Synergistic effect of chitosan derivative and DOPPO for simultaneous improvement of flame retardancy and mechanical property of epoxy resin

Junjie Wang

Wuhan Institute of Technology

Xuejun Yu

Three Gorges Public Inspection and Testing Center

Shengsong Dai

Wuhan Institute of Technology

Xinyu Wang

Wuhan Institute of Technology

Zhiquan Pan

Wuhan Institute of Technology

Hong Zhou (✉ hzhohu@126.com)

Wuhan Institute of Technology <https://orcid.org/0000-0003-2409-784X>

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Abstract

In this work, the effects of a chitosan-based derivative (CSA), DOPO and CSA-DOPO additives on the flammable properties of EP composites were systematically studied, where CSA was synthesized by a facile condensation between chitosan (CS) and 9-anthraldehyde and. DOPO was 9, 10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide. The mass ratio of CS and 9-anthraldehyde in CSA was determined by elemental analysis and theoretical calculation, which matched well with each other. Under the 8% addition in EP, EP/2.66%/5.34%DOPO sample was the only one, which passed the UL-94 rating and exhibited the highest LOI value of 36.4%. Compared with EP, the cone calorimeter test (CC) showed that the total smoke emission value and the peak heat release rate of the CSA and DOPO modified EP decreased 36.0% and 61.9%, respectively, and the residual char amount increased by 151%. The possible flame retardant mechanism of CSA/DOPO towards EP was proposed according to the results of the real time FTIR spectra at different pyrolysis temperatures, cone calorimeter and Py-GC/MS analysis for EP and EP/2.66%CSA/5.34%DOPO samples, and Raman spectra and XPS for their char residues. Moreover, the incorporation of CSA/DOPO effectively improved the mechanical properties, especially, the flexural strength was increased by 52.3%. It was proposed that CSA/DOPO plays roles in both vapor and condensed phases, and the synergistic effect of CSA and DOPO significantly improve the flame retardancy and mechanical strength of EP.

1. Introduction

Epoxy resin has been frequently used in many fields owing to its superior chemical resistance, excellent adhesion and good mechanical properties (Zhu et al. 2020; Tang et al. 2019; Yu et al. 2016). However, the widespread use of epoxy resin is severely limited due to its own flammability (Jin et al. 2019). In order to increase the fire resistance of epoxy resin materials, adding flame retardants in EP is considered as the most direct, efficient and economical method (Zhu et al. 2019).

Due to the flame retardancy function of DOPO in both gas and condensed phases, much work has been performed to synthesize DOPO-based derivatives for the purpose of upgrading the flame retardancy of EP (Selmera et al. 2015). The preparation of DOPO-based derivatives is usually based on the chemical reactions between P-H bond in DOPO and active groups in other substances. Some of the derivatives exhibited excellent flame retardancy toward EP. For examples, Carja and co-workers (Carja et al. 2014) synthesized the oligomer DOPO-PFR using DOPO, terephthalaldehyde and phenylphosphonyl dichloride as raw materials. When DOPO-PFR with the phosphorus content of 2 and 3% were added to EP system, the obtained epoxy matrix can reach UL-94 V-0 rating. Wang Xin et al. (Wang et al. 2010, 2011a, b, c, d) used phosphorus oxychloride, pentaerythritol and DOPO-based dihydric phenolic compounds as raw materials to synthesize a series of DOPO-based oligomers. When these oligomers were added in EP using 4, 4'-diaminodiphenylmethane as a curing agent, the amount of combustible gas, the total heat release and the maximum heat release rate in the combustion process were reduced significantly, and the LOI value was greatly increased. Yang Shuang et al. (Yang et al. 2015) used N-(4-hydroxyphenyl) maleimide and cyanuric chloride to synthesize a maleimide functional group-containing triazine

derivative TMT, and then reacted it with DOPO to synthesize the flame retardant DOPO-TMT. When the phosphorus content is 1.0 wt%, the LOI value of the modified EP reached 36.2% and passed the UL-94 V-0 test. Although some DOPO-based derivatives modified EP composites exhibited good flame retardancy, the complicated preparation process as well as the drawbacks in mechanical properties limited their industrial application. Easy preparation with lower cost and good mechanical properties is still the essential conditions for large scale production of EP. Aurelio Bifulco et al. (Aurelio et al. 2020) modified epoxy resin with the combined action of a DOPO-derivative, melamine and silica, the obtained epoxy resin composite achieved UL 94-V-0 classification at low P-content (2.0 wt%). The better flame retardancy of EP composites promoted by the combined action of several substances was worth to further study for industrial applications.

As a natural polysaccharide biomass polymer material (Dash et al. 2011; Yang et al. 2018), chitosan (CS) can be used as a charring agent due to the abundant hydroxyl groups in its structure (Chen et al. 2016). However, it has the disadvantages of low initial decomposition temperature, poor thermal stability and low flame retardant efficiency (Prabhakar and Jung-il 2018; Hu et al. 2012). The amine groups and hydroxyl groups possessed by chitosan can be used as active groups for chemical modification (Hirano et al. 2003; Huang et al. 2011). The salicylaldehyde modified chitosan combined with polyphosphate with the total content of 25% in polyurethane exhibited better flame retardancy (Liu et al. 2017). Chitosan derivative modified by gradually grafting -PO(OH)_2 and melamine and organic montmorillonite were used as an intumescent flame retardant (IFR) for EP (Yu et al. 2020a, b). There were some examples of chitosan as a flame retardant component of epoxy resins. Rao Tentu Nageswara et al. (Rao et al. 2019) reported that the introduction of ZrO_2 NPs, chitosan, boric acid, ammonium polyphosphate and melamine into EP can increase the LOI value and reach UL-94 V-0 rating, significantly. However, the flame retardants derived from CS were rarely reported due to its lower reaction activity. In our previous work, a flame retardant (CCD) was synthesized by two-step chemical reaction using chitosan, cinnamaldehyde and DOPO as raw materials, CCD exhibited better flame retardancy (Chen et al. 2020). We have also tried to synthesize other DOPO modified chitosan, however, it was difficult to get the designed products. It may be the reason why no other reports of DOPO-chitosan modified chitosan were found in literature.

Based on the charring function of chitosan derivative and the flame retardancy of DOPO, a Schiff base compound CSA was prepared by the condensation between the active amine groups of chitosan and aldehyde of 9-anthralaldehyde. The effects of different dosages of CSA and DOPO in EP on the combustion and mechanical properties of EP composites were studied, and the possible flame retardant mechanism of CSA/DOPO was proposed based on the results of TG-FTIR, cone calorimeter, Raman spectra, XPS and Py-GC/MS analysis. The superior properties of EP/2.66%CSA/5.34%DOPO in both flame retardancy and mechanical properties has not been found in chitosan containing flame retardants for EP. Moreover, the as prepared EP composites have the advantages of facile preparation, lower cost and improved flame retardancy and mechanical properties.

2. Experimental

2.1. Materials

DOPO (98.5%) and epoxy resin (DGEBA, E-44) were provided by Huangshi Hongsheng Reagent Co., Ltd, Huangshi, China. Diamino diphenylmethane (DDM), tetrahydrofuran (97%) and methanol (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Chitosan (Deacetylation degree $\geq 95\%$) and 9-anthracene aldehyde (99%) were obtained from Macklin reagent Co., Ltd, Shanghai, China.

2.2. Synthesis of CSA

The CSA was synthesized according to the literature method with some modifications (Kumar et al. 2009), the synthetic route was shown in Fig. 1a. First, chitosan (8.06 g, 0.05 mol) was dispersed in 150 ml methanol in a three-necked flask equipped with a condenser. A mixture of 9-anthraldehyde (20.73 g, 0.1 mol) and 150 ml of tetrahydrofuran was added dropwise through a constant pressure funnel within 60 minutes. The resulting mixture was heated to 75 °C and refluxed for 12 hours. Then it was cooled and filtered. The obtained filter cake was washed three times with a mixture of methanol and tetrahydrofuran (volume ratio 1:1). Finally, the product was dried at 60 °C for 6 hours under vacuum.

2.3. Preparation of EP mixtures

The preparation process of CSA/DOPO flame-retardant epoxy resin material was as follows (Fig. 1b): Firstly, DGEBA and CSA (or CS) were mixed uniformly in a two-necked flask. After it was heated under vacuum at 130 °C for about 40 min, a translucent liquid was obtained. Then, DOPO was added in a certain mass ratio, and stirred to get homogeneous. DDM was added under vigorous stirring and vacuum condition after the temperature dropped to 95 °C. Finally, the mixture was poured into the clean mold, cured for 2 hours at 100 °C and another 2 hours at 150 °C. The compositions of the modified EP samples were listed in Table 1.

2.4. Methods

FTIR spectra of CS, CSA and the char residue for EP/2.66%CSA/5.34%DOPO were recorded on a Thermo Nicolet 5700 FTIR spectrophotometer using the KBr disk in a wavenumber range of 4000 - 400 cm^{-1} .

The contents of carbon, hydrogen and nitrogen in CS and CSA were analyzed by a Vario MACRO cube elemental analyzer and phosphorus content in the char residue of EP/2.66%CSA/5.34%DOPO was detected additionally.

The surface morphologies studies of the char residual were performed on JEOL JSM-5900LV under vacuum at an acceleration voltage of 20 kV.

The thermal decomposition behavior of CS, CSA and epoxy resin thermosetting polymer samples were recorded by a thermogravimetric analyzer (NETZSCH STA449F3). The test was conducted by heating from 30°C to 790°C under nitrogen. The heating rate was 10°C/min.

The LOI value was obtained on a JF-3 oxygen index instrument, the sample size was $130 \times 6.5 \times 3.2 \text{ mm}^3$. The UL-94 rating was measured with the sample size $130 \times 13 \times 3.2 \text{ mm}^3$. The cone calorimeter (CC) test was carried out according to standard ISO 5660 with the sample size of $100 \times 100 \times 3.2 \text{ mm}^3$ under an external heat flux of 50 kW/m^2 .

X-ray photoelectron spectra of the char residues left behind after cone calorimeter tests were recorded on an ESCALAB 250xi (America) using AlK α radiation (1486.6 eV) as an excitation source.

Raman spectroscopy was recorded on LabRAMHR800 laser Raman spectrometer to characterize the types of the carbon under 532 nm helium-neon laser line at room temperature.

Pyrolysis products of EP composites were analyzed by Py-GC/MS in helium atmosphere. Firstly, the sample was pyrolyzed in a cracker (CDS 5200) at 600°C , and then the volatile products were transported to the Perkin-Elmer Clarus 680 GCSQ8MS gas chromatography-mass spectrometer via helium.

The flexural and tensile tests of the samples were recorded on CMT4104 universal testing machine (SANS) with a dumbbell shape of $75 \times 4 \times 2 \text{ mm}^3$ and a rectangle of $80 \times 10 \times 4 \text{ mm}^3$, separately, according to the standard of GB/T 9341-2008 and GB/T 1040.2-2006. Five samples were measured each time, and the average value was taken.

TG-FTIR was used to analyze the FTIR spectra of the gas components from the TGA, and the real time FTIR analysis of the pyrolysis gases was conducted on a Thermo Fisher IS50, the transfer line of gases from TGA to FTIR was heated at 280°C .

3. Results And Discussion

3.1. Characterization of CSA

Fig. 2 shows the FTIR spectra of chitosan and CSA. For chitosan, there is a wide frequency band in the range of $3400\text{--}3800 \text{ cm}^{-1}$, which was due to the stretching vibration of the O-H bond and the N-H bond, while the peak centered at 2907 cm^{-1} was assigned to the C-H bond. There were two obvious characteristic peaks at 1157 cm^{-1} and 1602 cm^{-1} , which were attributed to the tensile vibration of the sugar structure and amino groups, respectively. For CSA, a new stretching vibration absorption peak at 1645 cm^{-1} was detected, which was attributed to -C=N (Dubey et al. 2018), indicating the existence of Schiff base in CSA. It was noted that there was no aldehyde characteristic peak appeared at about 1680 cm^{-1} , revealing that CSA did not contain unreacted 9-anthraldehyde.

The chemical composition of CSA was further characterized by elemental analysis. According to the C, N and H atomic contents of CS and CSA in Table S1, the C contents in CS and CSA were 44.58 % and 68.04 %, respectively. Compared with CS, H and N contents in CSA decreased by 1.13 and 3.55 %, respectively. The reason for the increase of C content and the reduction of H and N contents can be attributed to the introduction of nitrogen-free anthracene unit with low H content and high C content in CSA. Chitosan

contains amino groups which can form Schiff base compounds with aldehyde substances under certain conditions. The reaction was generally carried out in ethanol solution, and the generated products were insoluble in ethanol. After the end of the reaction, the products were obtained by washing with ethanol for several times. Because of chitosan as a polymer, it can be treated as a mixture with different degree of polymerization. When it reacted with the aldehyde material, some chitosan molecules might have multiple amino groups participated in the reaction with aldehyde, some chitosan might not involved in the reaction. Considering that chitosan and the product were not soluble in ethanol, the unreacted chitosan as a product may mix in the final product. To confirm the composition of the product, the following calculations were used to calculate the mass ratio of chitosan and the amount of aldehydes involved in the reaction in this product.

In the Schiff base condensation reaction of chitosan with a substance containing aldehyde group, the chemical reaction of an amino group with an aldehyde group can be expressed as follow:

The masses of 9-anthraldehyde reacting with chitosan and chitosan added in the reaction system were set as m_1 and m_2 , respectively. The molar mass of 9-anthraldehyde was M_2 , then the mole number of R_2-CHO was m_2/M_2 , the total mass (m) of the product can be theoretically calculated according to the equation (1).

$$m = m_1 + m_2 - 1 \times \frac{m_2}{M_2} \times 18 \quad (1)$$

Where, m_1 and m_2 can be obtained from the following equations,

$$C\% = \frac{m_1 C_1\% + m_2 \times C_2\%}{m} \times 100\% \quad (2)$$

$$H\% = \frac{m_1 \times H_1\% + m_2 \times H_2\% - 2 \times \frac{m_2}{M_2} \times 1}{m} \times 100\% \quad (3)$$

$$N\% = \frac{m_1 \times N_1\%}{m} \quad (4)$$

Where C% and H% represent the percentage of C and H in the product, respectively, which can be obtained directly by measuring the element content of the product; $C_1\%$, $H_1\%$ and $N_1\%$ were the percentages of C, H and N in chitosan, which can be obtained directly by measuring the element content of chitosan. Among them, $C_2\%$ and $H_2\%$ were the percentage content of C and H in 9-anthraldehyde molecules, which can be directly calculated by the molecular formula of the aldehyde.

By solving equation (1-4), the mass ratio of chitosan (m_1) and the mass of 9-anthralaldehyde (m_2) involved in the reaction can be quantitatively determined, the calculation value was 1.0536, which was obtained as the followings: since the carbon content was the highest in the sample, the relative measurement error of carbon was relatively smaller than that of H and N in the sample. Therefore, the carbon content obtained by the elemental analysis and the theoretically inferred product quality calculation formula were selected to calculate the mass ratio (m_1/m_2). The theoretical values of H and N were calculated by substituting them into the theoretical content calculation formulas of hydrogen and nitrogen, and the theoretical values were compared with the actual measured percentage contents of H and N. The results showed that the calculated theoretical value was basically consistent with the actual measured value, indicating that the calculated ratio of m_1 to m_2 was correct. Therefore, the mass ratio of chitosan to 9-anthraldehyde involved in the reaction was obtained. The elemental analysis data of chitosan and CSA and the calculated values for CSA were listed in Table S1.

3.2. Thermal stability

In order to understand the thermal decomposition behavior of CSA and CSA/DOPO modified epoxy resins, CSA, EP, EP/8%CSA, EP/8%DOPO and EP/2.66%CSA/5.34%DOPO were studied by thermogravimetric analyzer. Fig. 3 showed the TGA and DTG curves of all the samples, the corresponding results were listed in Table S2. As seen from Fig. 3 that CSA has the highest residual char 34.6% at 750°C and lowest weight-loss rate at maximum weight loss temperature (T_{max}), indicating that CSA has excellent char-forming properties. However, the initial decomposition temperature $T_{5\%}$ and $T_{max\%}$ of CSA were the lowest ones among the tested samples, revealing that CSA has lower thermal stability than other EP composites. It was found that EP/8%CSA exhibited the highest T_{max} and char residue among the EP composites, revealing that the introduction of CSA improved the thermal stability and char-forming property of EP. In addition, the char residue of EP/8%DOPO was only 12.6% at 750°C, which was the lowest one in the tested samples. So, it can be concluded that the introduction of DOPO into EP greatly decreased the char-forming properties of EP. For EP/2.66%CSA/5.34%DOPO, it was observed that the residue char amount was increased 28.8% relative to EP/8% DOPO, reduced 12.7% relative to EP/8% CSA, exhibiting a comparable char-forming property with EP.

3.3. Flame retardancy performance

The LOI value and UL-94 test were adopted as the [frequently-used](#) methods for evaluating the flame retardancy of materials. The test results were summarized in Table 1. As shown in Table 1 that the LOI value of the EP sample was 22.6%, which was the lowest one in all the samples. Except the EP has the dripping phenomenon, all the other samples containing CSA, DOPO or CSA and DOPO in EP has no dripping in the combustion process. The LOI value of the EP/1.66%CSA/3.34%DOPO was 34.5%, which was increased by 52.6% compared with the EP sample. When the total content of CSA/DOPO was increased to 8wt% with the mass ratio of CSA to DOPO was 1:2, the LOI value of EP/2.66%CSA/5.34%DOPO samples was 36.4%, which was an increase of 61.1%, 31.9% and 6.4% relative to the EP, EP/8%CSA and EP/8%DOPO samples, respectively. The results show that the

synthesized flame retardant synergist CSA had a good synergistic effect with DOPO on the flame retardant properties of EP composites. In the UL-94 test, the EP samples were completely burned out and obtained no rating. EP/2.66%CSA/5.34%DOPO and EP/2.01%CSA/5.99%DOPO can pass the V-0 rating, while, EP/8%DOPO only reached V-1 rating and EP/8%CSA exhibited no rating. It indicated that the synergistic function of CSA and DOPO was contributed to the improvement of the flame retardant properties of EP.

Table 1 Composition of epoxy mixtures and the results of LOI tests and UL-94

Samples	EP	DDM	CSA	DOPO	LOI	UL-94	
	(g)	(g)	(g)	(g)	(%)	Dripping	Rating
EP	25.00	6.50	0	0	22.6	Y	No Rating
EP/5% CSA	25.00	6.50	1.66	0	25.7	N	No Rating
EP/5% DOPO	25.00	6.50	0	1.66	32.3	N	V-1
EP/2.5%CSA/2.5%DOPO	25.00	6.50	0.83	0.83	32.6	N	V-1
EP/1.66%CSA/3.35%DOPO	25.00	6.50	0.55	1.11	34.5	N	V-1
EP/1.27%CSA/3.74%DOPO	25.00	6.50	0.42	1.24	35.6	N	V-1
EP/8%CSA	25.00	6.50	2.74	0	27.6	N	No Rating
EP/8%DOPO	25.00	6.50	0	2.74	34.2	N	V-1
EP/4%CSA/4%DOPO	25.00	6.50	1.37	1.37	36.3	N	V-1
EP/2.66%CSA/5.34%DOPO	25.00	6.50	0.91	1.83	36.4	N	V-0
EP/2.01%CSA/5.99%DOPO	25.00	6.50	0.69	2.05	37.5	N	V-0

In addition, the combustion behavior of EP materials was tested with a cone calorimeter (CC). Fig. 4 showed the heat release rate (HRR), total heat release rate (THR), smoke generation rate (SPR) and total smoke generation (TSP) curves of EP and EP/2.66%CSA/5.34%DOPO samples. The CC test results were listed in Table 2. It showed that the TTI value of EP/2.66%CSA/5.34%DOPO samples increased from 59 s in EP to 82 s. The improvement of the ignition resistance of the matrix was attributed to the release of volatile products produced by the early decomposition of CSA/DOPO, which could capture or dilute oxygen. Relative to EP, EP/2.66%CSA/5.34%DOPO had much higher residual char amount, which increased by 151%, and very lower peak heat release rate (PHRR), which decreased by 36.0%.

In TGA test, the residue char of EP/2.66%CSA/5.34%DOPO was slightly lower than that of EP in N₂ atmosphere, while, in CC test, the obvious increase of the residue char amount of

EP/2.66%CSA/5.34%DOPO can be attributed to the existence of oxygen, which was the only difference in the two kinds of tests. It indicated that oxygen can improve the formation of more residue char of EP/2.66%CSA/5.34%DOPO, which was beneficial to resist fire. FIGRA was defined as the maximum value of HRR/t_p , which was equal to $PHRR/t_p$ in accordance with general practice. FIGRA was an important parameter for evaluating fire risk (Schartel et al. 2007). It can be seen from Table 2 that the FIGRA value of EP/2.66%CSA/5.34%DOPO was about 40 % lower than that of EP sample, indicating a significant function in reducing the fire risk. More importantly, it was worth noting that the peak smoke production rate (PSPR) and total smoke release (TSP) values of EP/CSA2.66%/5.34%DOPO were much lower than those of the EP sample, illustrating that the combination of CSA2.66% and 5.34%DOPO can significantly improve the smoke suppression effect of EP. The superior behavior of EP/2.66%CSA/5.34%DOPO both in smoke suppression and flame retardancy can be ascribed to the following reasons: 1) the lower thermal stability of CSA promotes the earlier escape of some non-flammable gases such as NH_3 and CO_2 , diluting combustible gases, 2) P containing radicals derived from the DOPO units in EP/2.66%CSA/5.34%DOPO help to capture the radicals of chain reactions (Schartel et al. 2008), 3) the rich and dense char layer also plays a role of isolation and quenching heat transfer.

Table 2 The CC test results of EP and EP/2.66%CSA/5.34%DOPO

Sample	EP	EP/2.66%CSA/5.34%DOPO
Time for ignitions(s) (TTI)	59	82
Time to peaks (s) (t_p)	130	140
Peak heat release rate($KW.m^{-2}$) (PHRR)	1063	680.8
Fire growth rate index (FIGRA)	8.17	4.9
Total heat release ($MJ.m^{-2}$) (THR)	97.6	83.7
Peak smoke produce rate ($m^2.s^{-1}$) (PSPR)	0.54	0.29
Total smoke release (m^2) (TSP)	71.4	27.2
Maximum average heat release rate (MARHE) ($KW.m^{-2}$)	301.8	258.7
Average CO yield ($kg.kg^{-1}$) (AV-COY)	0.054	0.14
Average CO_2 yield ($kg.kg^{-1}$) (AV- CO_2Y)	0.995	2.6
Char residue (%)	11.9	29.9

3.4 Analysis of char residue

Fig. 5 showed the macrostructure and microstructure of the char residues left behind after the CC test. Fig. 5a showed that the residual carbon left behind after EP combustion exhibited incontinuous fiber-like structure with large pores and low in quality. The char residue in this form cannot isolate the exchange of the produced combustion gases and cannot protect the substrate from burning. With the increase of the amount of CSA and DOPO in EP, it was found that the char residue became more denser with higher combustion char residue. It indicated that the addition of CSA/DOPO can increase the mass and compactness of residual char, playing a role in condensed phase flame retardant effect.

The residual carbon after CC test was systematically studied by elemental analysis, infrared spectroscopy and Raman spectroscopy. In Fig. 6, two significant peaks at 1594 cm^{-1} and 1374 cm^{-1} can be assigned to the G band and the D band, respectively. In general, G band is attributed to sp^2 -hybridized carbon atom, and D band belongs to amorphous carbon (Mauere et al. 2005). Therefore, the graphitization degree of the material can be reflected by the integral intensity ratio (I_D/I_G) of the D and G-band. With the decrease of the proportion, the graphitization degree increases, leading to better flame retardant performance (Sadezky et al. 2005). Fig. 6 shows that the I_D/I_G value (3.93) of EP was greater than that of EP/CSA2.66%/5.34%DOPO sample (3.52), indicating that the char layer formed by the combustion of EP/CSA2.66%/5.34%DOPO has a higher degree of graphitization than that of the char residue of EP, which was beneficial to better prevent heat transfer in the combustion process.

Fig. S1 showed the FTIR spectra of the char residues from EP/2.66%CSA/5.34%DOPO and EP. The two curves exhibited similar main absorption peaks at 2921 cm^{-1} and 1619 cm^{-1} , corresponding to the vibration of the aromatic ring. The signal peaks at 1080 cm^{-1} and 3422 cm^{-1} belonged to C-O and O-H bonds, respectively. There were three new absorption peaks at 1159 cm^{-1} , 1236 cm^{-1} and 1509 cm^{-1} in the char residues of EP/2.66%CSA/5.34%DOPO, which were assigned to the stretching vibrations of P-O-C, P=O and C-P, respectively. The results indicated that some phosphorus compounds existed in the char residue of EP/2.66%CSA/5.34%DOPO, which were not found in EP.

The results of elemental analysis of the char residues were listed in Table S3. Compared to EP char residue, the C content in the char residue of EP/2.66%CSA/5.34%DOPO was increased by 6.25%, and its O and N contents were decreased by 27.9% and 40.3%, respectively. The P content of 0.48% in the char residue of EP/2.66%CSA/5.34%DOPO was 37.7% lower than that in its precursor, which was 0.77% calculated from the addition mass of DOPO in the sample and P percentage in DOPO. The decrease of P content in the char residue illustrated that some P containing substances have escaped as gas phase in the combustion, which was proved by the Py-GC/MS analysis of the sample. Generally, the P element in the condensed phase would exist in the form of polyphosphoric acid and its derivatives, promoting the dehydration and carbonization and preventing further combustion.

Additional, XPS was further employed to analyze the composition of the various components of the char residue. Detailed data of C_{1s} , N_{1s} , O_{1s} , P_{2s} chemical bonds were listed in Table S4. As shown in Fig. 7, in the C_{1s} spectrum, the peaks at 284.4 eV was assigned to C-H and C-C bonds in the aliphatic and aromatic

components, and the peaks of C-N bond and C-OH bond were observed at 285.4 eV, and C-C and C-O bonds were observed at 288.7 eV. Compared with EP, the peak at 288.7 eV decreased (partially migrated to 290.2 eV), and the peak at 284.4 eV increased for the EP/2.66% CSA/5.34%DOPPO, showing that the compound of CSA and DOPPO could reduce the generation of oxidized substances during the combustion of EP materials (Levchik et al. 2005). In the N_{1s} spectrum, the peaks at 398.6 eV and 400.2 eV were assigned to the C-N and C=N bond, severally. In the O_{1s} spectrum of EP, the peak at 533.2 eV attributed to C-OH and C-O-C groups, while peak at 532.2 eV was assigned to C=O. For the EP/2.66%/5.34%DOPPO, the peaks at 532.2 and 533.2 eV were also observed, however, the peaks were wider than those of EP, which related to the formation of P-O-C group in the char residue of EP/2.66%/5.34%DOPPO. In the P_{2s} spectrum, the peak at 133.4 eV was attributed to P=O, and the peak at 134.2 eV can be attributed to P-OH and P-O-C bond, indicating that P containing substances were generated during the formation of residual carbon, while no P-containing peak shown in the char residue of EP.

According to reports in the literature, DOPPO undergoes thermal decomposition during the combustion process to release free radicals containing P, thereby playing a flame retardant effect in the gas phase (Li et al. 2020; Tang and Zhou 2019). Py-GC/MS was carried out for the EP sample and EP/2.66%CSA/5.34%DOPPO respectively, to dissect the gas flame-retardant mechanism at 500 °C. Fig. S2 exhibited the pyrolysis diagram of EP, and the main cracked products were listed in Table S5. As shown in Table S5, the pyrolysis products of EP samples were mainly derivatives of DDM and epoxy resin. Among them, thermal cracking produces $\cdot OH$ radicals and $\cdot H$ radicals were the main reasons for the inflammability of thermosetting epoxy resins.

The pyrolysis spectrum of EP/2.66%CSA/5.34%DOPPO was shown in Fig. 8. The identified specific products were listed in Table 3. Some characteristic products of the flame retardant pyrolysis of EP/2.66%CSA/5.34%DOPPO were as follows: methylaminoacetic acid (peak 1), L-alanylglycine (peak 2), paromomycin (peak 3), 4-hydroxy Phenyl phosphate (peak 4), o-cresol (peak 5), 2-isopropylphenol (peak 6), o-phenylphenol (peak 7), dibenzofuran (peak 8), fluorene (peak 9) and 9-hydroxy-4-methoxyacridine (peak 10). The existence of these substances can be explained by the structure of CSA/DOPPO flame retardant. The pyrolysis products 4, 7-9 can be attributed to the decomposition of DOPPO, accompanying with the production of PO and PO_2 radicals. These phosphorus-containing radicals can trap active free radicals during the combustion process and terminate radical chain reactions (Jellinek et al. 1977). Peak 1-3 were mainly corresponding to the cracking of chitosan fragments in CSA. The peaks located in the retention time more than 22.0 mins in the pyrolysis spectrum of EP/2.66%CSA/5.34%DOPPO were also found in that of EP, indicating that these substances related to these peaks come from the similar components with EP. The amino groups containing compounds can generate non-combustible gases, such as CO_2 , H_2O and NH_3 , diluting the combustion gases and reducing the heat release.

On the basis of the above analysis, the flame retardant mechanism of EP/2.66%CSA/5.34%DOPPO can be summarized as follows: with the increase of temperature, the gradual decomposition of DOPPO and CSA promoted the release of PO $\cdot$ radicals and non-combustible gases such as CO_2 , H_2O and NH_3 , thus

quenching in the gas phase. In the condensed phase, the polyhydroxyl and aromatic rings in CSA and the phosphorus-containing compounds generated by DOPO decomposition can accelerate the formation of a more uniform and dense coke layer, so as to realize the thermal oxygen barrier effect.

Table 3 Some characteristic products identified in the pyrolytic diagram of EP/2.66%CSA/5.34%DOPO

Peaks	Times	m/z	Chemical structure
1	1.07	89
2	2.22	160
3	2.92	615
4	9.35	174
5	10.07	108
6	12.32	136
7	16.33	170
8	16.46	168
9	17.21	166
10	21.03	225

3.6 TG-FTIR analysis of EP and EP/2.66%CSA/5.34%DOPO samples

TGA-FTIR spectra was used to obtain a further disclose of the flame-retardant behavior of the EP/2.66%CSA/5.34%DOPO. The FTIR spectra of the pyrolysis gas products of EP and EP/2.66%CSA/5.34%DOPO samples at 300, 350, 400, 450, 500, 550 and 600 °C from TGA were shown in Fig. 9. As shown in Fig. 9 (a, b), EP samples exhibited the characteristic absorption peaks of some thermally cracked molecules, such as hydrocarbons (2970 cm^{-1} , 1180 cm^{-1}), CO_2 (2360 cm^{-1}), $\text{C}=\text{O}$ (1740 cm^{-1}) and Ph-O-C (1260 cm^{-1}) (Kong et al. 2019; Wu et al. 2009; Sergei et al. 2004), respectively. The peaks at $4000\text{--}3500\text{ cm}^{-1}$ and $1300\text{--}1600\text{ cm}^{-1}$ were ascribed to water (Wu et al. 2009; Sergei et al. 2004; Liu et al. 2018). These small molecule compounds were mainly attributed to the thermal cracking of EP.

Particularly, as shown in Fig. 9 (c, d), the peak at 1130 cm^{-1} in the FTIR spectra of the gaseous products of EP/2.66%CSA/5.34%DOPO was attributed to the Ph-P bond (Li et al. 2018). What's more, the peak at 1260 cm^{-1} was assigned to Ph-O-C , which was probably overlapped with the characteristic absorbance of ether bonds (Li et al. 2018; Wang et al. 2010; Qian et al. 2011). It can be seen that there were phosphorus-containing fragments in the pyrolysis gas of EP/2.66%CSA/5.34%DOPO samples, indicating that the CSA/DOPO flame retardancy system plays an active role in the gas phase, which was consistent with the conclusion of Py-GCMS.

In order to further understand the changes of pyrolysis products, Fig S3 shows the changes in the absorbance of EP and EP/2.66%CSA/5.34%DOPO pyrolysis products over time (a) and the curve obtained from the first derivative (b). As can be seen from the figure that the pyrolysis products of EP/2.66%CSA/5.34%DOPO begin to be released about 30.2 min, while the pyrolysis products of EP begin to release around 31.4 min. Additionally, it can be observed from Fig. 9 (c, d) that the thermal cracking of EP/2.66%CSA/5.34%DOPO produces CO_2 not only earlier, but also the absorption peak was more obvious, indicating that CSA/DOPO began to decompose at the early stage of thermal degradation of EP/2.66%CSA/5.34%DOPO.

3.7 Mechanical properties

In order to study the effect of CSA/DOPO flame retardant on the mechanical properties of epoxy resin materials. The measurements of unnotched impact strength, tensile strength and flexural strength were conducted on EP, EP/8%DOPO and EP/2.66%CSA/5.34%DOPO. The results were presented in Table 4. It was observed that the mechanical properties increased according to the order of EP, EP/8%DOPO and EP/2.66%CSA/5.34%DOPO. The increase of the flexural strength of EP/2.66%CSA/5.34%DOPO was most obvious, which increased by 52.3%. The improved mechanical properties of the modified EP can be attributed to the reaction activity of CSA and DOPO with the epoxy groups in EP in the curing procedure. The $-\text{OH}$ and NH_2 in CSA and $-\text{P-H}$ groups in DOPO can participate in the ring opening reaction of epoxy groups in EP at high temperature, which were shown in Scheme 1, The formed strong interactions greatly improved the compatability of CSA and DOPO with EP. Moreover, the hydrogen bond interactions among

the polar groups such as -OH and -NH- in the modified EP were also beneficial to increase its mechanical strength. (see Scheme 1 in the Supplementary Files)

To the best of our knowledge, EP/2.66%CSA/5.34%DOPO was the first report for the CS-containing flame retardants, which simultaneously improve both the flame retardancy and mechanical properties of EP. For comparison, the relative data of flame retardancy and mechanical properties for the CS-containing flame retardants in EP was listed in Table S6. Compared with CCD modified EP composite (EP/10%CCD) (Chen et al. 2020), EP/2.66%CSA/5.34%DOPO exhibits comparable flame retardancy with higher LOI value and enhanced mechanical properties. It was worth mentioning that the preparation of the flame retardant in EP/2.66%CSA/5.34%DOPO was much easier than that of EP10%CCD. CSA was synthesized by Schiff base condensation, which was similar with the first step for the synthesis of CCD. However, the Schiff base compound needed to further react with DOPO to produce CCD, while, the flame retardant in EP/2.66%CSA/5.34%DOPO was the combined action of CSA and DOPO, which was prepared by simple mixing of CSA and DOPO.

Table 4 Mechanical properties of EP, EP / 8%DOPO and EP/2.66%CSA/5.34%DOPO

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Izod impact strength (KJ.m ⁻²)
EP	54±4	86±3	21±1
EP/8%DOPO	58±3	97±2	22±2
EP/2.66%CSA/5.34%DOPO	63±3	131±2	28±2

4. Conclusions

In this work, a flame retardant synergist (CSA) was successfully synthesized, and the EP/CSA/DOPO thermosetting material obtained by compounding DOPO and CSA with EP had good flame retardant properties. Based on the UL-94 test, EP/2.66%CSA/5.34%DOPO passed a V-0 rating and had the LOI value of 36.4 %, an increase of 61.06 % compared with 22.6 % for EP. In comparison with the EP, EP/2.66%CSA/5.34%DOPO composites exhibits the following merits, 1) the PHRR, PSPR and TSP values were significantly reduced, 2) the mechanical properties have been much improved, which are contributed to the reaction activity of the functional groups in CSA and DOPO with the epoxy groups in EP in the curing procedure, 3) the char residue amount increased by 151%. The analyses of TG-FTIR, CC tests and Py-GC/MS of EP composites further supported the synergistic significance of CSA and DOPO on flame retardant properties, which can release PO·radicals and non-combustible gases such as CO₂, H₂O and NH₃ in the gas phase and form a more uniform and dense coke layer to realize the thermal oxygen barrier effect. It can also be concluded that simple mixing of several substances with respective function according to a certain mass ratio can greatly improve the relative properties of the synthesized composites.

Declarations

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Code availability: No software application or custom code.

Authors' contributions: Junjie Wang, synthesis, writing and analysis; Xuejun Yu, [characterization](#); Shengsong Dai, analysis; Xinyu Wang, analysis; Zhiquan Pan, analysis; Hong Zhou, Design and revise of the work.

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Figures

Figure 1

Schematic diagram of the synthetic route of CSA (a) and the preparation process of EP composites (b)

Figure 2

FTIR spectra of CS and CSA

Figure 3

TGA curves and DTG curves of epoxy samples under N₂ atmosphere

Figure 4

The curves of HRR (a), THR (b), SPR (c) and TSR (d) of EP and EP/2.66%CSA/5.34%DOPO

Figure 5

The digital and SEM images of the char residues from EP (a, a-1,a-2), EP/1.66%CSA/3.35%DOPO (b-1, b-2) and EP/2.66%CSA/5.34%DOPO (c, c-1, c-2)

Figure 6

Raman spectra of char residues for EP (a) and EP/2.66%CSA/5.34%DOPO (b)

Figure 7

C1s, N1s, O1s and P2s spectra of char residues for EP and EP/2.66%CSA/5.34%DOPO 3.5 Py-GC/MS analysis of EP and EP/2.66%CSA/5.34%DOPO

Figure 8

The gas chromatography spectrum of EP/2.66%CSA/5.34%DOPO sample

Figure 9

The real time FTIR spectra and 3D TG-FTIR images of EP (a,c) and EP/2.66%CSA/5.34%DOPO (b,d) samples at different pyrolysis temperature

Supplementary Files

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