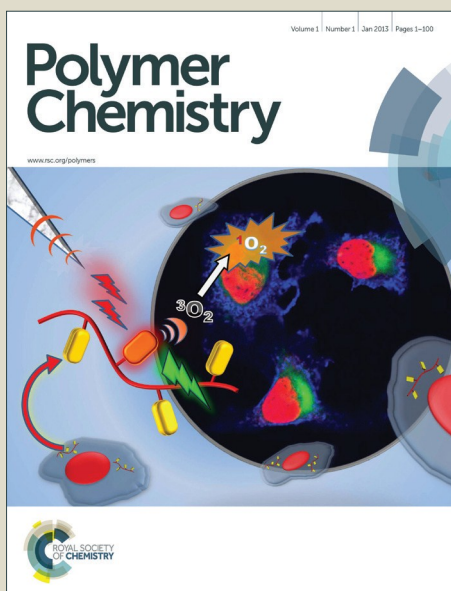


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Interfacial Carbonation for Efficient Flame Retardance of Glass Fiber-Reinforced Polyamide 6

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Wicking action, a typical physicochemical phenomenon, always causes high flammability of glass fiber (GF)-reinforced thermoplastic polymer composites due to the rapid and oriented flow of the polymer melt along the GF surface to the fire zone. This paper introduced an interfacial carbonation mode to solve the global challenge of flame resistance for these composites. Unlike the conventional bulk flame resistance mode, in which a high loading of phosphorus flame retardants must be added and evenly distributed in the polymer matrix and the acid sources released by the flame retardants would catalyze the resin into continuous and compact carbonate layer (the carbonates distributed in the bulk region are uncombined with the GFs), the interfacial mode enriches flame retardants in the GF-resin interfacial regions where wicking actions occur. After the composite burns, the released phosphorus acids can effectively carbonize the interfacial resin and the formed interfacial carbonate layer combining with the GF will convert the original smooth and high-energy GF surface to an inert and rough carbonate surface. The change of interfacial properties makes the adsorption, wetting, spreading and flow of the polymer melt along the GFs much more difficult, thus greatly weakening the wicking effects and improving the flame retardance efficiency of the composites.

1. Introduction

GF-reinforced polymer composites have been widely applied in modern society due to their greatly improved strength, rigidity, and heat distortion temperature compared with neat polymers¹⁻⁸. However, the composites have a notable disadvantage, i.e., high flammability caused by the wicking action of GFs⁹⁻¹². The burning mechanism of a candle is well known. During its combustion process, the wick itself does not flame but adsorbs and carries the melted wax to the fire zone, thus sustaining the combustion. Similarly, this wicking effect also exists in GF-reinforced thermoplastic polymer composites. Here, the GFs play the role of wicks, and polymer melts would wet and spread on the GF surface at the combustion temperature, which produces oriented interfacial flow of the melts, accelerates the fuel supply and intensifies the flame behavior. The direct result of the wicking effect is that GF/polymer composites exhibit much higher flammability than corresponding neat resins. Therefore, the improvement of flame retardance for the former is more difficult.

Currently, the main flame resistance method of GF-reinforced polymer composites is based on a bulk addition mode¹³⁻¹⁶. Some flame retardants containing acid sources can catalyze the polymer matrix into carbonates¹⁷⁻²², which construct a continuous and compact barrier covering the entire material surface to isolate oxygen, volatiles and heat, thus leading to the self-extinguish of fire. Certainly, this mode requires a high loading of flame retardants at the price of deteriorated processability and mechanical properties, as well as high cost. Over the past few years, researchers have mainly focused on the synthesis of efficient flame retardants²³⁻²⁶; however, successful commercialization of a novel flame retardant generally takes a long time and is expensive. Moreover, this strategy still cannot overcome the inherent limitations of bulk flame resistance mode: the flame retardance is basically the same at any region of the composite while the actual burning behaviors are different from the bulk to the interfacial resin. As a matter of fact, interfacial combustion is much more intensive due to the wicking effect. For this reason, if flame retardants can intensively act on the interfacial

region and effectively interfere with the wicking action, they would be more efficient than in the conventional bulk mode.

In view of the above consideration, we have proposed a novel interfacial carbonation flame resistance mode, in which, only a small amount of acid-release flame retardants is enriched on the GF-resin interface. At the combustion temperature of the composites, the released acids can quickly carbonize the interfacial resin, and the produced carbonates will encapsulate the adjacent glass fibers to form a coarse and inert surface in place of the original smooth and high-energy surface of the GF, thus effectively suppressing the wetting, spreading, and flowing behaviors of polymer melt on the interface. In this manner, it can almost eliminate all the wicking effect and result in facile flame retardance for the GF/polymer composites. In our earlier work²⁷, interfacial flame resistance mode has been successfully applied to GF-reinforced polymer composites through grafting a reactive flame retardant to GF surface, but the chemical method has some shortcomings including a relatively complicated process, limited choices and a low graft amount of the interfacial flame retardants. Accordingly, we developed here a more practical physical method that can enrich various flame retardants on GF surface. In addition, some advanced characterization techniques e.g., the contact angle of polymer melt on the carbonates glass, were employed in order to clearly reveal the mechanisms of the whole process.

2. Experimental

2.1 Materials

Polyamide 6 (PA6) with a relative viscosity of 3.2 was purchased from Balin Petroleum and Chemical Subsidiary Company, Petroleum and Chemical Co., China. Raw glass fibers (RGF) with a diameter of 10 μm , were provided by Jushi Group Co., China. Raw glass sheets (RGS) with dimensions of $1\times 3\times 4\text{ mm}^3$ were purchased from Sitong Chemical instruments Co., China. Melamine polyphosphate (MPP) was supplied by Sichuan Fine Chemical Engineering Institute, China. Phenolic aldehyde resin (PAR) with a molecular weight of 4200 was provided by Kelong Chemical Regent Co., Ltd.

2.2 Preparation of glass fibers and sheets coated with flame retardants

RGF and RGS were immersed into the flame retardant (FR) alcohol solution (concentration: 10%) composed of PAR and MPP (weight ratio of MPP/PAR=5/1) under sonication for 10 min and dried at 130 $^{\circ}\text{C}$ for 60 min to form a PAR film loaded with MPP on the RGF

and RGS surfaces. Thus, flame retardant-coated glass fibers and sheets (FRGF and FRGS) were obtained.

2.3 Preparation of PA6 resin-encapsulated glass fibers and sheets and their carbonation samples

RGF, RGS, FRGF and FRGS were coated with a PA6/formic acid solution (concentration: 20%) and dried in an oven at 180 $^{\circ}\text{C}$ for 2 h to remove the solvent. The obtained PA6 resin-encapsulated glass fibers and sheets (PA6E-RGF, PA6E-RGS, PA6E-FRGF and PA6E-FRGS) were flamed on an alcohol burner for sufficient ablation and carbonation of the interfacial PA6 resin.

2.4 Preparation of the composites

PA6 pellets, GF (FRGF or RGF, its content kept a fixed 30 wt% in the entire composite) and FRs (MPP/PAR) (only added in the bulk mode formulation) were premixed in a mixer. Then, the mixture was extruded at 230-250 $^{\circ}\text{C}$ in a TSSJ-25/33 co-rotating twin-screw extruder ($\Phi=25\text{ mm}$, $L/D=33$, Chenguang Research Institute of Chemical Industry, China) with a rotation rate of 150 rpm. The extruded granulates were cooled in a water bath, cut into pellets, and dried in a drier at 100 $^{\circ}\text{C}$ for 5 h. The dried granulates were injected into standard test bars of PA6/RGF, PA6/RGF/FR, and PA6/FRGF at 250 $^{\circ}\text{C}$ under 60 MPa pressure in an injection molding machine ($\Phi=30\text{ mm}$, MA1200-SMS-A, Haitian Plastics Machinery Ltd., China).

2.5 Characterization

X-ray fluorescence (XRF) was performed using an instrument from Shimadzu Corporation (XRF-1800) and was used to analyze the content of P on the RGF and FRGF surfaces. The Underwriters Laboratories-94 (UL-94) vertical burning test was conducted on a HK-HVR vertical burning tester (Zhuhai Huake Testing Equipment Co., Ltd) with bar dimensions of $127\times 12.7\times 1.6\text{ mm}^3$ according to the American National UL-94 test (ASTM D3801-10). The LOI was measured using an automatic oxygen index analyzer (Shandong Textile Science Research Institute) according to ASTM D2863. The sample dimensions were $120\times 6.5\times 3.0\text{ mm}^3$. Cone calorimetry (Fire Testing Technology Ltd, UK) was employed to investigate the combustion behaviors at an incident radiant flux of 50 kW/m^2 according to ISO5660. The surface morphologies of the burned samples (PA6E-RGF, PA6E-FRGF, PA6E-RGS and PA6E-FRGS) were observed using a polarizing microscope (Leica DM2500P) and a scanning electronic microscope (SEM) (JSM-5900LV, JEOL Ltd., Tokyo, Japan) with a conductive gold layer coating and an accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) analysis of the carbonate layer was performed by a

Shimadzu/Kratos AXIS Ultra DLD Multifunctional X-ray Photoelectron Spectrometer (Manchester, UK). Contact angle measurements of the samples were conducted on a Kruss DSA-100 goniometer (PA6 granulates were heated to the melting point on the surface of the burned PA6E-RGS and PA6E-FRGS).

3. Results and discussion

3.1 Characterization of FRGF

XRF measurements were first used to quantify the actual interfacial FR content by detecting variations in the concentrations of the characteristic elements on the FRGF surface. From Fig. 1, an obvious absorption peak at 141° assigned to P from MPP was observed in the XRF spectrum for FRGF (there was almost no P element in RGF). According to the determined P content on the FRGF surface, the FR content of the entire composite was calculated as 5.4%.

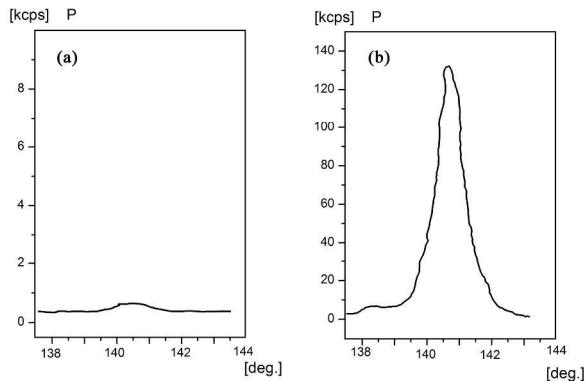


Fig.1 XRF spectra of (a) RGF and (b) FRGF

3.2 Flame Retardance

The conventional flame retardance evaluation methods, LOI and UL94 vertical flame test, were employed to evaluate the flame retardance of the composites. Fig. 2 indicates the variations of LOI values and UL94 rating with different FR contents in bulk mode. There was almost no improvement of the flame retardance when 5.4% FR was added compared with the non-flame retardant sample. The contents only reached 25%, then 24.3% of the LOI value and the UL94 V2 rating could be achieved. In contrast, with the same low FR content (5.4%), the interfacial mode system reached 26.4% and V1 rating (Table 1), displaying equivalent flame retardance of the bulk mode with 30% FR loaded (LOI: 26.1%, UL94 rating: V1). Clearly, the interfacial mode resulted in much higher efficiency.

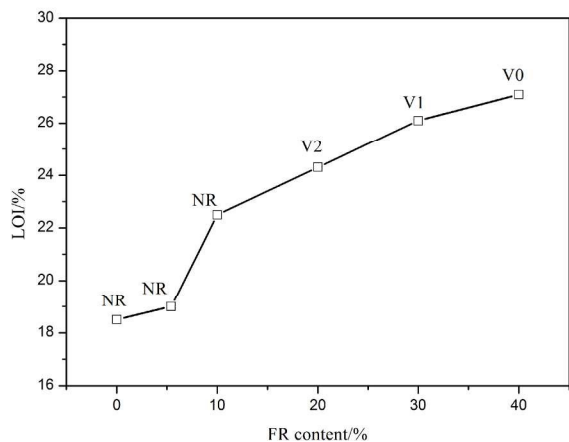


Fig. 2 The flame retardance variation with FR content in bulk mode (NR: no rating)

Table 1 The LOI and UL-94 testing results of the composites

Systems	LOI (%)	UL94 (1.6 mm)	
		t_1/t_2 (s)	Rating
PA6/RGF/FR	19.4	No self-extinction/-	NR
PA6/FRGF	26.8	5.1/10.4	V-1

(t_1/t_2 : the average time after the first and second applications of the flame, NR: no rating, the same FR content (5.4%) in the bulk and interfacial systems)

In addition to the LOI and the UL94 vertical flame test, cone calorimetry is a quantitative method to evaluate the combustion behaviours of materials in real fire disasters. The following cone calorimetry data for the above bulk and interfacial systems further confirmed the impact of the FR dispersion modes on the flame retardance. In Fig. 3, the interfacial mode system showed remarkably decreased heat release rate (HRR), total heat release rate (THR), mass loss rate (MLR) and smoke production rate (SPR) compared with the bulk mode. These results indicated greatly improved flame retardance and lower fuel consumption rate of the interfacial mode system during combustion.

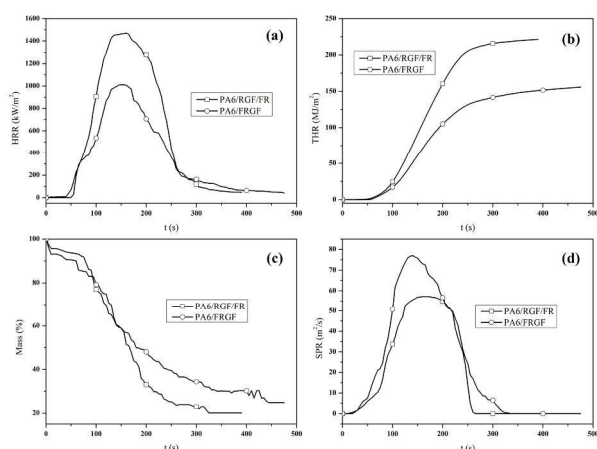


Fig. 3 Cone calorimetry curves of PA6/RGF/FR and PA6/FRGF: (a) HRR, (b) THR, (c) MLR and (d) SPR (5.4% FR content in bulk and interfacial systems)

3.3 Mechanism analysis of interfacial flame resistance mode

The mechanism of phosphorus-containing flame retardants like MPP is to release phosphorus acids that carbonize polymers into an inert char barrier to isolate the fire. The dispersion of the FR in the composites has a profound impact on the final distribution of the produced carbonates, which can greatly influence the flame retardance. Bulk and interfacial dispersion of the FR were shown in Fig. 4. MPP particles (arrows) were distributed in the resin matrix for the bulk system (a), whereas they were enriched on the glass fiber surface (encapsulated by PAR) for the interfacial mode (b).

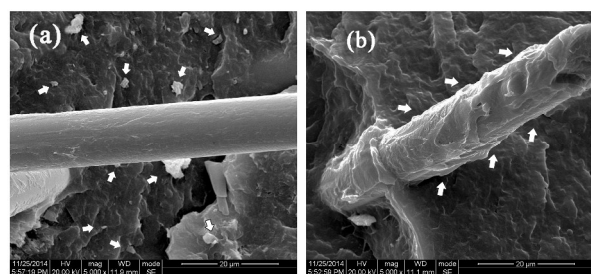


Fig. 4 Dispersion morphology of the FR in the composites of (a) bulk and (b) interfacial mode

Accordingly, during the chemical carbonation, the independently produced carbonates in bulk resin regions hardly combined with the glass fibers in the bulk system, therefore the contribution to weakening the interfacial wicking effect was low. However, in the case of the interfacial system, the FR concentrated on the FRGF surface mainly catalyzed the interfacial resin to form a carbonate layer combined with the GFs.

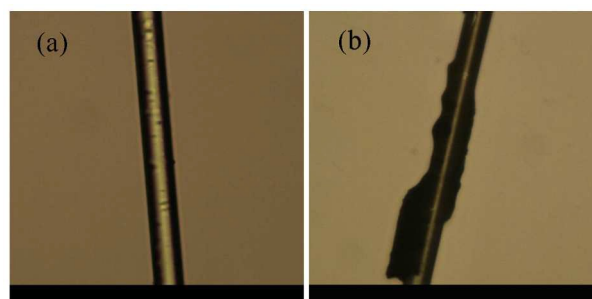


Fig. 5 The surface morphologies of (a) PA6E-RGF and (b) PA6E-FRGF after flame

The interfacial carbonation behaviors were simulated by burning a single PA6E-RGF and PA6E-FRGF bar. Fig. 5 shows that the interfacial PA6 resin coated on the RGF surface was almost burned out for the bulk FR system. In contrast, the produced continuous carbonates encapsulated the surface of the glass fiber in the interfacial FR system.

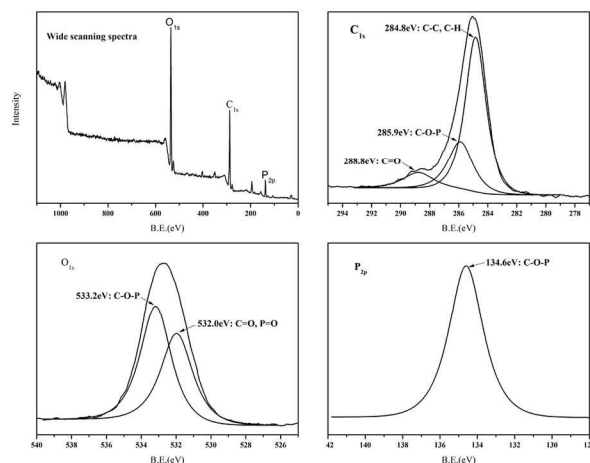
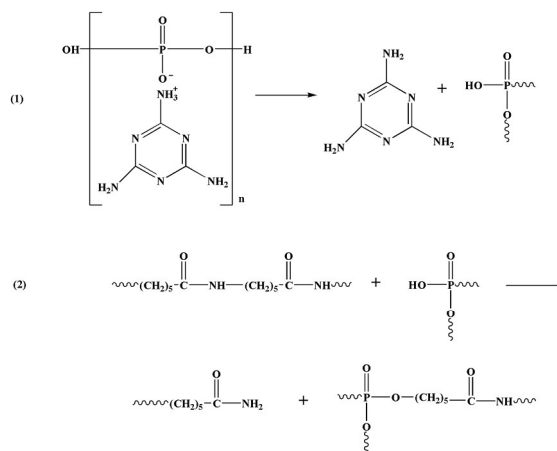


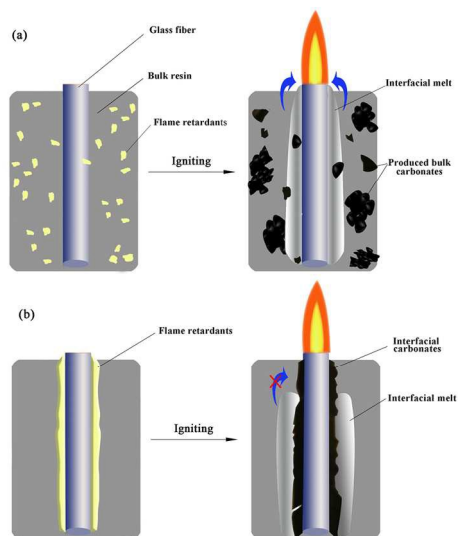
Fig. 6 XPS spectra of carbonate layer



Scheme 1 The interaction mechanism of carbonation

The elements composition and chemical bond forms of the char were also determined by XPS. From Fig. 6, C_{1s} spectrum had three peaks with binding energy at 284.8 eV (assigned to the C-C and C-H groups), 285.9 eV (C-O-P) and 288.8 eV (C=O). Two peaks were observed with binding energy around 532.0 eV and 533.2 eV in O_{1s} spectrum, which were the contributions of C=O, P=O and C-O-P groups respectively. The binding energy measured at 134.6 eV in P_{2p} spectrum could be assigned to P-O-C and/or P=O groups²⁸⁻³¹. The observation of C-O-P group in char layer indicated that MPP participated in the charring reaction and the possible interaction mechanism could be described by Scheme 1. The above analysis concerning the carbonation processes of MPP are also agreement with the researches of other researchers³²⁻³⁴.

The result of the interfacial carbonation is to change the original smooth and high-energy GF surface into a rough and low-energy carbonate surface. The interface qualities conversion means that either dynamic (surface roughness) or thermodynamic (surface polarity) factors inducing the wicking action are weakened. On such a carbonate layer, the PA6 melt became much more difficult to adsorb, wet and spread. The mechanisms were described in Scheme 2.



Scheme 2 Interfacial behaviors of the PA6 melt in (a) bulk and (b) interfacial mode

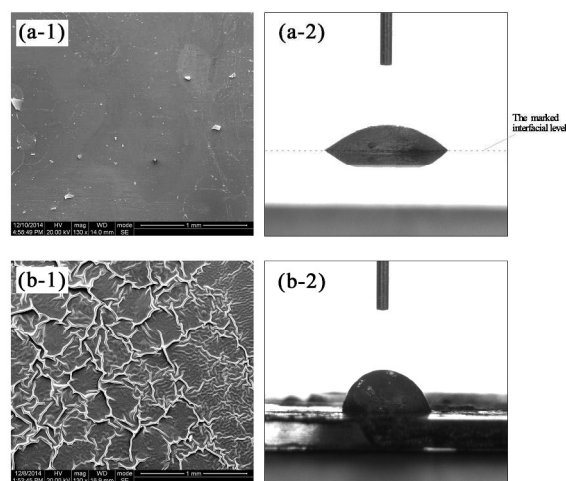


Fig. 7 The surfaces of (a-1) burned PA6E-RGS and (b-1) burned PA6E-FRGS and the corresponding contact angles (a-2, b-2) of the PA6 melts on them

To further confirm the above mechanisms, contact angle experiments of the PA6 melt on smooth and carbonation glass surfaces were designed. Considering the difficulties of the contact angle test on a fine glass fiber, glass sheets were used as an alternative. Fig. 7 shows the surface morphologies of the burned PA6E-RGS and PA6E-FRGS and the corresponding contact angles (θ) of the PA6 melts on them. The former θ was only 32.4° ; however, the latter was as high as 84.2° (90° is the critical angle determining the occurrence or non-occurrence of wetting behavior), which means that the PA6 melt more easily wets the relatively smooth and high-energy glass sheet (the resin of PA6E-RGS was almost burned out) but hardly wets the inert and low-energy carbonation glass surface.

4. Conclusions

In our designed interfacial carbonation mode, the produced rough and inert carbonates surface replaced the smooth and high-energy surface of RGF, effectively blocking the adsorption, wetting, spread and flow of the PA6 melt on the glass fiber surface. In this manner, this system eliminated the thermodynamic and dynamic factors causing the wicking action and remarkably improved the flame retardance (26.4% of LOI and V1 rating) with a very low flame retardant content (5.4%). The interfacial carbonation mode indicated distinct advantages compared with the conventional bulk mode and provided an efficient and economic flame resistance technology to prepare flame-retarded GF/polymer composites with high performances.

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Notes and references

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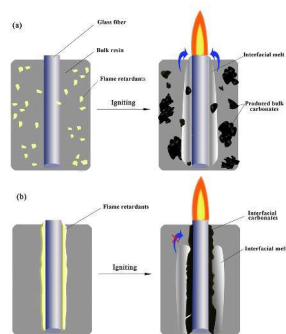
Fax: +86-28-85402465

- [1] S. K. Kumar, R. Krishnamoorti, *Annu. Rev. Chem. Biomol.*, 2010, **1**, 37.
- [2] M. Chauzar, S. Tateyama, T. Ishikura, K. Matsumoto, D. Kaneko, K. Ebitani, T. Kaneko, *Adv. Funct. Mater.*, 2012, **22**, 3438.
- [3] N. Y. Ning, S. R. Fu, W. Zhang, F. Chen, K. Wang, H. Deng, Q. Zhang, Q. Fu, *Prog. Polym. Sci.*, 2012, **37**, 1425.
- [4] C. Kuttner, A. Hanisch, H. Schmalz, M. Eder, H. Schlaad, I. Burgert, A. Fery, *ACS Appl. Mater. Inter.*, 2013, **5**, 2469.
- [5] K. Makyla, C. Müller, S. Lörcher, T. Winkler, M. G. Nussbaumer, M. Eder, N. Bruns, *Adv. Mater.*, 2013, **25**, 2701.
- [6] Y. Yoo, M. W. Spencer, D. R. Paul, *Polymer*, 2011, **52**, 180.
- [7] E. B. Murphy, F. Wudl, *Prog. Polym. Sci.*, 2010, **35**, 223.
- [8] M. J. Clifford, T. Wan, *Polymer*, 2010, **51**, 535.
- [9] W. Yang, Y. Hu, Q. Tai, H. D. Lu, L. Song, R. K. K. Yuen, *Compos. Part A-Appl. Sci. Manuf.*, 2011, **42**, 794.
- [10] U. Braun, B. Schartel, M. A. Fichera, C. Jager, *Polym. Degrad. Stabil.*, 2007, **92**, 1528.
- [11] Y. H. Chen, Q. Wang, *Polym. Degrad. Stabil.*, 2006, **91**, 2003.
- [12] Y. Liu, Q. Wang, *Polym. Degrad. Stabil.*, 2006, **91**, 3103.
- [13] P. Kiliaris, C. D. Papaspyrides, *Prog. Polym. Sci.*, 2010, **35**, 902.
- [14] S. Bourbigot, S. Duquesne, *J. Mater. Chem.*, 2007, **17**, 2283.
- [15] N. Bitinis, M. Hernández, R. Verdejo, J. M. Kenny, M. Lopez-Manchado, *Adv. Mater.*, 2011, **23**, 5229.
- [16] A. Dasari, Z. Z. Yu, G. P. Cai, Y. W. Mai, *Prog. Polym. Sci.*, 2013, **38**, 1357.
- [17] Q. Tai, Y. Hu, R. K. K. Yuen, L. Song, H. D. Lu, *J. Mater. Chem.*, 2011, **21**, 6621.
- [18] W. Jin, L. Yuan, G. Liang, A. J. Gu, *ACS Appl. Mater. Inter.*, 2014, **6**, 14931.
- [19] B. Wang, Q. Tang, N. Hong, L. Song, L. Wang, Y. Q. Shi, Y. Hu, *ACS Appl. Mater. Inter.*, 2011, **3**, 3754.
- [20] A. A. Muleja, X. Y. Mbianda, R. W. Krause, K. Pillay, *Carbon*, 2012, **50**, 2741.
- [21] P. J. Liu, W. H. Chen, Y. Liu, S. B. Bai, Q. Wang, *Polym. Degrad. Stabil.*, 2014, **109**, 261.
- [22] W. H. Awad, C. A. Wilkie, *Polymer*, 2010, **51**, 2277.
- [23] P. Müller, Y. Bykov, M. Döring, *Polym. Advan. Technol.*, 2013, **24**, 834.
- [24] B. K. Kandola, M. H. Akonda, A. R. Horrocks, *Polym. Degrad. Stab.*, 2005, **88**, 123.
- [25] D. X. Zhuo, A. J. Gu, G. Z. Liang, J. T. Hu, L. Yuan, X. X. Chen, *J. Mater. Chem.*, 2011, **21**, 6584.
- [26] J. Sun, X. Wang, D. Wu, *ACS Appl. Mater. Inter.*, 2012, **4**, 4047.
- [27] Y. Han, Y. Xu, Y. Liu, Q. Wang, Z. J. Zhang, Z. Y. Wang, *J. Mater. Chem. A*, 2013, **1**, 10228.
- [28] Y. Nakayama, F. Soeda, A. Ishitani, *Carbon*, 1990, **28**, 21.
- [29] S. D. Gardner, C. S. K. Singamsetty, G. L. Booth, G. R. He, *Carbon*, 1995, **33**, 587.
- [30] S. Duquesne, M. Le Bras, C. Jama, E. D. Weil, L. Gengembre, *Polym. Degrad. Stabil.*, 2002, **77**, 203.
- [31] S. Bourbigot, M. Le Bras, R. Delobel, L. Gengembre, *Appl. Surf. Sci.*, 1997, **120**, 15.
- [32] F. Samyn, S. Bourbigot, *Polym. Degrad. Stabil.*, 2012, **97**, 2217.
- [33] R. D. Davis, J. W. Gilman, D. L. VanderHart, *Polym. Degrad. Stabil.*, 2003, **79**, 111.
- [34] S. Jahromi, W. Gabriëlse, A. Braam, *Polymer*, 2003, **44**, 25.

Graphical Abstract

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Wenhua Chen, Pengju Liu, Yuan Liu*, Qi Wang



The interfacial carbonation mode is introduced to solve the high flammability of GF-reinforced polymer composites through produced interfacial char.