 96.

Cone calorimeter (Fire Testing Technology, UK) was used to investigate combustion behaviour at an incident radiant flux of 50 kW/m² on the specimen according to ISO 5660. Each specimen including three bars with a dimension of 100.0 × 100.0 × 2.0 mm³, were mounted in an aluminium foil and placed on a ceramic fiber blanket, so that only the upper face was exposed to the radiant heater. The final data are the averages of triplicate measurements.

Mechanical properties, including tensile strength and flexible strength, of the composites were tested at ambient temperature using a university machine of RGM-4010 (ShenZhen Reger Instrument Co. Ltd, China) according to ASTM D638-10 and ASTM D790-10, respectively.

3 Results and discussion

3.1 Surface flame-retardant elemental analysis

The amount of flame retardant grafted on the glass fabric surfaces was first detected. As the raw glass fabrics (RGF) lacked phosphorus, the detected P content of the grafted glass fabric (GGF) reflected the actual amount of grafted DOPO. Two methods of surface element quantification, EDS and XRF, were employed. Absorption peaks assigned to P can be observed at 2.4 keV in the EDS spectrum (Fig. 2(b)) and at 141° in the XRF spectrum (Fig. 3(b)) for the GGF. In addition, both results suggested similar P contents (Table 1), 5.82% (EDS) and 5.17% (XRF). According to the quantified P content of the glass fiber surface, the DOPO content of the entire composite was calculated as 4.2-4.6%.

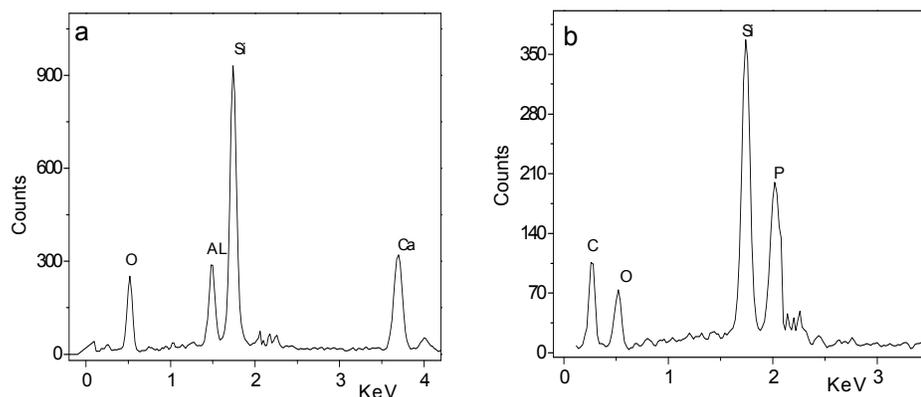


Fig. 2 EDS spectra of RGF (a) and GGF (b)

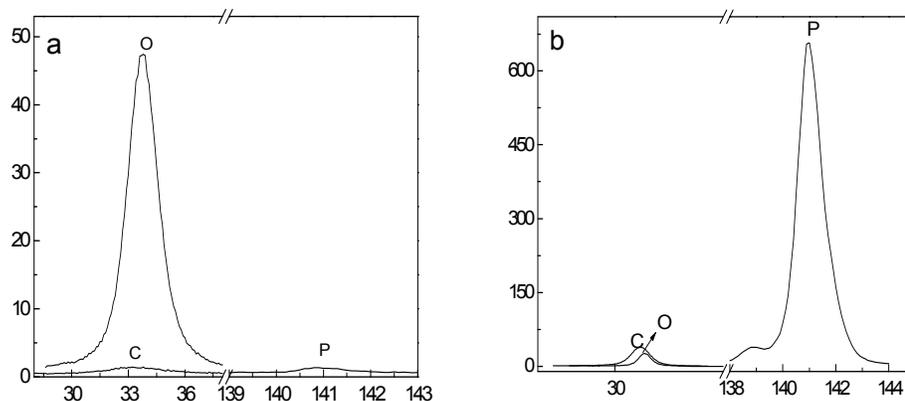


Fig. 3 XRF spectra of RGF (a) and GGF (b)

Table 1 Surface element content of RGF and GGF detected by EDS and XRF

Samples	Spectra	Element content detected (%)		
		O	P	C
RGF	EDS	50.32%	Not detected	Not detected
	XRF	51.20%	0.01%	2.08%
GGF	EDS	29.57%	5.82%	47.41%
	XRF	30.25%	5.17%	46.18%

3.2 Flame retardance and interfacial intergrowth charring properties

Vertical flame and LOI tests were performed to evaluate the flame retardance of neat EP, RGF/EP, RGF/EP/DOPO (the same DOPO content (4.6%) as GGF-EP was directly added into the bulk resin) and GGF/EP. Table.2 shows the above test results. Neat EP had a very fast combustion rate in the vertical flame test, with an LOI of only 19. For the RGF/EP composite, although the vertical flame did not self-extinguish, its flame rate slowed down: moreover, the LOI increased, indicating that compounds of the non-combustible glass fabric have improved flame retardance by decreasing the release of combustible volatiles and entrance of heat and oxygen to some degree. For the RGF/EP/DOPO system based on the bulk mode, the LOI also increased slightly, but the vertical flame retardance remained unchanged. In contrast, the interfacial mode for EP/GGF exhibited greatly improved flame retardance; the LOI of the former was enhanced to 31, and the vertical flame self-extinguished after two ignitions, achieving a V-1 rating.

Table 2 LOI and vertical burning tests

Samples	LOI,%	Vertical burning test			
		Afterflame time after the first 10s ignition	Afterflame time after the second 10s ignition	Flaming drips	Rating
Neat EP	19	No self-extinction	-	None	NR*
EP/RGF	21	No self-extinction	-	None	NR
EP/RGF/DOPO	24	No self-extinction	-	None	NR
EP/GGF	31	18.3	3.7	None	V-1

* No rating

Cone calorimetry is a quantitative test method that can effectively evaluate the combustion behaviours of materials in real fire disasters. The cone calorimetry test results for the above systems further confirmed the impact of the charring modes on flame retardance. Fire safety properties, including heat release rate (HRR), smoke production rate (SPR), CO₂ release rate and specific extinction area (SEA), are shown in Fig. 4. The EP/GGF interfacial-mode system had a much lower HRR, SPR and CO₂ release rate than the EP/RGF/DOPO bulk-mode system. The maximum values of the former decreased 19.7% in HRR, 37.1% in SPR and 5.9% in CO₂ release respectively. It indicates that interfacial-mode system performs much higher efficiency in improving the fire safety properties of the composites.

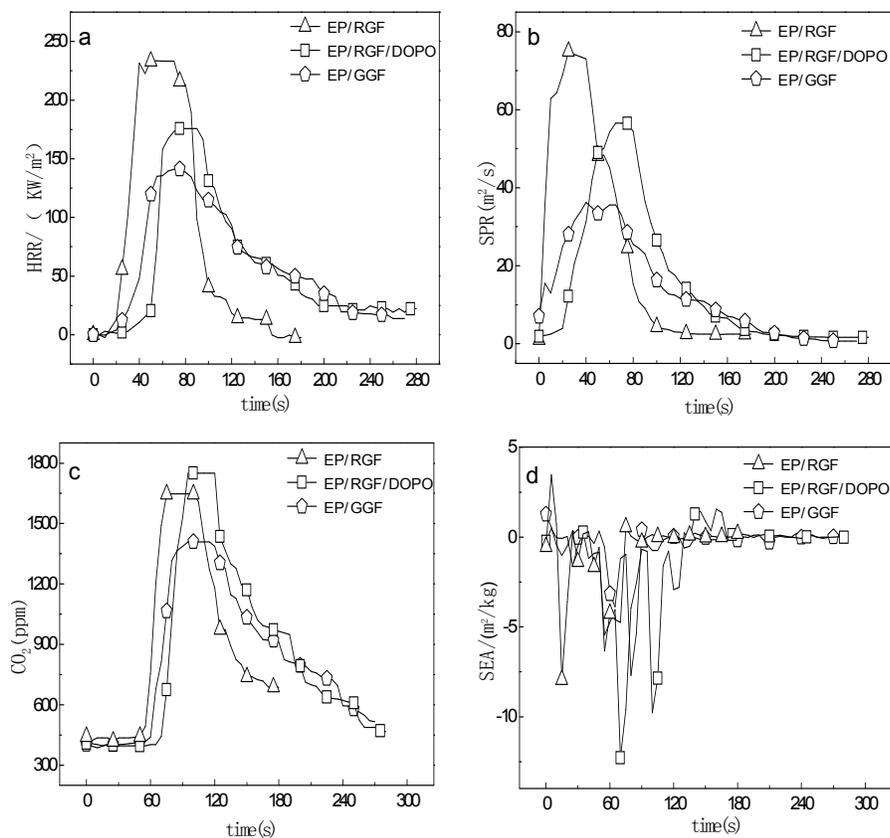


Fig. 4 HRR (a), SPR (b), CO₂ concentration (c) and SEA (d) curves of EP/RGF, EP/RGF/DOPO and EP/GGF composites

The mechanism of phosphorus flame retardants involves the release of phosphorus-containing acids that catalyze conversion of the polymer into char to form a fire-proof shield, which is so-called flame retardance in the condensed phase. Accordingly, the quantity and quality of produced char determine the final flame retardance. In general, only a continuous, dense and consolidated char layer encapsulating the entire material surface can effectively block heat and oxygen as well as retard the impact of heated expandable gases. To obtain an ideal char layer, a high-loading flame retardant is generally needed in bulk mode. The interfacial charring mode can effectively take advantages of the inherent glass-fiber shield to make the produced char intergrow on the glass fiber. When the produced chemical char jams and closes the original gaps of the glass fabrics, a perfect barrier shield can be formed. The required amount of char to fill the glass fabric grids for interfacial mode is much smaller than that which independently constitutes a compact shield in bulk mode. Simultaneously, the glass fiber encapsulated by resin carbides can also support the char layer and greatly enhance its strength.

The interfacial morphologies of EP/RGF/DOPO and EP/GGF after the flame test were observed by SEM (Fig. 5). For the bulk system, the gaps of the glass fabric were exposed again after the interfacial resin was nearly burned out, with only a small amount of char combined with the glass fiber. However, for EP/GGF, the intergrown char layer from the adjacent glass fibers merged and completely filled up the gaps and grids of the glass fabric to obtain a perfect barrier.

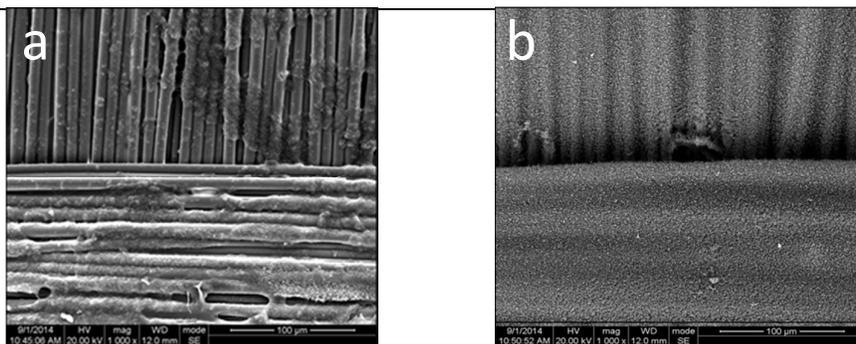


Fig. 5 Morphology of residual glass fabric from burned RGF/EP/DOPO (a) and GGF/EP (b) bars

An atmosphere permeability test verified the notable difference in the isolation effects of the two residual glass fabrics. As shown in Table 3, the permeability value of the barrier from the interfacial system was as high as 31.4, almost three times that of the bulk one, meaning that the former system more efficiently isolates oxygen and combustible volatiles that support the combustion process.

Table 3 Atmosphere permeability test of residual glass fabrics after flame test

Residual glass fabric	Atmosphere permeability value
EP/RGF/DOPO system	10.3
EP/GGF system	31.4

3.3 Elimination of stress concentration for interfacial mode

Interfacial properties greatly influence the performance of composites. For bulk mode, in which fillers such as flame retardants are directly dispersed in a resin matrix, a heterogeneous system is formed. Accordingly, defects are easily generated in the filler-resin interfacial region due to inadequate wetting of the glue or shrinking of the cured resin. The interfacial defects result in interfacial stress concentration; therefore, the composites undergo interfacial breakage with the exerted load, which is often the main failure mechanism for composites. Even for the reactive flame retardant system like DOPO, the rigid phenanthrene rings distributed in the bulk EP backbone also lead to notable stress concentration, thus increasing the brittleness of the material.

In the case of the interfacial distribution mode, with flame retardant grafted on the fiber surface rather than distributed in the resin matrix, the stress concentration in the resin by flame retardants was effectively eliminated. Moreover, the grafted organic side chains with polar groups on the inorganic glass fiber surface can extend into EP macromolecular chains to further enhance the resin-glass fiber interfacial combinations.

Table 4 reports the variation of mechanical properties due to stress elimination. The tensile strength and flexural strength of EP/RGF/DOPO were decreased by 23.7% and 22.3% relative to those of EP/RGF, showing that the stress concentration due to the rigid phenanthrene rings seriously deteriorated the mechanical properties even at a very low loading level (4.6%) of the bulk flame retardant. By comparison, the EP/GGF interfacial mode system had a little increase relative to the non-flame retardant system. Consequently, interfacial flame-retardant composites display outstanding advantages to maintain mechanical performance.

Table 4 Mechanical properties of EP/RGF, EP/RGF/DOPO and EP/GGF

Composite	Tensile strength(MPa)	Flexural strength(MPa)
EP/RGF	186.4	310.8
EP/RGF/DOPO	142.6	241.5
EP/GGF	187.3	312.5

4 Conclusions

A flame resistance mode through interfacial intergrowth charring was successfully applied to glass fabric-reinforced EP composites. The interfacial flame retardant grafted on the non-combustible glass fabric catalysed the conversion of EP resin into intergrown char that could quickly jam and close the inherent gaps and grids of the RGF, thus constructing a compact and sealed composite fire-proof barrier. With a much higher isolating effect on flammable volatiles, oxygen and combustion heat than independently produced chemical char layers in the bulk flame-retardant mode, the interfacial system demonstrated remarkably higher flame retardance properties, including LOI, vertical flame rating and cone calorimetry data. Meanwhile, the interfacial system also overcame the interfacial stress concentration caused by flame retardants directly dispersed in the resin matrix and endowed the composites with markedly improved mechanical properties. In summary, this interfacial flame resistance mode presents an efficient approach to the preparation of flame-retardant glass fabric-reinforced thermoset polymers with high performance.

5 Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 51473095) NSAF Fund (No.U1330122), Foundation for Innovative Research Groups of the National Natural Science Foundation of China (51121001) and State Key Laboratory of Polymer Materials Engineering (No. sklpme2014-3-11) is gratefully acknowledged.

6 References

1. S. Liu, H. Yan, Z. Fang and H. Wang, *Composites Science and Technology*, 2014, **90**, 40.
2. M. Sponton, J. C. Ronda, M. Galia and V. Cadiz, *Journal of Polymer Science Part a-Polymer Chemistry*, 2007, **45**, 2142.
3. C. S. Wang and C. H. Lin, *Journal of Polymer Science Part A: Polymer Chemistry*, 1999, **37**, 3903.
4. W. Zhang, X. Li and R. Yang, *J Appl Polym Sci*, 2013, **130**, 4119.
5. Y. L. Liu, C. S. Wu, K. Y. Hsu and T. C. Chang, *Journal of Polymer Science Part a-Polymer Chemistry*, 2002, **40**, 2329.
6. L. A. Mercado, J. A. Reina and M. Galia, *Journal of Polymer Science Part a-Polymer Chemistry*, 2006, **44**, 5580.
7. Q. L. Tai, Y. Hu, R. K. K. Yuen, L. Song and H. D. Lu, *Journal of Materials Chemistry*, 2011, **21**, 6621.
8. J. Alongi and G. Malucelli, *Journal of Materials Chemistry*, 2012, **22**, 21805.
9. X.-e. Cheng and W. Shi, *J Therm Anal Calorim*, 2011, **103**, 303.
10. M. Espinosa, M. Galia and V. Cadiz, *Journal of Polymer Science Part A: Polymer Chemistry*, 2004, **42**, 3516.
11. G.-H. Hsiue, W.-J. Wang and F.-C. Chang, *J Appl Polym Sci*, 1999, **73**, 1231.
12. C. H. Lin, *Polymer*, 2004, **45**, 7911.
13. C.-H. Lin and C.-S. Wang, *Polymer*, 2001, **42**, 1869.
14. J. Sun, X. Wang and D. Wu, *ACS applied materials & interfaces*, 2012, **4**, 4047.
15. C. S. Wang and C. H. Lin, *Polymer*, 1999, **40**, 747.
16. X. H. Zhang, S. Chen, Y. Q. Min and G. R. Qi, *Polymer*, 2006, **47**, 1785.
17. S. Allauddin, R. Narayan and K. Raju, *ACS Sustainable Chemistry & Engineering*, 2013, **1**, 910.
18. F. Gao, L. Tong and Z. Fang, *Polymer degradation and stability*, 2006, **91**, 1295.
19. X. X. Chen, J. H. Ye, L. Yuan, G. Z. Liang and A. J. Gu, *Journal of Materials Chemistry A*, 2014, **2**, 7491.
20. D. Wang, K. Zhou, W. Yang, W. Xing, Y. Hu and X. Gong, *Ind. Eng. Chem. Res.*, 2013, **52**, 17882.
21. D. Wang, Q. Zhang, K. Zhou, W. Yang, Y. Hu and X. Gong, *J. Hazard. Mater*, 2014, **278**, 391

-
22. Perret, B.; Schartel, B.; Stoss, K.; Ciesielski, M.; Diederichs, J.; Doring, M.; Kramer, J.; Altstadt, V. *Macromolecular Materials and Engineering* 2011, **296**, 14.
 23. Muller, P.; Bykov, Y.; Doring, M. *Polym. Adv. Technol.* 2013, **24**, 834.
 24. Kandare, E.; Chukwudole, C.; Kandola, B. K. *Fire and Materials* 2010, **34**, 21.
 25. Kandola, B. K.; Horrocks, A. R.; Myler, P.; Blair, D. J. *App. Polym. Sci.* 2003, **88**, 2511.
 26. Kandola, B. K.; Akonda, M. H.; Horrocks, A. R. *Polym. Degrad. Stab.* 2005, **88**, 123.
 27. Y. Han, Y. Xu, Y. Liu, Q. Wang, Z. Zhang and Z. Wang, *Journal of Materials Chemistry A*, 2013, **1**, 10228.