Thermal degradation and intumescent flame retardation of cellulose whisker/epoxy resin composite

Kun Wu · Min-Min Shen · Yuan Hu · Weiyi Xing · Xin Wang

Abstract The morphology, thermal degradation, and flame retardancy of epoxy (EP) composites containing microcrystalline cellulose whisker (MCW) and microencapsulated ammonium polyphosphate (MFAPP) were investigated using optical microscopy, limiting oxygen index (LOI), UL-94, thermogravimetry (TG), microscale combustion calorimeter, and TG-FTIR. EP/MFAPP/MCW composites can pass V-0 in UL-94 test at 6 wt% loading, and its peak heat release rate decreases when compared with EP and EP/MFAPP. The reason is that the presence of MCW strengthens the charring capacity of EP composites in a fire. The results of TG and TG-FTIR show that at low temperature, MFAPP stimulates the dehydration of MCW and EP, and produces gas which is helpful for the formation of an intumescent char. Moreover, the residue at high temperature does not release any flammable gas and is a good insulation layer on the surface of the sample, which protects the underlying material in a fire.

Keywords Epoxy resin · Thermal degradation · Flame retardancy · Ammonium polyphosphate · Microcrystalline cellulose whisker

K. Wu (✉) · M.-M. Shen
Key Laboratory of Cellulose and Lignocellulosics Chemistry,
Guangzhou Institute of Chemistry, Chinese Academy of
Sciences, Guangzhou 510650, Guangdong, China
e-mail: wukun@gic.ac.cn

Y. Hu · W. Xing · X. Wang
State Key Laboratory of Fire Science, University of Science and
Technology of China, Hefei 230026, Anhui, China

Introduction

Modifying epoxy resins (EP) to improve their thermal properties and reduce their brittleness and cost has been of considerable interest for the last 20 years. [1] Due to a variety of specific properties of natural cellulose fibers, such as low cost, lightweight nature, renewable character, high specific strength, and modulus, etc., the natural cellulose fiber is considered as an excellent replacement of conventional glass fibers [2]. It is reported that reinforcement of the epoxy by cellulose fiber resulted in a increase in its physical mechanical properties, such as strain at failure, fracture toughness, impact toughness, flexural strength, and flexural modulus, etc. [3–6]. Because of the high flammability of EP, the fiber reinforced epoxy composite is easily flammable and its development and application in many fields is limited. Some literature focus on the flame retardancy of glass or carbon fiber reinforced epoxy composites using non-halogen flame-retardant additives [7–10]. However, very few studies are found on the thermal degradation and flame-retardant properties of EP/cellulose fiber composites.

In our previous work, to utilize the charring capacity of epoxy resin, APP is added in EP and shows good flame-retardant properties. The LOI value of the composite containing 20 wt% APP is as high as 38.0% and its UL-94 rating is raised to V-0 [11]. In this study, to expand our previous study, microencapsulated ammonium polyphosphate (MFAPP) with melamine–formaldehyde (MF) shell was selected to replace APP to prepare flame-retarded EP/cellulose composite. It is well known that intumescent flame retardant (IFR) is a promising halogen-free flame-retardant method and are usually composed of an acid agent, a carbon agent, and a blowing agent. MFAPP may show better flame-retardant properties when compared with APP in EP, due to the flame-retardant synergism of acid agent (APP) and

blowing agent (MF resin). In another aspect, from the viewpoint of intumescent flame-retardant mechanism, cellulose is a hydroxyl-containing compound with high molecular mass and can act as a carbon source. Hence, cellulose can be used to improve the charring capacity of the modified resin system.

The aim of this study is to investigate the effect of MFAPP on the thermal degradation and flame-retardant properties of EP composites containing microcrystalline cellulose whisker (MCW). Optical microscopy was used to investigate the morphology of EP/MFAPP/MCW composites. The flame retardancy and thermal properties of intumescent flame-retarded EP/MCW is evaluated by limiting oxygen index (LOI), UL-94, thermogravimetry (TG), and microscale combustion calorimeter (MCC). Moreover, to study the flame-retardant mechanism of EP composites, thermal degradation behaviors of EP and EP/MFAPP/MCW composite are evaluated by TG-Fourier transform infrared spectra (FTIR).

Experimental

Materials

The epoxy resin system used in this study was diglycidyl ether of biphenol A (DGEBA, E-44, Jiangsu Wuxi Resin Plant, China) and a hardener based on modified aliphatic amines (WK-6683, Guangzhou Wells Sheng Chemical Products Co., Ltd., China). The mass ratio of hardener and resin was 0.38:1. MFAPP, microencapsulated APP (degree of polymerization > 1000) with shell of melamine–formaldehyde, was purchased from Hangzhou JLS Flame Retardants Chemical Corporation. Its mean diameter is about 20 μm and mass percentage of the shell in MFAPP is 7.9%. Commercial microcrystalline cellulose whisker (MCW) used in this study was purchased from Guangdong Gaoli Chemical Company, China. The average length of this cellulose was about 50 μm.

Preparation of EP and its composite

Required mass fraction of MFAPP and/or MCW was added to the mixture of epoxy resin (E-44) and curing agent (WK-6683), while stirring with a mechanical mixer under high shear (1000 rpm) for 15 min at room temperature. Then the mixtures were poured into preformed molds of dimensions $100 \times 100 \times 3$ mm^3 and heated at 100 °C for 4 h. The formulations of the samples are listed in Table 1.

Measurements

Optical microscopy

MFAPP and MCW was added to the mixture of epoxy resin (E-44) and curing agent (WK-6683), while stirring with a

Table 1 Formulations of EP and its composites

Sample code	EP/wt%	MFAPP/wt%	MCW/wt%
EP	100	0	0
EM	94	6.0	0
EMC1/1	94	3.0	3.0
EMC3/1	94	4.5	1.5
EMC5/1	94	5.0	1.0
EMC7/1	94	5.25	0.75
EMC9/1	94	5.4	0.6

mechanical mixer under high shear (1000 rpm) for 15 min at room temperature. The mixture was dripped onto a piece of glass and heated at 100 °C for 4 h. The optical microscopy image of the EP composite was recorded using an optical microscope (Orthoplan, Leitz, Germany) equipped with a digital camera (Nikon-4500).

Limiting oxygen index

LOI was measured on a limiting oxygen index chamber (Dynisco, Germany) according to ASTM D2863-77. The specimens used for the test were of dimensions $100 \times 6.5 \times 3.0$ mm^3.

UL-94 testing

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL-94 test standard. The specimens used were of dimensions $130 \times 13 \times 3$ mm^3.

Thermogravimetry (TG)

Each sample was examined under air flow on a TGA-6 apparatus (PerkinElmer, USA) at a heating rate of 20 °C min^{-1}. The mass of all samples was kept within 3–5 mg in an open Al pan.

Mixture of MFAPP and MCW was manually blended in 1:1 mass proportion at room temperature to avoid any degradation reaction. Concerning thermal analysis of the mixture, theoretical TG curves are computed as follows:

$$W_{th}(T) = 50\% \times W_{exp}(T)_{[MFAPP]} + 50\% \times W_{exp}(T)_{[MC]}$$

(1)

In Eq. 1, $W_{exp}(T)_{[MFAPP]}$, $W_{exp}(T)_{[MC]}$ are the TG curves of MFAPP and MCW in air.

Microscale combustion calorimeter

The heat release rate (HRR) and the total heat release (THR) were measured in a microscale combustion calorimeter

(MCC-2, GOVMARK) for studying the fire behaviors of materials. About 5 mg samples were heated at a heating rate of 1 K s^{-1} in nitrogen stream flowing at 80 cm^3 min^{-1}. The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a 20 cm^3 min^{-1} stream of pure oxygen prior to entering a 900 °C combustion furnace.

Thermogravimetry-Fourier transform infrared spectra

The TG-FTIR instrument consists of TG analyzer (TGA-Q5000, TA Company, USA) coupled with Fourier transform spectrometer (Nicolet 6700) via the transfer line. The investigations were carried out under nitrogen atmosphere at a flow rate of 35.0 mL min^{-1} for TG, with heating rate of 20 °C min^{-1}. In order to reduce the possibility of gases condensing along the transfer line, the temperature in the gas cell and transfer line were set to 230 °C.

Results and discussion

Morphology of EP/MCW/MFAPP

Optical microscopy (OM) was employed to characterize the dispersion and morphology of MFAPP and MCW in EP matrix. The OM image of EP/MCW/MFAPP is shown in Fig. 1. It is clearly observed that the appearance of MCW is fiber-like and its length/diameter ratio is above 10. However, many irregular polygonal MFAPP particles with a size distribution in the range of about 10–25 μm are dispersed around MCW in the matrix.

Flammability study of EP and its composites

The effect of MCW and MFAPP on the LOI values and UL-94 testing results of EP composites is presented in Fig. 2. Pure epoxy resin (EP) is easily flammable and its LOI value is just 21.5%. The LOI value increases when
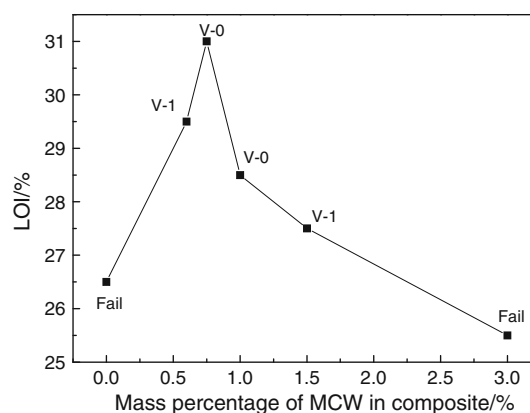
Fig. 1 Optical microscopy image of EP/MCW/MFAPP (EMC7/1)

Fig. 2 Effect of MCW and MFAPP on LOI and UL-94 results of EP composite (total additive level = 6 wt%)

MFAPP is added into EP and the LOI value of EP/MFAPP (EM in Table 1) is 26.5%. However, EM cannot pass any rating in UL-94 testing. The reason is that the weak charring capacity of the modified resin system compared with MCW.

MCW is introduced to improve the charring capacity of epoxy resin. A synergistic effect occurs when MCW and MFAPP are both present in the composites. From Fig. 2, it can be found that at the same additive level (6 wt%), the LOI values of most EP/MCW/MFAPP composite are higher than that of EP/MFAPP. For example, the values of EP/MCW/MFAPP composites (EMC5/1, EMC7/1) containing 1.0 and 0.75% MCW are 28.5 and 31.0%, respectively. Moreover, the UL-94 ratings for the composites (EMC5/1, EMC7/1) are raised to V-0. Here it should be noted that with increasing mass percentage of MCW, LOI value and UL-94 rating increases and then decreases. The reason can be explained that a suitable mass ratio of phosphorus, nitrogen, and carbon in flame-retardant system is very important for the flame retardancy of polymer composites. It can be concluded that the influence of MCW and MFAPP on the flame retardancy of EP composite is remarkable.

MCC study

Microscale combustion calorimeter (MCC) is an effective approach to obtain the information regarding combustibility and fire hazard of plastics, wood, textiles, and composites. It can quickly and easily measure the key fire parameters from just a few milligrams of specimen in minutes.

Heat release rate (HRR) results of EP and its composites are shown in Fig. 3. The presence of MFAPP and MCW change the combustion behaviors and reduce the peak HRR values of EP significantly. The shape of the HRR curve for neat EP is a low peak followed by a sharp peak. The first peak is caused by the degradation of main chain of EP, and the second one can be assigned to the further thermal

degradation of the residual char. Associated data for EP are: peak HRR = 171.1, 378.5 W g^{-1}, total heat release (THR) = 24.8 kJ g^{-1}.

In case of the EM composite, its HRR curve shows a sharp peak followed by a low slope. Associated data for the EM are: peak HRR = 316.8 W g^{-1}, THR = 21.9 kJ g^{-1}. However, the ignition temperature (IT) of EM composite (285 °C) is less than that of EP (301 °C). This is because beyond 285 °C, MFAPP begins to degrade and stimulates the decomposition of EP. As a result, EM shows higher HRR value compared with EP at the earlier stage. However, a char residue is formed due to the reaction between MFAPP and EP. With the increase of the temperature, HRR value of EM is decreased and lower than that of EP.

For EMC7/1 composite, its curve shows the similar shape with that of EM. However, the presence of MCW decreases the peak HRR value slightly when compared with EM at lower and higher temperature. The first peak is assigned to the reaction between MFAPP, MCW, and EP and the slope is explained by the destruction of the precursor char and the formation of a carbonaceous residue. Associated data for EMC7/1 are: peak HRR = 309.0 W g^{-1}, THR = 21.8 kJ g^{-1}. The combination of MFAPP and MCW can further stimulate the formation of a char with better thermal resistance and insulation compared with EM, and the char may prevent underlying materials from further degradation and leads to a decrease in the HRR value at high temperature.

Thermal analysis of MFAPP, MCW, and MFAPP/MCW

The experimental and calculated TG curves of MFAPP, MCW, and MFAPP/MCW (1:1 by mass) are shown in Fig. 4. MFAPP starts decomposing at about 295 °C. At the beginning, the mass loss of MFAPP is initiated by the thermal oxidative degradation of APP (core) and MF resin (shell). The MF resin on heating produces gases, such as NH$_3$ and CO$_2$, which are helpful in forming an expanded char. For APP, its evolution products at this step are mainly ammonia and water, and crosslinked polyphosphoric acids (PPA) are formed simultaneously [12]. From the DTG curves of MFAPP shown in Fig. 5, the T_{max} value of MFAPP at this stage is 359 and 413 °C, respectively. Beyond the temperature of 500 °C, the char decomposes further to a complex structure containing P=O and P–O [12].

In the case of MCW, only one pyrolysis process was observed in the DTG curve above 293 °C. Below the temperature of 100 °C, MCW loses about 2.5 wt% mass which is caused by the release of free water. At high temperature, the thermal degradation of MCW is brought about by the decrease in polymerization degree and the development of new saturated and unsaturated structures (aromatic C=C, aromatic C–H, carbonyl, etc.). [13] The corresponding T_{max} of MCW at this stage is 365 °C.

In order to investigate the occurrence of reaction between MFAPP and MCW under heating, MFAPP and MCW were blended at room temperature with a mass ratio 1:1, and the mixture was characterized by TG under experimental and calculated conditions. For experimental TG curve of MFAPP/MCW, it is clear that the mixture begins to decompose at about 260 °C which is lower than that of MFAPP and MCW. However, beyond the temperature of 354 °C, MFAPP/MCW is more thermally stable than MCW. According to the literature, it is representative of a non-interacting behavior among the components if the calculated curve is a linear combination of the TG curves of the individual components of the system [14]. In Fig. 4, it can be found that the experimental curve is different from the calculated one, which indicates the occurrence of an interaction between MFAPP and MCW during the thermal degradation. Moreover, the residual char mass of the mixture in experimental curves is 36.3%, which is higher than that of calculated curve (31.1%). Conclusion can be drawn that the reaction between MFAPP and MCW may lead the formation of a char with a better thermal
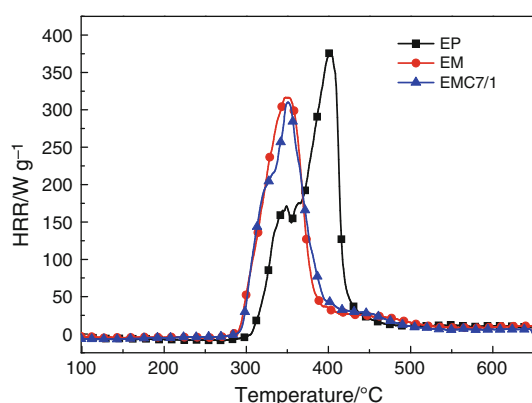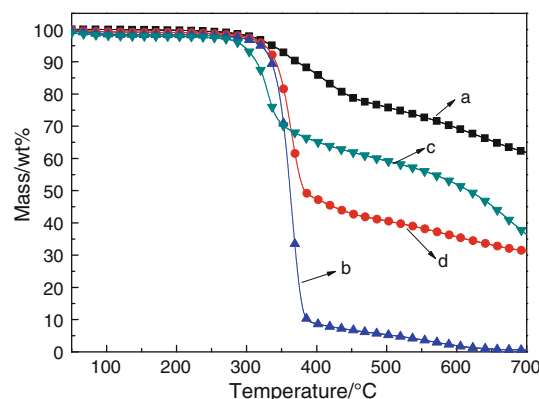

Fig. 3 HRR curves of EP, EM and EMC7/1

Fig. 4 TG curves of MFAPP (*a*), MCW (*b*) and mixture (experimental *c*; calculated *d*) of MFAPP/MCW (1:1 by mass)
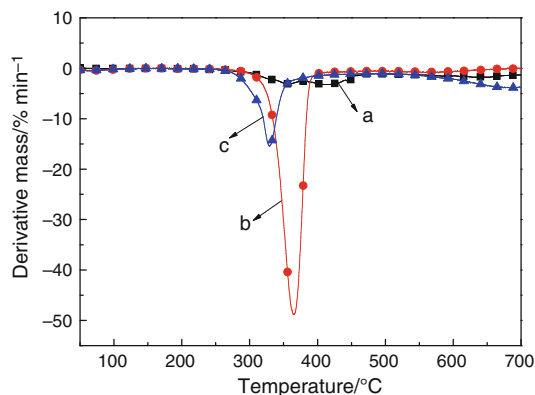
Fig. 5 DTG curves of MFAPP (*a*), MCW (*b*) and MFAPP/MCW (*c*, 1:1 by mass)

stability which has positive effect on the flame-retardant properties of EP composites during the combustion. The results of samples containing optimum ratios of MFAPP and MCW are according with the data in LOI, UL-94, and MCC testing.

Thermal oxidative degradation of EP and its composites

The thermal oxidative behaviors of EP and its composites were studied. TG and DTG curves of EP, EM, and EMC7/1 under air atmosphere are reported in Fig. 6. The temperature of 5 wt% mass loss ($T_{-5\%}$), the mid-point temperature of the degradation ($T_{-50\%}$) and the solid residue left at 700 °C were obtained from the TG curve; the temperature of the maximum mass loss rate (T_{max}) of samples was obtained from the DTG curve. These data are shown in Table 2.

EP degrades in a two-step process, with maximum degradation rate temperatures centered at 407 and 607 °C, respectively.

The decomposition behavior changes significantly for the composite containing MFAPP. EM decomposes earlier with T_{max} of 377 °C which shifts to a lower temperature when compared with EP. The decrease in initial decomposition temperature and increase in mass loss rate is due to the reaction between EP and polyphosphoric acid which is released by MFAPP. As a result, a precursor char is formed. Meanwhile, MF shell outside MFAPP can produce gases, such as CO_2 and NH_3, which can swell the formed char. The swollen char may retard the transfer of mass and heat between the materials and the flame in a fire. The char plays a very important role in flame-retarded polymeric materials through condensed-phase mechanisms. Above 414 °C, EM shows better thermal stability when compared with EP, as shown in Fig. 6. Moreover, char residue of EM at 700 °C is 19.5% which is much higher than that of EP.

In Fig. 7, the mass difference curve of EMC7/1 (difference = Mass$_{EMC7/1}$ − Mass$_{EP}$) shows an important

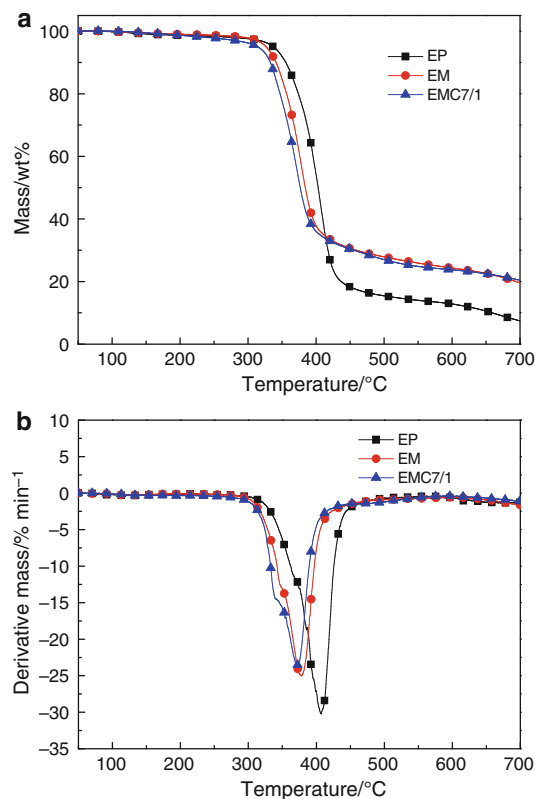**Fig. 6** TG (**a**) and DTG (**b**) curves of EP, EM, and EMC7/1

Table 2 TG and DTG data under air atmosphere

Sample	$T_{-5\%}$/°C	$T_{-50\%}$/°C	T_{max}/°C	Solid residue, %, at 700 °C
EP	337	403	407, 670	7.4
EM	326	384	377, –	19.5
EMC7/1	314	376	372, –	20.4

zone of destabilization in the temperature range of 250–413 and 250–640 °C when compared with EP and EM. The presence of MCW in EMC7/1 leads to a lower initial decomposition temperature and higher mass loss rate when compared with EP and EM at earlier stage. It is because that MFAPP may react with MCW and EP to form a char with better thermal stability above the temperature of 314 °C. In Fig. 7, beyond the temperature of 413 and 640 °C, EMC7/1 is more thermally stable than EP and EM. The residual mass of EMC7/1 at 700 °C is the highest (20.4%) among the samples. The results reveal that the introduction of MCW can further improve the charring capacity of EP in its intumescent flame-retarded composite. This is the reason that EMC7/1 shows higher LOI value, UL-94 rating and lower peak HRR when compared with EP and EM.
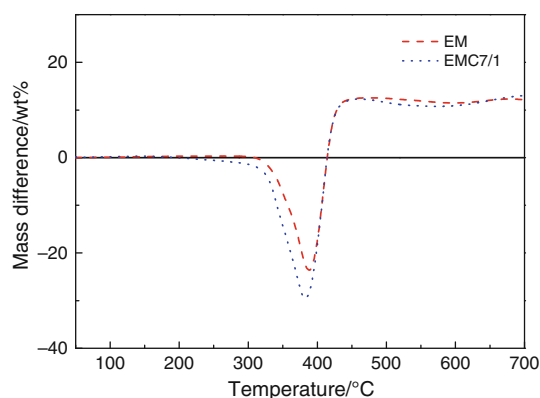
Fig. 7 Difference in mass loss between EM, EMC7/1, and EP

TG-FTIR analysis of EP and EP/MFAPP/MCW

From the above results, it can be found that the combination of MFAPP and MCW shows excellent flame-retardant properties in EP composites. TG-FTIR is an effective method for analysis of the gaseous products during thermal decomposition, used here to study EP and EMC7/1.

Figure 8 shows the 3D TG-FTIR spectrum of gas products in the thermal degradation of EP. As shown in Fig. 9, the main gas products of the thermal decomposition of EP are compounds containing –OH (such as H_2O, phenol; 3500–4000 cm^{-1}), CO_2 (2360 cm^{-1}), CO (2180, 2117 cm^{-1}), compounds containing $CH/CH_2/CH_3$ group (2800–3100 cm^{-1}), compounds containing carbonyl (1680–1800 cm^{-1}), compounds containing aromatic ring (1300–1600 cm^{-1}), aromatic ethers (asymmetric stretching of the C–O–C bands; 1042 cm^{-1}) and CH_3OH (671 cm^{-1}), etc. [15–17]. Moreover, the intensity curve of gas products for EP in Fig. 10 presents two peaks. Associated with the analysis of Figs. 9 and 10, it can be found that at earlier stage, it is the thermal degradation process of EP main chains and the gas products composed of H_2O, compounds containing $CH/CH_2/CH_3$ group, carbonyl and aromatic
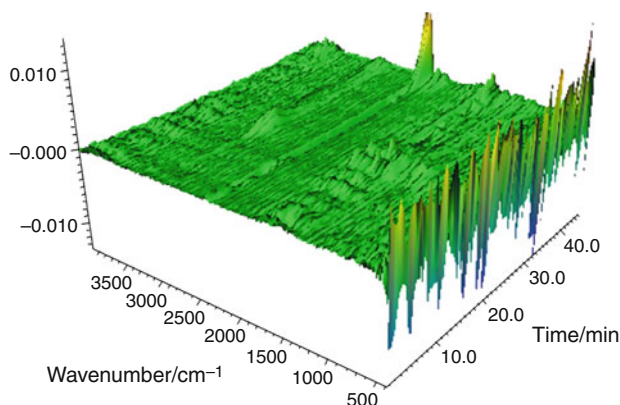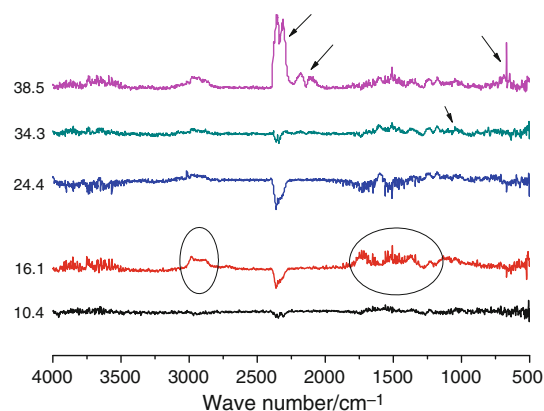

Fig. 9 FTIR spectra of gas products for EP at different times
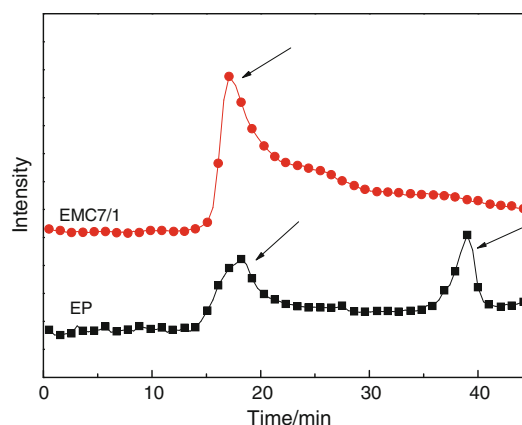

Fig. 10 The intensity of gas products for EP and EMC7/1 versus time

ring, etc., are released. At higher temperature, the second peak of EP curve in Fig. 10 can be ascribed to the further degradation of precursor char and small molecular gaseous species, CO_2, CO, and CH_3OH are released. Among the pyrolysis products at high temperature, CO and CH_3OH are flammable gas which is responsible for the second sharp peak in the HRR curves of EP in MCC testing.

The 3D FTIR spectrum of the evolved gases of EMC7/1 is shown in Fig. 11. The characteristic FTIR spectra of the volatile pyrolysis products evolved at different times are shown in details in Fig. 12. Compared with the data of EP, it is clear that EMC7/1 decomposes entirely in a different way. As shown in Figs. 11 and 12, the main evolved gas products containing –OH group (e.g., H_2O, phenol; 3500–4000 cm^{-1}), CH/CH_2 group (3000–3150 cm^{-1}), –CH_3 group (2800–3000 cm^{-1}), CO_2 (2360 cm^{-1}), carbonyl (1620–1820 cm^{-1}), aromatic ring (1250–1610, 1509 cm^{-1}), and aromatic ether (1050–1220 cm^{-1}) were easily identified by their characteristic absorbance [15–17]. It should be noted that, at the beginning, the release of NH_3 (968, 928 cm^{-1}) was detected. It is aroused by the

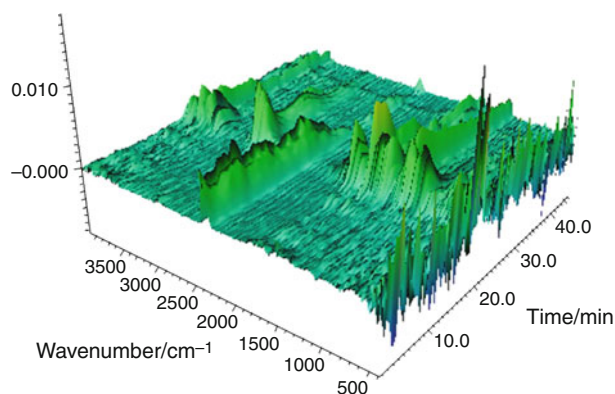**Fig. 8** 3D TG-FTIR spectrum of gas products of EP
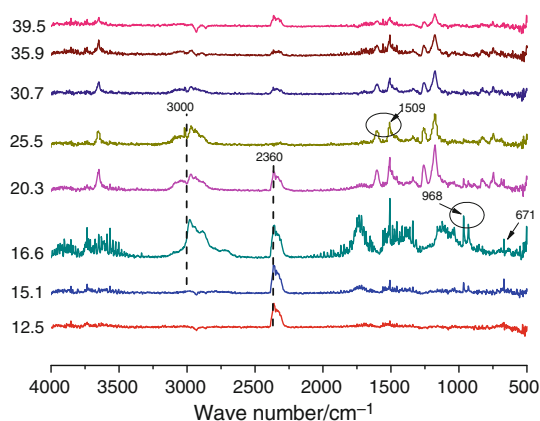
Fig. 11 3D TG-FTIR spectrum of gas products of EMC7/1

Fig. 12 FTIR spectra of gas products for EMC7/1 at different times

decomposition of MFAPP. Moreover, EMC7/1 releases H_2O (3200–3500 cm^{-1}), compounds containing $CH/CH_2/CH_3$ group, carbonyl, aromatic ring, aromatic ethers, and CH_3OH (671 cm^{-1}) at this stage. The reason is that the MFAPP degrades and releases polyphosphoric acid which stimulates the degradation of MCW and EP main chain. As a result, a precursor char is formed. Later, it is the further degradation of the precursor char. In Fig. 12, it is interesting that, after 16.6 min, the evolved gases show the characterized absorption peak of $CH/CH_2/CH_3$ group, and $–CH_3$ (2800–3000 cm^{-1}) is the main component. However, with the increase of temperature, the content of CH/CH_2 (3000–3150 cm^{-1}) containing compound increases. The pyrolysis products at higher temperature are mainly composed of phenol, aromatic ether, and compounds containing carbonyl and aromatic ring. This is the reason that the intensity curve of gas products for EMC7/1 shows a peak following by a long slope in Fig. 10.

The presence of MFAPP and MCW change the thermal degradation behavior of EP remarkably. The main pyrolysis products of EP at high temperature are composed of flammable gas, CO, and CH_3OH, etc., which are responsible for the high HRR value in MCC test. However, for

EMC7/1, MFAPP release PPA which stimulate the degradation of MCW and EP, and produces gases (NH_3 and CO_2) which is helpful for the formation of an intumescent char. Moreover, the gas products of EMC7/1 at higher temperature are composed of phenol, aromatic ethers, and compounds containing carbonyl and aromatic ring which shows low flammability when compared with that of EP.

From above results, the fire-retardant mechanism of MFAPP in EP/MCW composites can be described as follow: MFAPP can release polyphosphoric acid and stimulate the formation of a char at low temperature. Meanwhile, a lot of gas (NH_3 and CO_2) are released. As a result, an intumescent char is formed. On one hand, the char at high temperature does not release high flammable gas. On the other hand, due to the excellent thermal stability of the char, it can be used as a good insulation layer of heat and substance to suppress the further combustion of underlying materials in a fire.

Conclusions

In this study, epoxy composites containing microcrystalline cellulose whisker (MCW) and microencapsulated ammonium polyphosphate (MFAPP) were prepared. From the optical microscopy image of EP/MCW/MFAPP, it can be seen that the appearance of MCW is fiber-like and MFAPP shows irregular polygonal shape in EP. In LOI and UL-94 test, it can be found that combination of MFAPP and MCW (MCW7/1) in EP can improve its LOI value (31.0%) and UL-94 rating (V-0) sharply at low additive levels (6 wt%). The presence of MFAPP and MCW decreases the peak heat release rate and total heat release of EP in MCC testing.

In TG and TG-FTIR study, the main pyrolysis products of EP at high temperature are composed of flammable gas, CO, and CH_3OH, which are responsible for the high HRR value in MCC test. However, for EP/MCW/MFAPP, MFAPP release polyphosphoric acid which stimulate the dehydration of MCW and EP, and releases gases (NH_3 and CO_2) which is helpful for the formation of an intumescent char with excellent thermal stability. Moreover, the vapor products of EP/MCW/MFAPP at higher temperature are composed of phenol, aromatic ethers, and compounds containing carbonyl and aromatic ring which shows low flammability when compared with that of EP. The intumescent char is a good insulation layer of heat and substance which can prevent underlying materials from further destruction during combustion.

References

1. Raj MM, Raj LM, Shah TB, Patel PM. Synthesis, characterization of Mannich base oligomers used with epoxy resin for glass fibre-reinforced laminates. J Therm Anal Calorim. 2010;101:1003–9.

2. Sbiai A, Kaddami H, Fleury E, Maazouz A, Erchiqui F, Koubaa A, Soucy J, Dufresne A. Effect of the fiber size on the physico-chemical and mechanical properties of composites of epoxy and date palm tree fibers. Macromol Mater Eng. 2008;293:684–91.

3. Satyanarayana KG, Arizaga GGC, Wypych F. Biodegradable composites based on lignocellulosic fibers—an overview. Prog Polym Sci. 2009;34:982–1021.

4. Kong K, Hejda M, Young RJ, Eichhorn SJ. Deformation micromechanics of a model cellulose/glass fibre hybrid composite. Compos Sci Technol. 2009;69:2218–24.

5. Eichhorn SJ, Baillie CA, Zafeiropoulos N, et al. Review: current international research into cellulosic fibres and composites. J Mater Sci. 2001;36:2107–31.

6. Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. Prog Polym Sci. 1999;24:221–74.

7. Kandola BK, Horrocks AR, Myler P, Blair D. Mechanical performance of heat/fire damaged novel flame retardant glass-reinforced epoxy composites. Composites A. 2003;34:863–73.

8. Schartel B, Braun U, Balabanovich AI, Artner J, Ciesielski M, Doring M, Perez RM, et al. Pyrolysis and fire behaviour of epoxy systems containing a novel 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-(DOPO)-based diamino hardener. Eur Polym J. 2008;44:704–15.

9. Braun U, Balabanovich AI, Schartel B, et al. Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites. Polymer. 2006;47:8495–508.

10. Perez RM, Sandler JKW, Altstadt V, et al. Effective halogen-free flame retardants for carbon fibre-reinforced epoxy composites. J Mater Sci. 2006;41:4981–4.

11. Song L, Wu K, Wang Y, Wang ZZ, Hu Y. Flammability and thermo-oxidative decomposition of epoxy resin containing ammonium polyphosphate and metallic oxide. J Macromol Sci A. 2009;46:290–5.

12. Wu K, Wang ZZ, Liang HJ. Microencapsulation of ammonium polyphosphate: preparation, characterization, and its flame retardance in polypropylene. Polym Compos. 2008;29:854–60.

13. Soares S, Ricardo NMPS, Jones S, Heatley F. High temperature thermal degradation of cellulose in air studied using FTIR and ^{1}H and ^{13}C solid-state NMR. Eur Polym J. 2001;37:737–45.

14. Michel LB, Bourbigot S. New intumescent formulations of fire-retardant polypropylene: discussion of the free radical mechanism of the formation of carbonaceous protective material during the thermo-oxidative treatment of the additives. Fire Mater. 1996;20:191–203.

15. Braun U, Schartel B, Fichera MA, Jager C. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6, 6. Polym Degrad Stab. 2007;92:1528–45.

16. Baker RR, Coburn S, Liu C, Tetteh J. Pyrolysis of saccharide tobacco ingredients: a TGA–FTIR investigation. J Anal Appl Pyrol. 2005;74:171–80.

17. Colthup NB, Daly LH, Wiberley SE. Introduction to Infrared and Raman Spectroscopy. Boston: Academic Press; 1990.