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Influence of eco-friendly calcium gluconate on the intumescent flame-retardant epoxy resin: Flame retardancy, smoke suppression and mechanical properties

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ABSTRACT

In this work, calcium gluconate (CaG) as an eco-friendly additive was subtly incorporated into intumescent flame-retardant epoxy resin (EP) aiming to increase the flame-retardant efficiency. As expected, CaG exhibited synergistic effect in combination with APP, which could further decrease the heat release of epoxy thermosets including peak of heat release rate (PHRR), as well as the smoke production covering smoke production rate (SPR) and total smoke production (TSP). Typically, EP81 with 10 wt% flame retardants (8:1, the mass ratio of APP and CaG) easily passed a UL-94 V-0 rating, and got the highest LOI value of 31.8%; besides, during combustion it displayed PHRR value at 336 kW/m^2 with a reduction of 39.7% compared to EP/10 wt% APP. In addition, its TSP value was further reduced to 9.2 m^2 from 18.1 m^2 of EP/10 wt% APP. According to the analyses of char residues, it indicated that the presence of APP-CaG was beneficial for EP to form more continuous and compact char which was more effective to insulate the transfer of heat and the diffusion of fuels. Besides, despite the introduction of CaG the tensile strength of EP/APP material was well maintained.

1. Introduction

Epoxy resins (EP) as one of the most important thermosetting polymer have been broadly applied to the fields of coating, adhesive, composites et al. owing to its fine adhesive strength, chemical resistance, and excellent mechanical properties [1–3]. Nevertheless, like other polymers EP is also severely suffering from the defects of flammability and smoke/toxic gases-releasing during combustion, which significantly limits its applications related to automobile, electricity & electronics, et al. [4–6]. Thus, how to realize the simultaneous improvement in the flame retardancy and smoke/toxic-gases reduction has become an important issue.

In the past decades, researchers have developed various flame retardants (FRs) to solve the aforementioned problem of EP, such as intumescent flame-retardants (IFRs) [7–11], phosphorus-based FRs [12–17] including DOPO-based FRs [18–24] and phosphazene-based FRs [25,26], and nano FRs [27–29] et al. Although phosphorus-based FRs show high flame-retardant efficiency, they are still lack of the ability to reduce the smoke/toxic-gases production of EP in a way. To date, IFRs have been known as a promising method on endowing polymers simultaneously with flame-retardant and smoke-suppression properties, as they could induce polymers to form intumescent chars as an obstruction to inhibit the transfer of heat and fuels [30]. Generally, conventional IFRs are commonly comprised of acid sources, carbonization agents, and blowing agents [31]. Conventionally, APP usually acts as an acid and gas source in IFRs because it can generate phosphoric/polyphosphoric acid and release inert gases such as ammonium. Because amine-cured epoxy thermosets contain a great amount of hydroxyl and nitrogen-containing groups which can be considered as a carbonization agent, it is a feasible way to solve the referred problems of

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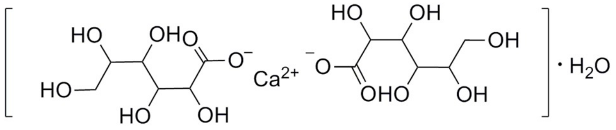

Scheme 1. The chemical structure of CaG.

Table 1
The formulations of IFR-EP and the UL-94 and LOI results.

Sample	DGEBA (wt%)	DETA (wt%)	IFR (wt %)	Mass ratio of APP and CaG	UL-94 (3.2 mm)	LOI (%)
EP	92.2	7.8	0	–	NR	19.0
EP01	83.0	7.0	10	0:1	NR	22.2
EP21	83.0	7.0	10	2:1	V-1	26.5
EP41	83.0	7.0	10	4:1	V-1	30.5
EP61	83.0	7.0	10	6:1	V-0	30.9
EP81	83.0	7.0	10	8:1	V-0	31.8
EP10	83.0	7.0	10	1:0	NR	30.9
EP1.1	91.2	7.7	1.1	0:1.1	NR	19.9
EP8.9	84.0	7.1	8.9	8.9:0	NR	30.1

EP through incorporating APP [32–34]. However, even in the presence of APP, the fire still could not self-extinguish during the combustion of epoxy thermosets in some cases. In this regard, some researchers selected to introduce heavy metal compound such as cuprous oxide [35, 36] and copper/nickel/cobalt acetate [37] to epoxy resins, in order to further enhance the flame-retardant efficiency of APP and reduce the release of smoke and toxic gases of epoxy resins. Nevertheless, it should be noted that heavy metal compounds are not eco-friendly and would definitely bring heavy-metal pollution to the environment. Meanwhile, the abovementioned method might further deteriorate the mechanical properties of epoxy resins. Therefore, it is meaningful to adopt the suitable alternatives of metal compounds. Interestingly, it is found that during combustion calcium gluconate (CaG) can dehydrate and simultaneously release CO_2, which prompts the residues (mainly CaO or $CaCO_3$) to gradually expand leading to the formation of a swelling and continuous char [38–41]. This phenomenon is also proven through comparing the morphologies of CaG before and after combustion as shown in Fig. S1. Such phenomenon makes it promising to be used as a carbonization and blowing agent. Besides, CaG is a green and environment-benign additive derived from the glucose which exists widely in the nature world [38]. Therefore, the combination of CaG and APP is brought forward to modify epoxy resin.

In this paper, the compounds composed of different mass ratios of APP and CaG were prepared to modify epoxy resins. The flame retardancy and fire performance of EP, EP/APP and EP/APP-CaG system were compared. Besides, cone calorimetric tests (CCT) were conducted to monitor the change of the heat release, CO/CO_2 production, and smoke production with the prolonged time. Finally, by virtue of SEM-EDX and Raman analyses, the reasonable flame-retardant mechanism of APP-CaG was proposed. Moreover, the thermo-mechanical and mechanical properties of materials were also determined.

2. Experimental

2.1. Materials

CaG as shown in Scheme 1 was bought from Macklin Biochemical Co., Ltd, Shanghai, China. CF-APP201 (form II) was sourced from Shifang Changfeng Chemical Co., Ltd, Sichuan, China. Diglycidyl ether of bisphenol A (DGEBA, E44) was commercially available from Xingchen Synthetic Material Co., Ltd., Nantong, China. Diethylenetriamine (DETA) as the hardener was available from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the relevant materials were directly used without further purification.

2.2. Preparation of IFR-EPs

Firstly, the mixtures of APP and CaG were fed into DGEBA under stirring at 90 °C until a homogeneous epoxy solution was formed. Thereafter, the solution was cooled down to 60 °C; meanwhile, DETA was rapidly poured into the former solution accompanied with vigorous stirring. After stirred for 30 s, the as-obtained solution was transferred to a preheated mold with different dimensions, and the curing process was completed successively at 80 °C and 100 °C for every 2 h. Besides, EP, EP/APP and EP/CaG as the control were also prepared. Finally, the resultant specimens were demolded and coded EP, EP01, EP21, EP41, EP61, EP81, EP10, EP1.1 and EP8.9 which are listed in Table 1.

2.3. Characterization

The flame-retardant tests in terms of the LOI, UL-94 vertical burning tests and CCT were conducted in accordance with ASTM D2863, ASTM D3801 and ISO5660-1. LOI tests were carried out on a HC-2C oxygen index meter (Jiangning, China). In addition, UL-94 vertical burning tests were experimented on a CZF-2 instrument (Jiangning, China). Fire performances were monitored at a heat flux of 35 kW/m^2 through a FTT cone calorimeter device. The dimension of specimens for LOI, UL-94 and CCT testing were $130.0 \times 6.5 \times 3.2$, $130.0 \times 13.0 \times 3.2$, and $100.0 \times 100.0 \times 3.0$ mm^3, respectively.

Thermal stabilities of neat EP and IFR-EPs were tested in the temperature range of 30–600 °C with 10 °C/min in nitrogen and air atmosphere on a METTLER TGA/SDTA 851 thermal analyzer.

SEM-EDX observation on a HITACH S4800 with energy-dispersive X-ray spectrometer was used to investigate the morphologies and composition of chars of EP and IFR-EPs after cone tests, as well as the dispersion of APP and APP-CaG in epoxy resins.

X-ray diffraction (XRD) was used to study the crystallization change of the residues of CaG and APP-CaG after heat-treated at 600 °C through XPERT-PRO diffractometer with Cu Kα ($\lambda = 0.1542$ nm).

DXR laser Raman spectrometer (LRS) was used to characterize the char residues of IFR-EPs with a 532 nm Helium-Neon laser line.

Thermal-dynamic mechanical analyses (DMA) were investigated using DMA Q800 apparatus. The specimens were treated in the temperature range of 40–220 °C with 10 °C/min on the mold of a single cantilever clip. The dimensions of neat EP and IFR-EP are $40 \times 10 \times 4$ mm^3, the oscillation amplitude was adjusted at 20.0 μm, and the frequency of testing was set as 1.0 Hz.

The flexural and tensile properties were determined according to GB/T 9341-2008 and GB/T 1040.2–2006 on universal testing machine (CMT4104). The dumbbell-shaped samples with the size of $75 \times 5 \times 2$ mm^3 were employed for tensile testing. The rectangular samples with the dimension of $80 \times 10 \times 4$ mm^3 were used for three-point bending tests. The testing speeds are both set as 2 mm/min.

3. Results and discussion

3.1. Flame retardancy

The flame-retardant efficiency of IFR in epoxy thermosets are evaluated by LOI values and UL-94 rating as shown in Table 1. Indeed, EP is very inflammable, as its LOI value is as low as 19.0%, and it cannot pass any UL-94 rating. Although the LOI values have some improvement when APP or CaG is added individually, for instance, the LOI value of EP10 increases to 30.9%, epoxy thermosets still exhibit disappointed results in the UL-94 tests. Excitedly, the combination of APP and CaG shows a synergistic effect on upgrading the UL-94 rating of epoxy resins, and EP21 as well as EP41 achieve UL-94 V-1 ratings. In addition, EP61 and E81 both pass UL-94 V-0 ratings. Moreover, EP81 gets the highest LOI value of 31.8% among the tested samples, indicating the aforementioned mass ratio of APP and CaG is the optimal. Herein, we use Lewin's concept of synergistic effectivity (E_s) [42,43] shown in formula

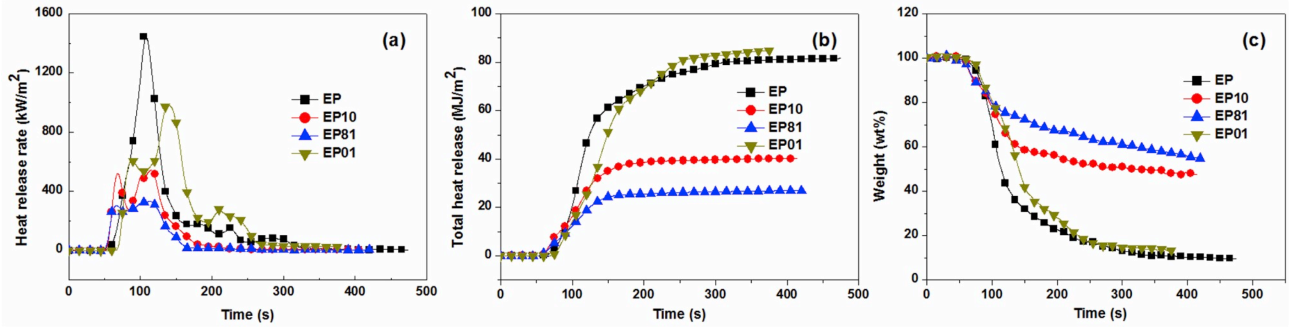

Fig. 1. HRR (a), THR (b) and residue mass (c) curves of EP, EP10, EP81 and EP01.

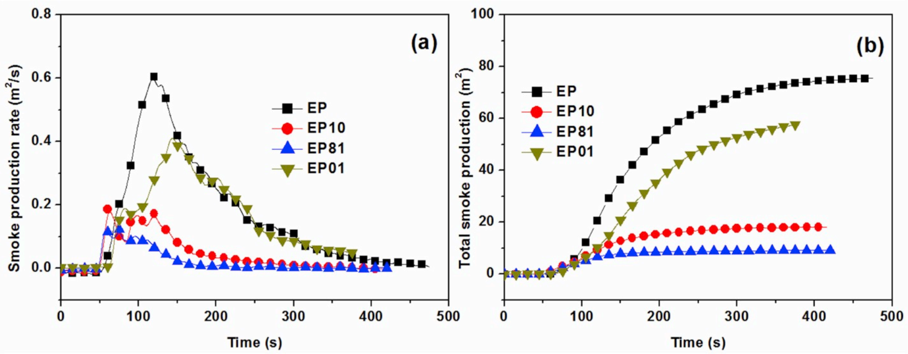

Fig. 2. SPR (a) and TSP (b) curves of EP, EP10, EP81 and EP01.

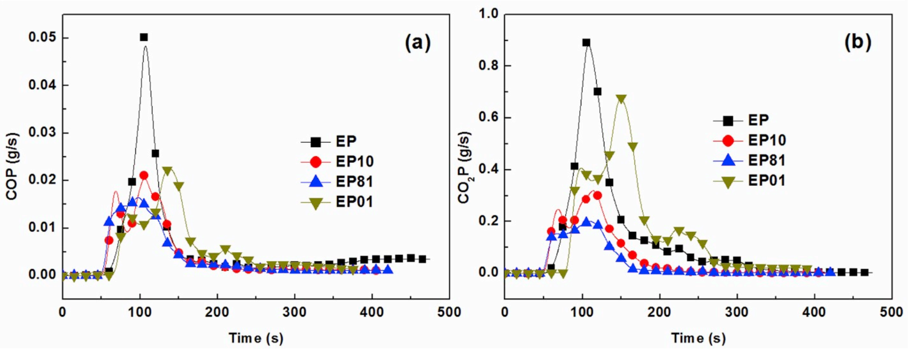

Fig. 3. COP and CO_2P curves of EP, EP10, EP81 and EP01.

Table 2
Combustion performance of EP, EP10, EP81 and EP01.

Samples	TTI (s)	THE (MJ/m^2)	PHRR (kW/m^2)	FIGRA (kW/m^2/s)	MARHE (kW/m^2)	EHC (MJ/kg)	Av-COY/Av-CO_2Y (%)	Residue (wt%)
EP	52	82	1462	13.3	419.9	23.0	0.047	9.7
EP10	50	40	556	7.9	237.9	20.2	0.068	46.8
EP81	50	27	336	4.8	166.7	19.4	0.096	54.2
EP01	60	84	986	7.2	337.1	22.5	0.035	14.0

(1) to enable a quantified synergism of CaG and APP in EP81.

$$E_s = \{LOI_{[APP+CaG]} - LOI_{EP}\}/\{(LOI_{APP} - LOI_{EP}) + (LOI_{CaG} - LOI_{EP})\} \quad (1)$$

where LOI_{EP}, LOI_{CaG}, LOI_{APP} and $LOI_{[APP+CaG]}$ are the respective values of EP, EP plus CaG, EP plus APP and EP plus the combined CaG and APP. Through incorporating LOI values of EP, EP1.1, EP8.9 and EP81 into (1), E_s value of EP81 can be calculated as 1.1 higher than 1, indicating the synergistic effect between CaG and APP. Hence, it is concluded that the combination of APP and CaG with a suitable mass ratio plays a positive role in enhancing the flame-retardant properties of epoxy resin, and there is an obviously synergistic effect between APP and CaG that can effectively reduce the flammability of EP.

CCT is now widely used to give an detailed assessment of the fire hazard of polymers during combustion [44,45]. It can provide useful information related to heat release, smoke and toxic gases, etc. As EP81 presented the best performance in the flame-retardant tests, it is chosen to be experimented on CCT along with EP, EP10 and EP01 taken as the

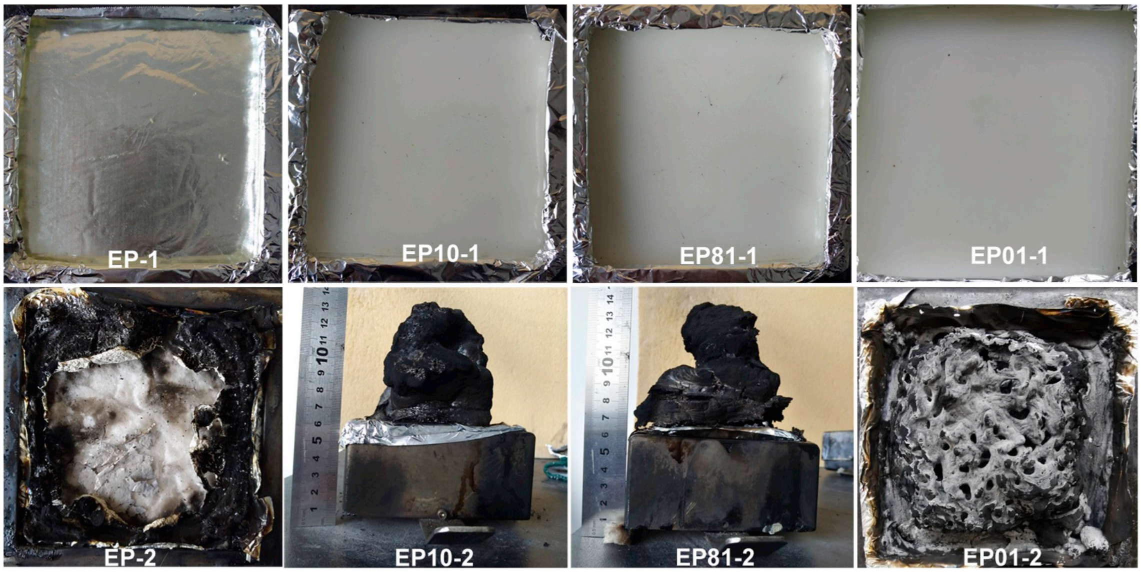

Fig. 4. Digital photos of EP, EP10, EP81 and EP01 before (1) and after (2) CCT.

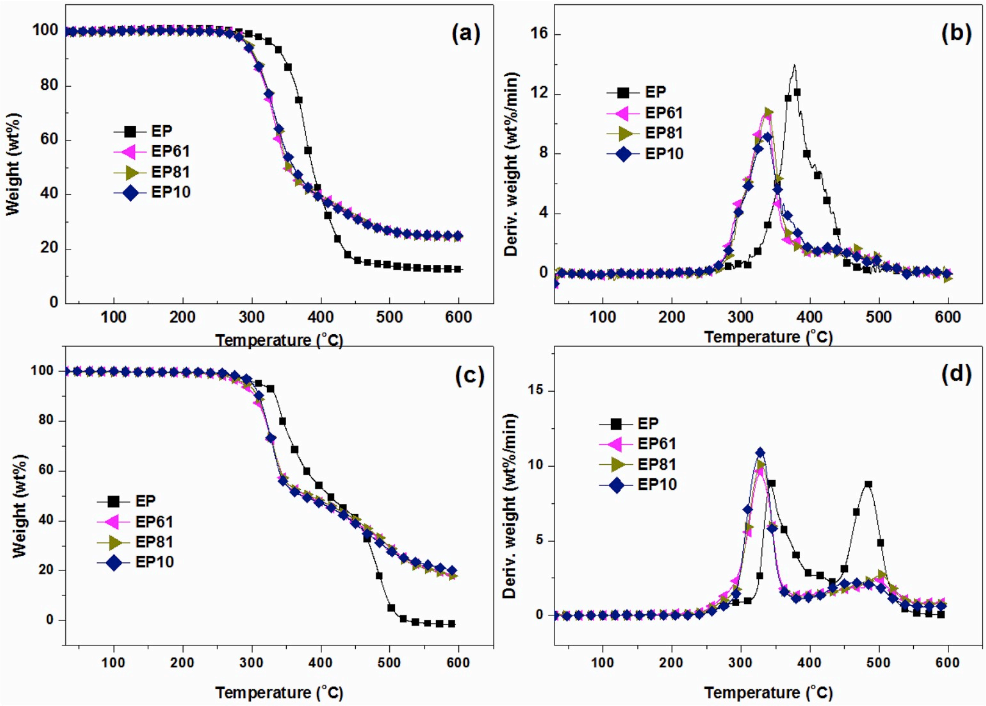

Fig. 5. TG (a, c) and DTG (b, d) curves of EP and IFR-EPs in nitrogen (a, b) and air (c, d) condition.

Table 3
Thermal-stability parameters derived from TG and DTG curves.

Samples	Nitrogen				Air			
	$T_{5\%}$ (°C)	T_{max} (°C)	Residue at T_{max} (wt%)	Residue at 600 °C (wt%)	$T_{5\%}$ (°C)	T_{max} (°C)	Residue at T_{max} (wt%)	Residue at 600 °C (wt%)
EP	332	377	64.2	12.6	310	345	79.8	0
EP61	293	334	63.0	24.7	287	328	72.4	17.8
EP81	296	338	63.2	24.5	292	328	73.5	17.5
EP10	293	334	63.1	24.9	298	328	73.1	19.8

controls. The curves of heat-release, residue mass, smoke-production and CO/CO_2-production or yield parameters are respectively illustrated in Fig. 1, Fig. 2 and Fig. 3. In addition, the detailed results including ignition time (TTI), PHRR, total heat release at the end of tests (THE), MARHE, FIGRA and mass are listed in Table 2.

It is found that there is some difference in TTI value for flame-retardant EP as compared to neat EP. Owing to the lower decomposition temperature of APP, phosphoric acids are firstly produced and then

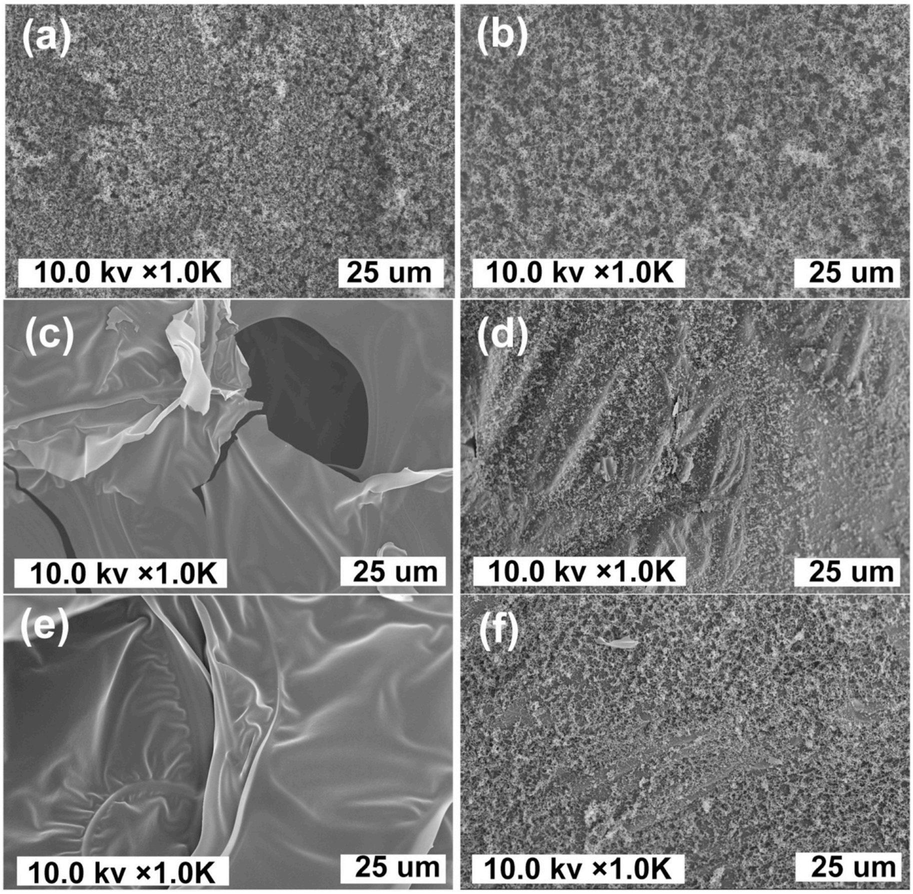

Fig. 6. Micro-morphologies of char residues for EP (a, b), EP10 (c, d) and EP81 (e, f) after CCT: inner-surface (a, c, e); outer-surface (b, d, f).

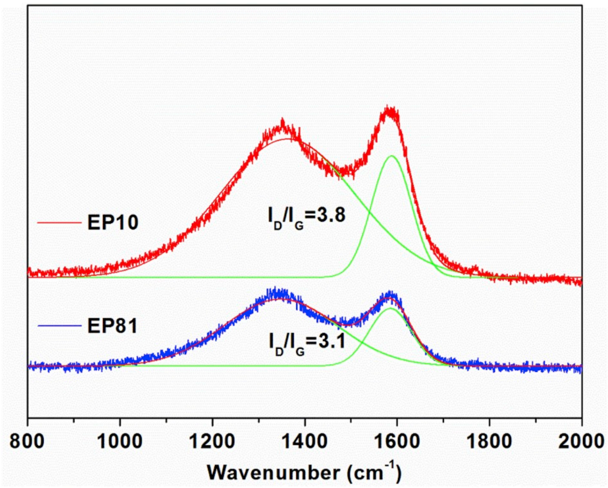

Fig. 7. The Raman spectra of EP10 and EP81.

promote the decomposition of epoxy thermosets in advance, which causes the early ignition of EP10 and EP81. As for EP01, although CaG decomposes earlier than EP, EP01 still has a higher TTI value as compared to other materials probably. It might be related to the release of CO_2 derived from the decomposition of CaG, which decrease the concentration of fuels and oxygen.

As is known, HRR is recognized as a useful parameter to evaluate the fire safety of polymers. It is notable that when APP, CaG or APP-CaG added, obvious reduction in PHRR value comes out. In detail, PHRR

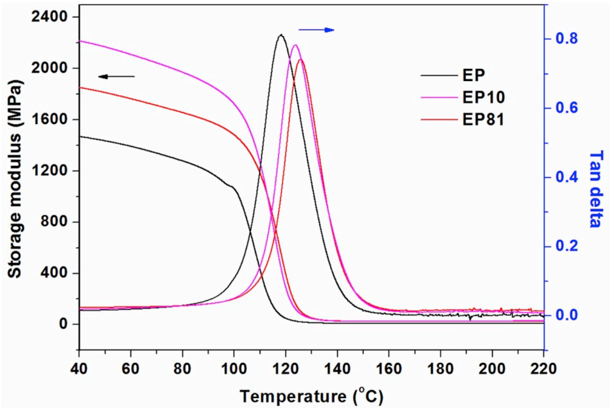

Fig. 8. The storage modulus and tan delta vs. Temperature of EP, EP10 and EP81.

Table 4
Thermo-mechanical and mechanical parameters of neat EP, EP10 and EP81.

	EP	EP10	EP81
T_g at the maximum tan delta (°C)	118	124	126
E′ at 40 °C (MPa)	1468	2215	1851
Tensile strength (MPa)	54 ± 8	51 ± 5	53 ± 4
Flexural strength (MPa)	108 ± 2	84 ± 11	76 ± 5
Flexural modulus (MPa)	3076 ± 146	2755 ± 48	2793 ± 102

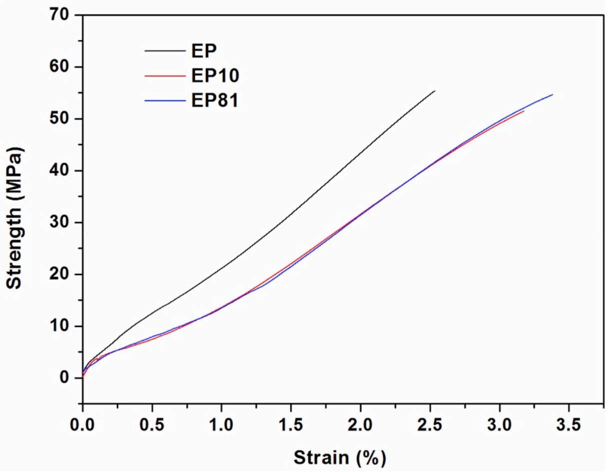

Fig. 9. The curves of tensile strength vs. strain for neat EP, EP10 and EP81.

value of EP is as high as 1462 kW/m^2, while EP10 and EP01 display lower PHRR values at 556 and 986 kW/m^2, respectively. Moreover, EP/APP shows a better result in the presence of CaG, as PHRR value of EP81 is obviously dropped to 336 kW/m^2 by 77% as compared to neat EP. The phenomenon reveals a synergistic effect between APP and CaG. Besides, average rate of heat emission (ARHE) determined by THR(t)/t, and fire growth rate (FIGRA) equal to the maximum value of HRR(t)/t are used to assess the fire hazards of materials [44]. In this work, FIGRA values are calculated by using the respective HRR and time at the first peak where HRR(t)/t is the maximum during the whole combusiton, which are collected in Table 2. It should be referred that if the FIGRA value becomes lower, it suggests the time to flashover of materials is delayed, which promises more time for people to escape from the fire scene. By comparison, FIGRA of EP81 is obviously decreased to 4.8 kW/m^2/s from 13.3 kW/m^2/s of EP, 7.9 kW/m^2/s of EP10, and 7.2 kW/m^2/s of EP01. In addition, the maximum value of ARHE (MARHE) of EP81 is 166.7 kW/m^2, which is the lowest among the tested materials. The lower FIGRA and MARHE values of EP81 mean that the combination of APP and CaG can further enhance the fire safety of epoxy resins as compared to EP10 and EP01. Moreover, EP81 also displays the lowest THE value of 27 MJ/m^2 and there are more char residues left as compared to EP, EP10 and EP01 according to Table 2 and Fig. 1. It supposes that a part of material is not pyrolyzed due to the protection of char layer, indicating EP81 shows more protective efficiency than EP10 although both of them can form a swelling char as shown in Fig. 4. Meanwhile, EHC is equal to the value of HRR against mass loss rate, and can be used to suggest the mechanism of flame retardants. It could be found that the average EHC value (av-EHC) of EP81 is the lowest and decreased from 23.0 MJ/kg of EP, 20.2 MJ/kg of EP10 and 22.5 MJ/kg of EP01 to 19.4 MJ/kg as compared to EP, EP10 and EP01 respectively. In other words, the burning degree of volatiles of EP81 is lowest among the tested thermosets. Hence, except the condensed activity of APP-CaG, there is some gaseous activity. The abovementioned phenomena reflect epoxy thermosets possibly undergoes more perfect formation process of swelling char under the reaction of APP and CaG.

As discussed before, the combustion of epoxy resin always accompanies with large heat release and production of heavy smoke. The smoke production parameters including SPR and TSP are illustrated in Fig. 2. Obviously, the trend of the curve of SPR versus time is similar to the curve of HRR versus time, and EP modified with APP and CaG individually both show the decreased SPR and TSP values than EP. Moreover, combined with APP and CaG, EP81 further suppresses the smoke production in the whole combustion as compared to EP10 and EP01. It is deduced that the promotion of smoke-inhibition is attributed to the lower decomposition rate of EP81 and more compact intumescent char layer formed in the existence of APP-CaG, and thus less fuels were released.

CO and CO_2 are the main toxic gases generated from the complete and incomplete combustion of polymers, respectively. As shown in Fig. 3, it is found that after the addition of APP both COP and CO_2P of EP10 decrease to some extent, owing to the condensed char-formation behavior of APP. While, the char layer of EP10 might be not enough compact to prevent the diffusion of CO_2 and CO, since there are two peaks in the curves of COP and CO_2P versus time, and the same phenomenon is found in the curves of HRR and SPR versus time of EP10 as well. The phenomenon also appears for EP01, since its char residue is also porous and not compact. Besides, EP01 presents relatively higher CO_2P as compared to EP10 and EP81, which is possibly due to the further decomposition of $CaCO_3$ proven by Fig. S4. Therefore, the av-COY/av-CO_2Y ratio of EP01 is the lowest. Nevertheless, EP81 displays the lowest COP and CO_2P among the tested materials, indicating that the combination of APP and CaG exerts more positive effect on increasing the char residues leading to the production of less fuels so as to further reduce the COP and CO_2P of epoxy thermosets. Besides, the av-COY/av-CO_2Y ratio of EP81 is 0.096 higher than 0.047 of EP, 0.068 of EP10 and 0.035 of EP01, suggesting that EP81 experiences more incomplete combustion probably because of the effective insulation of char residues.

Based on the discussions above, the simultaneous improvements in the flame retardancy and reduction of heat release as well as smoke/toxic gases production are obtained when CaG is incorporated into EP/APP system, indicating APP-CaG actually exerts synergistic effect on promoting the formation of improved char.

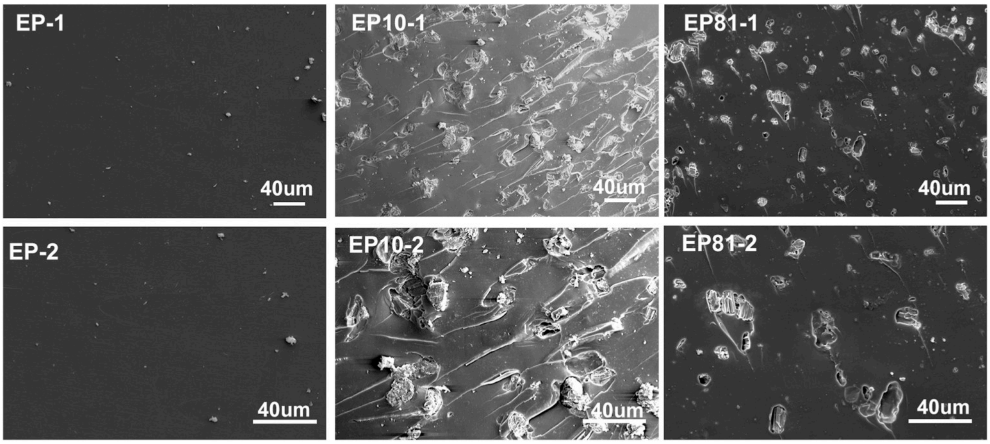

Fig. 10. The micro-morphologies of the cross-section for EP, EP10 and EP81.

3.2. Thermal stabilities

As CaG is beneficial to enhance the flame-retardant properties of EP/APP, it is noteworthy to explore how it will affect the thermal properties of EP and EP/APP. Hence, TG tests are experimented under nitrogen and air atmosphere for EP, EP61, EP81 and EP10, which are illustrated in Fig. 5 and Table 3. Under nitrogen atmosphere, it is clear that in the presence of IFRs the thermal stabilities of materials all decrease to some extent, since $T_{5\%}$ corresponding to the temperature of 5 wt% loss decrease from 332 °C of EP to 293, 296 and 293 °C for EP61, EP81 and EP10 respectively. Besides, T_{max} considered as the temperature of the maximum mass loss for all modified EP also decrease, as well as the residues at T_{max}. The phenomenon is related to the lower thermal stabilities of APP and CaG (Fig. S3) as compared to EP, which will promote the decomposition of epoxy resins. Nevertheless, it is found that the residues for EP containing APP or APP-CaG are all higher than neat EP, indicating the remarkable carbonization effect of APP or APP-CaG. Besides, the thermal parameters including $T_{5\%}$, T_{max} and residual mass, and decomposition trends of EP/APP-CaG (as seen in Fig. S2 and Table S1) are similar to that of EP10, suggesting that the addition of CaG does not obviously affect the thermal stability of EP modified with APP individually. While under air atmosphere, there is almost no residue left for EP owing to the further oxidation of unstable char in the range of 400–550 °C. As for modified EP, both the $T_{5\%}$ and T_{max} of them are significantly decreased, and it is shown that $T_{5\%}$ of epoxy thermosets modified with APP-CaG are all lower than EP/APP, which is caused by the lower thermal decomposition temperature of CaG. However, it is interesting that the residues mass of IFR-EPs are much higher than that of EP, and the dramatic weight loss is not found in IFR-EPs although there is a gentle weight-loss step, that is to say, the immediate generated before 400 °C is more stable than that of EP. Based on the above, it is speculated that APP and APP-CaG can promote the formation of more stable residues at high temperature.

3.3. Flame-retardant mechanism

According to TG analyses, it is known that CaG would not show obvious effect on the thermal stability of EP/APP. Thus, it is a question what is the difference of char residues between EP modified with APP individually and EP containing APP-CaG causing the different results in terms of LOI, UL-94 and CCT. To make it clear, SEM-EDX was utilized to analyze the char residues as shown in Fig. 6.

The char residue of neat EP exhibits loose micro-morphology both in the inner-surface and outer-surface, which is not beneficial to insulate heat and fuel. After modification of APP, the outer-surface of char is more compact and continuous. Although the inner-surface of char is more continuous, it seems not strong enough to prevent the released gases such as water and ammonium derived from APP to break through the char layer. As a consequence, the char layer is not perfect to inhibit the transfer of heat and diffusion of fuels, so that EP10 cannot pass UL-94 rating and double peaks are existed in the curves of HRR and SPR vs time. With the help of CaG, the quality of char layer is improved that the inner-surface of char is more compact and continuous, and there is no cavity existing. It suggests that the reaction between CaG with APP plays a dominant role in improving the char quality. Because of the thermal decomposition of CaG, CaO is released [39,40] and then reacted with phosphoric, pyrophosphoric and polyphosphoric acid derived from APP [14] to produce calcium phosphate, and it is proved by FTIR and XRD spectra of the residues of APP-CaG after heat-treated at 800 °C in muffle (Fig. S4). Actually, we find that CaO and $CaCO_3$ both exist in the residue of CaG according to the XRD spectra. However, after blended with APP, CaO or $CaCO_3$ are not found any more in the residue of CaG according to the relevant FTIR and XRD spectra. In contrast, some diffraction peaks at 12.1, 25.0, 33.7 and 59.7° related to $Ca_2P_2O_7$ appear in the XRD spectrum of the residue for APP-CaG, and the characteristic absorption peaks at about 490 and 1000 cm^{-1} are related to PO_4^{3-}, and the peaks at 720 and 920 cm^{-1} belong to pyrophosphates [46]. Therefore, it is confirmed that the reactions between CaO or $CaCO_3$ and some phosphoric acids like pyrophosphoric or polyphosphoric acid happen, which lead to the formation of calcium phosphate. As seen, the presence of inorganic calcium phosphate as a protective ceramic like shield is beneficial for the quality of chars [47,48], and the existence of calcium is confirmed by EDX shown in Table S2. Accordingly, the combination of APP and CaG helps to further enhance the quality of char layer.

In order to further study the difference of the char residues, the order degree of chars for EP10 and EP81 were characterized by LRS. It could be seen from Fig. 7 that there are two peaks at approximately 1360 and 1590 cm^{-1} which belong to D- and G-band respectively. In general, the existence of D band is caused by the vibrations of amorphous char, while the appearance of G band is on account of the vibration of sp^2-hybridized carbons. Through calculating the area ratio R of D-band and G-band it helps to identify the graphitization degree of char, as the value of $R = ID/IG$ has inversely proportional relationship with the graphitization degree of the chars [49]. Besides, graphitization-char as a compact and effective barrier is more beneficial to isolate the fuels and even insulate the transfer of heat and oxygen. As seen, the value of I_D/I_G for EP81 is 3.1 lower than that of EP10, indicating more graphitization-char is formed during combustion. As a consequence, the combination of APP-CaG contributes to flame-retard epoxy resin.

3.4. Mechanical properties

It is known that although polymers modified by physical methods would have obvious improvement in flame retardancy, it would always accompany with the deterioration of mechanical properties. Hence it is of significance to explore the effect of APP-CaG on the mechanical properties of EP. Firstly, DMA is adopted to study the thermo-mechanical behaviors of EP and EP containing APP-CaG. As seen in Fig. 8 and Table 4, it is clear that the glass transition temperatures (T_g) of EP10 and EP81 are higher than that of EP, which might be related to that APP or APP-CaG particles could restrict the motion of chain segment of epoxy. Accordingly, the storage modulus (E′) of EP10 and EP81 are both increased remarkably to 2215 and 1851 MPa.

Besides, mechanical properties related to tensile and flexural parameters were also tested. As seen in Fig. 9, pure EP is very brittle, anddoes not yield during the tensile tests. EP10 and EP81 display the same behavior during testing, while the slope of the tensile strength vs. strain curves are lower than that of EP possibly due to the lower rigidity of them. After fracture, EP gets a tensile strength of about 54 MPa. As for EP10, although tensile strength has no obviously decrease, its flexural strength and modulus are markedly decreased from 108 to 3076 MPa of EP to 84 and 2755 MPa. It is clear from Fig. 10 APP is dispersed evenly in the epoxy matrix, while some cavities and bad interface are found, and it indicates a weak interfacial action between APP and epoxy matrix. After CaG is incorporated, although the dispersion of APP is not improved much, tensile strength of EP81 is close to that of EP10 and EP. However, flexural strength of EP81 is further decreased from about 84 MPa of EP10 to approximately 76 MPa. Nevertheless, EP81 still possesses a high strength in consideration of tensile strength.

4. Conclusions

Eco-friendly calcium gluconate (CaG) was incorporated into the intumescent flame-retardant epoxy resin based on APP, and it was found that EP containing APP and CaG (mass ratio, 8:1) showed the best flame retardancy that it achieved the highest LOI value of 31.8%, passed a UL-94 V-0 rating, and greatly enhanced the effect on suppressing the production of smoke, and CO/CO_2. During the whole combustion, EP81 exhibited a large reduction in terms of SPR, TSP, COP and CO_2P. Besides, heat-release parameters including HRR and THE also showed an obvious decrease that THE value of EP81 dramatically decreased to 27 MJ/m^2 and the PHRR value to 336 kW/m^2. According to the analyses of char residues, the better flame retardancy and enhanced ability of smoke suppression was attributed to the more continuous and compact char residues. Moreover, the introduction of CaG didn’t show obvious effect on the mechanical properties of EP/APP, and tensile strength of EP81 was still maintained at a high value.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2019.107200.

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