Thermal properties and combustion behaviors of flame retarded epoxy acrylate with a chitosan based flame retardant containing phosphorus and acrylate structure

Shuang Hu a, Lei Song a, Haifeng Pan a, Yuan Hu a,*, Xinglong Gong a, b, **

a State Key Lab of Fire Science, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui, PR China
b CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui, PR China

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Functional materials prepared from natural resources arouse a great interest recently. Herein, a novel natural material based flame retardant chitosan phosphate acrylate (GPCS) containing phosphorus and acrylate structure has been prepared. Its effect on thermal properties and combustion behaviors of epoxy acrylate (EA) has been investigated. Microscale combustion calorimeter (MCC) data showed that GPCS reduced the peak heat release (PHRR) and total heat release (THR) of samples greatly, which meant that GPCS was efficient in reducing the flammability of EA. The results of thermogravimetric analysis (TGA) exhibited that GPCS improved the thermal stability of materials at high temperature. Investigation of real time Fourier transform infrared (RT-IR) and thermogravimetric analysis/infrared spectrometry (TGA-IR) revealed that GPCS promoted the formation of char and reduced the release of combustible gas. Thermomechanical properties data showed that the storage modulus of samples increased then decreased with increasing GPCS content while the glass transition temperature continued reduced.

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1. Introduction

Functional material prepared from natural resources is an effective way to circumvent the confrontations of pollution, waste disposal and depletion of conventional petroleum-based resources [1–5]. Much attention has been paid to prepare such materials today [6].

Chitosan, the fully or partially deacetylated form of chitin, the principal component of living organisms such as fungi and crustaceans, one of the most abundant biomaterials in the world, is considered as one of the most studied materials in recent years due to the renewable property, non-toxicity, high biocompatibility and so on. A number of researches focus on its application in clinics, drug delivery systems and surfactants [7–9]. It should be noticed that chitosan possesses the structure of multi-hydroxyl groups just like pentaerythritol and cyclodextrins, which promote the formation of char during burning [10–13]. It is well known that the char forming on the surface of the burning materials acts as a heat insulator, limiting the heat transfer from the heat source to the polymer and the mass transfer from the polymer to the flame.

Flame retardant technology develops quickly in decades. The intumescent flame retardant system, composed of acid agent, char forming agent and blowing agent is a focus in recent years owing to its efficiency and environment friendly characteristic. A number of flame retardants have been prepared. However, in these materials, the segment used as char forming source root in petroleum based materials, such as pentaerythritol [14–19]. Because of the petroleum crisis and the deterioration of ecological environment, it is necessary to search for the replacement of petroleum based materials. Some work has been done on investigating environmental-friendly and sustainable char forming agent, such as starch, lignin and cyclodextrins [20–26]. But in these researches, the materials were just applied as char forming additives alone. It is well known that flame retardant combining with char former and acid agent in one molecular structure shows higher efficiency on fire resistance [27,28]. Hence, it is useful to prepare the flame retardant that contain more than one component.

Epoxy acrylate (EA), as a UV curing resin is popular due to its rapid cure, solvent-free characteristics, application versatility, low energy requirements, and low temperature operation [29–31]. However, it is so combustible that its application is narrowed. A number of methods have been used to improve the fire retardancy of epoxy acrylate and reactive type flame retardant has been proved to be an efficient way because that the flame retardant segments are bonded to the polymer backbone [32–35].
In this paper, we have prepared a novel chitosan based flame retardant material (GPCS) containing phosphorus and acrylate structure. Herein, phosphorus knowing as one of the most effective flame retardant element was used as acid agent. Acrylate structure was introduced to graft on the backbone of polymer matrix to enhance its compatibility. SEM was applied to reveal the dispersion performance of GPCS in matrix. The characteristic of flammability was presented by MCC. Thermal and mechanical properties were showed by TGA, RT-IR, TGA-IR and DMA.

2. Experiment

2.1. Materials

Chitosan (viscosity 50–800 mPa·s, degree of deacetylation 80–95%), phosphorus pentoxide (AR), methanesulfonic acid (99%) were provided by Sinopharm Chemical Reagent Co., Ltd. Glycidyl methacrylate (GMA), supplied from Dong-fang Chemical Co., Beijing, China, was distilled before used.

2.2. Synthesis of GPCS

GPCS can be prepared as the following process. Firstly, phosphorylated chitosan (PCS) can be synthesized by the reaction of chitosan (CS, 2 g) with phosphorous pentoxide (10 g) in methanesulfonic acid in ice water bath under nitrogen for 3 h. The residue was washed with ether, acetone, methanol and ether, and then dried to obtain PCS [36–38]. Then, PCS (2 g) was dispersed in 1,4-Dioxane for 15 min before glycidyl methacrylate (20 g) was added. The reaction occurred at 60 °C for 12 h and 100 °C for 3 h. After filtration, the product was washed by 1,4-Dioxane several times to remove the extra GMA. Finally, the white powder can be obtained, after it was dried. Scheme 1 exhibited the reaction scheme.

2.3. Preparation of samples

The ultraviolet light source used for irradiation is a lamp (80 W/cm; Lantian Co., Beijing, China) that emits light in the near UV (characterized wavelength, 340–360 nm). The UV irradiation was carried out in air atmosphere. The polymerization mixture was prepared by adding 3 wt% photoinitiator (Darocur 1173, Ciba-Geigy, Switzerland) into the GPCS/EA system.

2.4. Characterization

FTIR spectroscopy (Nicolet 6700, Nicolet Instrument Company, USA) was employed to characterize samples using thin KBr as the sample holder. Solid-state 31P NMR was performed with Bruker AVANCE 400 WB spectrometer. Atomic absorption spectrometry (AAAnalyst 800, Perkin Elmer) was used to test the content of phosphorus.

Scanning electron microscopy (SEM) (JSM–6700F, JEOL, Japan) was used to study morphological features of the fracture face (treated in liquid nitrogen) of GPCS/EA system, which was used to evaluate the compatibility.

MCC test was carried out using a Govmak MCC-2 microscale combustion calorimeter; samples were heated to 650 °C at a heating rate of 1 °C/s in a stream of nitrogen flowing at 80 cm³/min. The volatile anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³/min stream of pure oxygen prior to entering a 900 °C combustion furnace.

Thermogravimetric analysis (TGA) was carried out using a Q5000IR thermoanalyzer instrument from 50 to 700 °C at a linear heating rate of 20 °C/min under an air flow of 60 cm³/min. Real time Fourier transform infrared (RT-IR) method was used to study the thermo-oxidative degradation of the samples. Powders of the cured sample were mixed with KBr powders, and the mixture was pressed into a tablet, which was then placed into the oven. The temperature of the oven was raised at a heating rate of about 10 °C/min. Thermogravimetric analysis/infrared spectrometry (TGA-IR) was performed to analyze the volatilized products after the pyrolysis of samples under a nitrogen flow of 35.0 cm³/min. Thermomechanical properties of the sheets were tested with a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA) using a double cantilever measuring mode. The sample size was 50mm × 8mm × 3 mm. Tests were performed from room temperature to 160 °C at a heating rate of 5 °C/min and an oscillation frequency of 10 Hz.

3. Results and discussion

3.1. Characterizations of GPCS

FTIR spectra of CS, PCS and GPCS were showed in Fig. 1. For CS, characteristic peak at 1600 cm⁻¹ was ascribed to N-H group. The broad peak observed at 3500 cm⁻¹ has the contribution of the OH group. The other peaks at 2890 and 1380 cm⁻¹ were assigned to CH stretching and CH₃ symmetric deformation, respectively. Phosphorylation led to an emerging shoulder at 1200 cm⁻¹, which can be attributed to the P=O asymmetric stretching. New peaks at 1050 and 484 cm⁻¹ can be attributed to the P–O structure, such as P–O–C and P–OH. The above phenomenon suggested phosphorylation of hydroxyl groups on CS. The absorption at 1600 cm⁻¹ was replaced by a new absorption at 1634 cm⁻¹. Wang reported that lots of amino groups in chitosan could change into ammonium groups in methanesulfonic acid medium while some amino groups underwent the reaction to form phosphorylamine groups [39]. Then, the reaction happened with the addition of glycidyl methacrylate. It can be observed from the FTIR curve of GPCS that a new peak at 1720 cm⁻¹ was found, which was attributed to C=O group of glycidyl methacrylate. Moreover, the peak assigning to P–O structure shifted to higher wavenumber, increasing from 1050 and 484 cm⁻¹ to 1070 and 513 cm⁻¹, respectively. Meanwhile, P=O band moved from 1200 to 1250 cm⁻¹. The above results indicated that glycidyl methacrylate group has been grafted on the PCS.

Fig. 2(a) showed the solid state 31P NMR spectrum of GPCS. According to the space hindrance and migration situations [40], a strong peak around –1 ppm meant that phosphorylation occurred on C-6 hydroxyl groups of chitosan mainly. Besides, another small peak appeared around –11 ppm implied that part hydroxyl groups
on C-3 of chitosan took part in the reaction to yield P-chitosan [39]. Fig. 2(b) exhibited the solid state $^{13}$C NMR spectrum of GPCS. C1–C6 belonged to different carbon chemical shifts on the chitosan structure of GPCS. Besides, the shifts at 168 ppm (C=O), 136 ppm (C=C=O), 126 ppm (C=O), 57 ppm (C–O–C=O), 37–40 ppm (C=O, C=OH) and 18 ppm (C=C=C) were attributed to different carbon chemical shifts on the acrylate structure of GPCS. Furthermore, atomic absorption analysis revealed that the content of phosphorus for GPCS was 6.6 wt%.

In conclusion, the above information indicated that it was successful to synthesize GPCS.

3.2. Morphological analysis of GPCS/EA system

Since the various properties of samples are remarkably dependent on the compatibility between the matrix and fillers, it is necessary to determine the compatibility between EA matrix and GPCS. The fracture morphology of 20 wt% GPCS/EA was investigated by SEM analysis. Fig. 3 showed a homogeneous morphology to the fracture face of the sample and no agglomeration of particles can be observed. It revealed that the compatibility between EA matrix and GPCS was good, which can be explained that GPCS has been grafted on the backbone of EA through the acrylate structure.
3.3. Flammability properties

The limiting oxygen index (LOI) data of EA and GPCS/EA were given in Table 1. The LOI value increased gradually with the increasing of GPCS loading, which ascended from 21 to 26. The results indicated that GPCS exhibited good flame retardancy. Microscale combustion calorimeter (MCC) was an effective bench scale method for investigating the combustion properties of polymer materials. The flame retardancy of GPCS/EA system was interpreted in terms of its heat release properties.

Fig. 4 described the heat release rate (HRR) curves of GPCS/EA samples and the corresponding combustion data were presented in Table 1. It can be observed that the GPCS led to the PHRR value descend significantly compared to the pure EA. With the increase of GPCS, PHRR decreased from 332 to 145 W/g. The 56% reduction in PHRR can be considered as a significant improvement in flame retardancy.

Total heat release (THR) calculated from the area under the HRR curve was another important parameter for fire hazard evaluation. Compared to the THR value of 21.2 kJ/g in neat EA, increasing content of GPCS caused the THR value decreased to 10.7 kJ/g. It implied that GPCS as flame retardant for EA can effectively reduce the THR value of the samples. Otherwise, Table 1 noted that the $T_{\text{max}}$ (temperature at peak heat release rate) shifted to lower temperature with the increasing content of GPCS decreasing from 441°C to 363°C. This phenomenon was because of the low initial thermal stability of GPCS.

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of GPCS and GPCS/EA blended samples was investigated. Fig. 5 showed two stages possessed in the thermal decomposition of GPCS. The first section occurred around 200°C with the onset temperature ($T_{10\%}$, temperature of 10% weight loss) at 221°C corresponding to the loss of absorbed water and the broken of the organic phosphonate group of GPCS [41]. Then, further thermal degradation happened with the increase of temperature, containing pyrolysis of polysaccharides, which started by a random split of the glycosidic bonds, followed by a further decomposition forming acetic and butyric acids and a series of lower fatty acids [42].

Fig. 5 also showed TGA curves of GPCS/EA system and Table 2 listed data related to the results. GPCS changed the thermal degradation process of EA. It was observed that the flame retardant reduced the onset temperature of samples, decreasing from 373°C to 324°C, which was owing to the degradation of GPCS. However, when the temperature increased to 450°C, all GPCS/EA samples exhibited better thermal stability than that of pure EA. With more addition of GPCS, samples showed better thermal stability. The value of residual char at 700°C can exhibit the above results directly, increasing from 4.1 wt% to 8.2 wt%, while that of pure EA was 1.8 wt%. GPCS accelerated the formation of char during thermal degradation process. As a result, the resin with higher flame retardant content yielded more char and was more stable at high temperature. It is well known that char layer can block the transfer of oxygen and heat, which retarded thermal decomposition of underlying materials. Therefore, GPCS improved thermal stability of materials.

3.5. Real time FTIR analysis

Real time Fourier transform infrared spectra (RT-IR) was employed to give some details in the thermo oxidative degradation process of 20 wt% GPCS/EA showing in Fig. 6.

As the pyrolysis temperature increased, the peak at 1250 cm$^{-1}$ assigning to the stretching vibration of $\text{P=O}$ bond, shifted to 1300 cm$^{-1}$. The peak at 1300 cm$^{-1}$ was ascribed to the stretching

### Table 1
Flammability properties.

<table>
<thead>
<tr>
<th>Samples</th>
<th>LOI</th>
<th>PHRR (W/g)</th>
<th>THR (kJ/g)</th>
<th>Reduct-MCC (%)</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>21</td>
<td>332</td>
<td>21.2</td>
<td>NA</td>
<td>441</td>
</tr>
<tr>
<td>5 wt% GPCS/EA</td>
<td>22.5</td>
<td>204</td>
<td>14.3</td>
<td>39</td>
<td>406</td>
</tr>
<tr>
<td>10 wt% GPCS/EA</td>
<td>24</td>
<td>186</td>
<td>11.2</td>
<td>44</td>
<td>378</td>
</tr>
<tr>
<td>20 wt% GPCS/EA</td>
<td>26</td>
<td>145</td>
<td>10.7</td>
<td>56</td>
<td>363</td>
</tr>
</tbody>
</table>

PHRR, peak heat release rate; THR, total heat release; Reduct-MCC = (PHRR$_{\text{EA}}$ − PHRR$_{\text{GPCS/EA}}$)/PHRR$_{\text{EA}}$; $T_{\text{max}}$, temperature at peak heat release rate.

- Table 2
TGA curves of GPCS/EA samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{10%}$ (°C)</th>
<th>Residual char at 700°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>373</td>
<td>1.8</td>
</tr>
<tr>
<td>GPCS</td>
<td>221</td>
<td>17.2</td>
</tr>
<tr>
<td>5 wt% GPCS/EA</td>
<td>359</td>
<td>4.1</td>
</tr>
<tr>
<td>10 wt% GPCS/EA</td>
<td>341</td>
<td>5.5</td>
</tr>
<tr>
<td>20 wt% GPCS/EA</td>
<td>324</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Fig. 4. HRR curves of GPCS/EA.

Fig. 5. TGA analysis.
vibration for P—O—Φ structure, where Φ represented the graphite-like polynuclear aromatic structure [43,44]. This change indicated that the phosphate group deviated from the aliphatic structure and formed the P—O—Φ structure around 400 °C. The peak at 1100 cm⁻¹ assigning to the stretching vibration of P—O bond moved to lower wavenumber. It can be observed that P—O bond shifted to 1080 cm⁻¹ around 400 °C and a new peak appeared at 880 cm⁻¹ at the same temperature. These absorption peaks used to be assigned to the symmetric and asymmetric stretching vibration of the P—O—P band [44]. These phenomenon implied that phosphate group in the samples can degrade at lower temperature to form poly(phosphoric acid) structure that can promote the formation of char at higher temperature. Therefore, GPCS/EA system exhibited better thermal stability than that of pure EA at high temperature, just as the TGA data showed to us.

3.6. Volatilized products analysis

Thermogravimetric analysis/infrared spectrometry (TGA-IR) was performed to analyze the volatilized products after thermal decomposition of samples, which contributed to understand the thermal degradation process. Fig. 7 exhibited the TGA-IR curves of 20wt% GPCS/EA in different time.

Some small molecular gaseous species can be observed at the early stage of thermal degradation. The first volatilized product can be identified as CO₂ (characteristic peaks at 2360 cm⁻¹). Chen et al. ascribed the formation of CO₂ to the scissions of unstable P—O—C structure in flame retardant [45]. Besides, the thermal degradation of small part of EA also contributed to the release of CO₂. As time went on, other peaks came up later. The peak around 1750 cm⁻¹ indicated the volatilized products containing carbonyl compounds. Specifically, the carboxylic acid, RCOOH (characteristic peaks at 2815 cm⁻¹ and 1727 cm⁻¹) can be observed firstly. Then, the peak shifted from 1735 cm⁻¹ to 1780 cm⁻¹, which was attributed to acid anhydride. It can be explained that acid anhydrides were formed at high temperature in result of the reactions among the carboxylic acid molecules. Otherwise, the compounds of acid anhydrides can form polynuclear aromatic structures through the catalysis of phosphoric compounds. And polynuclear aromatic structures will form char in high temperature [46].

In order to further understand the effect of GPCS on EA, total and some specific volatilized products were selected to study. The intensities of absorbance were all normalized to the samples’ content. Fig. 8 showed the whole change of pyrolysis products of EA and 20wt% GPCS/EA in different time. It can be found that absorbance peak of pure EA appeared around 20 min, while that of GPCS/EA showed around 15 min, which advanced 5 min. It was because that GPCS was unstable when heated. The same thing happened to other three specific products, CO₂, aromatic compounds and carbonyl compounds. This phenomenon accorded with the TGA results. Specifically, GPCS degraded at lower temperature and some small molecular released. Meanwhile, it should be noticed that GPCS made the intensities of volatilized product drop greatly. It was because that GPCS accelerated the formation of char. And the char can be used as a shield to prevent the release of volatilized products. Volatilized products such as carbonyl compounds were flammable. So the reduction of such combustible products can improve the flame retardancy of materials.

3.7. Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) was used to investigate the dynamic mechanical behavior of samples. The storage modulus (E’) of the samples with different GPCS contents was showed in Fig. 9. It should be noticed that E’ ascended firstly, then descended with increasing GPCS content. Two main competitive factors had an impact on the modulus of samples. To begin with, the reinforcement effect of GPCS enhanced the modulus. Then, the decrease of the crosslinking density of the GPCS/EA system, inducing by the concentration of double bond decreased and the viscosity increased as the GPCS content raised, caused the decline of the storage modulus. The storage modulus in GPCS/EA network with the GPCS content below 10wt% was higher than that of pure EA, indicating that the reinforcement balanced the influence of reduced crosslinking density on the storage modulus. However, further adding of the GPCS content decreased E’. It was because that the reduced crosslinking density controlled the main influence.

The curves of loss factor (tan δ) were also showed in Fig. 9. The glass transition temperature (Tg) of a crosslinked material was determined as the relaxation peak of the tan δ. Tg reduced with the increase of GPCS. Such decrease was attributed to the lower crosslinking density and the flexibility and mobility of the phosphate ester group. Besides, the analysis on the width of relaxation peaks shows the homogeneity for the samples with different GPCS contents. No significant difference on the width of relaxation peaks among all the samples, which confirmed the good miscibility of GPCA with EA matrix.
4. Conclusions

A novel chitosan based flame retardant GPCS containing phosphorus and acrylate structure has been prepared successfully. It was applied in EA to improve the thermal properties and reduce the flammability of the matrix. The morphological analysis of the GPCS/EA system revealed that the compatibility between EA matrix and GPCS was good. LOI values increased with the addition of GPCS, indicating that GPCS improved the flame retardancy of EA matrix. MCC data showed the flammability properties of samples, which revealed that GPCS was efficient in reducing the PHRR and THR during burning. Thermal analysis of samples exhibited that GPCS improved the thermal stability of materials at high temperature and increasing content of flame retardant further enhanced the thermal stability in that area. RT-IR and TGA-IR revealed that the flame retardant promoted the formation of char, and prevented the release of combustible volatilized products. The storage modulus of samples increased then decreased with increasing GPCS content owing to competition between crosslinking density and the reinforcement of the flame retardant. While, the glass transition temperature continued reduced, which was due to the lower crosslinking density and the flexibility and mobility of the phosphate ester group. In summary, the above results confirmed that GPCS can be used as an effective flame retardant in EA.

Acknowledgments

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