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Synergistic SiO₂@DPPA flame retardancy for enhancing flame retardancy and thermal insulation in epoxy resin

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Abstract

Novel and environmentally flame-retardant epoxy resin coating that maintain outstanding physical performance are urgently needed for high-tech fields. In this work, SiO₂@DPPA was successfully synthesized and incorporated together with SiO₂ aerogel and OMMT into EP to prepare EP/SiO₂@DPPA composite coatings. Increasing the SiO₂@DPPA content progressively enhances the flame retardancy, with a 2wt% SiO₂@DPPA content yielding the optimal flame retardancy performance for EP. Compared to EP composite coating, the peak heat release rate (pHRR), total heat release (THR) and total smoke production (TSP) values of EP/SiO₂@DPPA composite coatings decreased effectively by 47.6%, 47.6% and 41.5%, respectively. The excellent heat and smoke reduction performance of the composite coatings was further validated through condensed and gas phase flame retardancy mechanism. Moreover, the EP/SiO₂@DPPA composite coatings has good mechanical properties, including the tensile strength of 11.1 MPa. This work further validates the feasibility of preparing flame-retardant high-performance polymer materials by adding organically modified SiO₂.

Keywords: Flame retardancy, Composite coatings, Thermal insulation, Epoxy resin

1. Introduction

Epoxy resin (EP) possesses numerous advantages, including high mechanical strength, excellent thermal stability, strong adhesion, and low shrinkage. Additionally, it offers good processability and high reactivity. However, the flammability of EP restrict its application under increasingly stringent flame-retardant regulations. The

development of flame-retardant modification for EP has become crucial in expanding its application field^[1-3].

In recent years, nano-fillers have emerged as promising flame retardants, including aerogel, layered double hydroxides, carbon material, and others^[4,5]. Among them, aerogel is the most prominent due to its low bulk density, low required addition levels, ultra-low thermal conductivity and high flame-retardant efficiency. Recently, SiO₂ aerogel has emerged as a promising non-toxic, environmentally friendly flame retardant additive in the development of flame-resistant polymer composites. The composite coatings with SiO₂ aerogel would serve as an effective flame retardant that impedes the transfer of heat and flammable volatiles^[6-8]. Xue et al.^[9] prepared a SiO₂/PI/AF aerogel composite and reported that the aerogel incorporation effectively lowered its thermal conductivity and enhanced its flame retardancy. The surface modification of SiO₂, achieved through either physical adsorption or chemical bonding, not only improves its dispersibility but also allows for the incorporation of flame-retardant functional groups, thereby enhancing its overall flame retardancy^[10-12]. The DPPA is an organophosphorus flame retardant, which imparts flame retardancy to EP via free radical trapping. Meanwhile, the organophosphorus flame retardant can also catalyze carbonization, reinforcing the char layer structure and consequently reducing the release of heat and smoke^[13-16]. Therefore, integrating SiO₂ aerogel with other flame-retardant functional groups to construct an efficient flame-retardant system represents a promising research direction.

In this work, DPPA was modified onto SiO₂ to leverage the synergistic effect of gas-phase and condensed-phase flame retardancy. The thermal stability, flame retardancy, and mechanical properties of the EP/SiO₂@DPPA composite coatings were systematically evaluated. Based on these results, the flame-retardant mechanism of SiO₂@DPPA was proposed and confirmed.

2. Experimental

2.1 Materials

SiO₂ aerogel (SA 20-40 nm) was purchased by Needleless Technology Group Co., Ltd. (Hebei, China). Sodium montmorillonite (Na-MMT, K10 grade) was purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Tetraethyl orthosilicate (TEOS, 98% purity), and diphenyl azidophosphate (DPPA, 97% purity) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

Anhydrous ethanol (analytical grade) and acetone (analytical grade) were acquired from Shenyang Xinhua Chemical Reagent Factory.

2.2 Synthesis of SiO₂@DPPA

Deionized water (7.2ml) and anhydrous ethanol (23.6 mL) were combined and mixed thoroughly. Subsequently, TEOS (4.46 mL) was added to the mixture under continuous stirring. After magnetic stirring for 3 h, a cross-linked transparent silica sol-gel was obtained. DPPA (4.36g) was introduced into the prepared SiO₂ sol-gel. The resulting mixture was transferred into a 100 mL autoclave and heated at 160 °C for 12 h under vacuum conditions. After cooling to room temperature, the solution was filtered, and the supernatant was removed. The precipitate was washed several times with deionized water, anhydrous ethanol, and acetone, followed by drying in a vacuum oven at 80 °C for 10 h. The particles were obtained, ground into powder (SiO₂@DPPA) and stored in a sealed container. The reaction process is shown in Fig. 1a.

2.3 Preparation of composite coatings

First, 41.07wt% deionized water (all percentages are by mass unless specified) was mixed with 2.03wt% dispersant SN-5040, 0.05wt% defoamer NXZ, 0.38wt% pH regulator (alkaline polyamine), 7wt% SA. The mixture was then subjected to high speed dispersion at 5000 rpm for 30 min using a high-shear mixer. Subsequently, 49.54wt% curing agent 235B was added and further dispersed at 5000 rpm for 10 min to obtain the SA slurry. For the final composite coating preparation, specified amounts of functional fillers, flame retardants, and 33.3wt% epoxy resin were incorporated into the prepared silica aerogel slurry. The mixture underwent intermediate speed dispersion at 3000 rpm for 10 min to yield the thermally insulating and flame-retardant composite coating. The preparation process is shown in Fig.1. Through controlled variable methodology, the optimal additive concentrations were determined as: 7 wt% SA, 2 wt% OMMT, with SiO₂@DPPA incorporated at three different loadings (1wt%, 2 wt%, and 3 wt%). The composite coatings were designated as 7-2-1, 7-2-2, and 7-2-3 respectively, corresponding to their SA-OMMT-SiO₂@DPPA mass ratios.

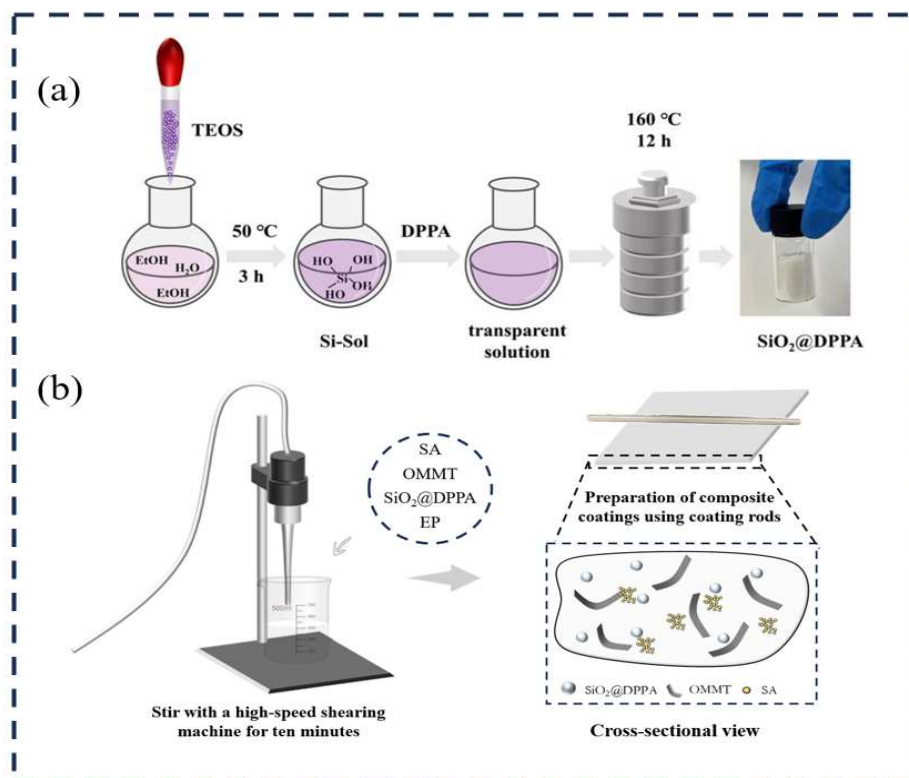


Fig. 1 (a) Scheme illustration for the preparation of SiO₂@DPPA. (b) Preparation of composite coatings

2.4 Characterizations

Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Tensor 27 spectrometer (Bruker Corporation, Germany) to analyze the chemical composition of the coatings. X-ray photoelectron spectroscopy (XPS) analysis of the synthesized flame retardant was conducted using a Nexsa Thermo Scientific spectrometer (Thermo Fisher Scientific, USA) equipped with a 0.5-5 keV Ar⁺ ion source. The analysis employed an ion beam spot diameter of 1-10 mm with a sputtering rate ranging from 0.1 to 50 nm/min. Morphological characterization of the dispersed fillers was carried out using field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma 300, Germany). Phase composition analysis of post-combustion coating samples was performed by X-ray diffraction (XRD, Bruker D8 Advance, Bruker Corporation, Germany) using Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. Thermal insulation performance was evaluated using a multi-channel temperature tester (VG1008S, China) according to standard testing protocols. Electrochemical corrosion resistance was assessed following the method described by a literature^[17]. Coating specimens were immersed in 3.5wt% NaCl solution, and polarization curves were recorded using an electrochemical workstation.

3. Results and discussion

3.1 Microstructure of SiO₂@DPPA

Fig.2 shows the FTIR spectra of DPPA, SiO₂, and SiO₂@DPPA. A comparison of the FTIR spectra of SiO₂@DPPA with those of SiO₂ and DPPA reveals a significant reduction in the -OH stretching vibration peak^[18], while the absorption vibration peak of Si-O-Si at 1085 cm⁻¹ is present. Additionally, a new peak corresponding to Si-O-P appears at 1068 cm⁻¹, indicating that Si-OH has been replaced by organic groups and that the organosilicon phosphorus-containing compound SiO₂@DPPA has been successfully prepared^[19].

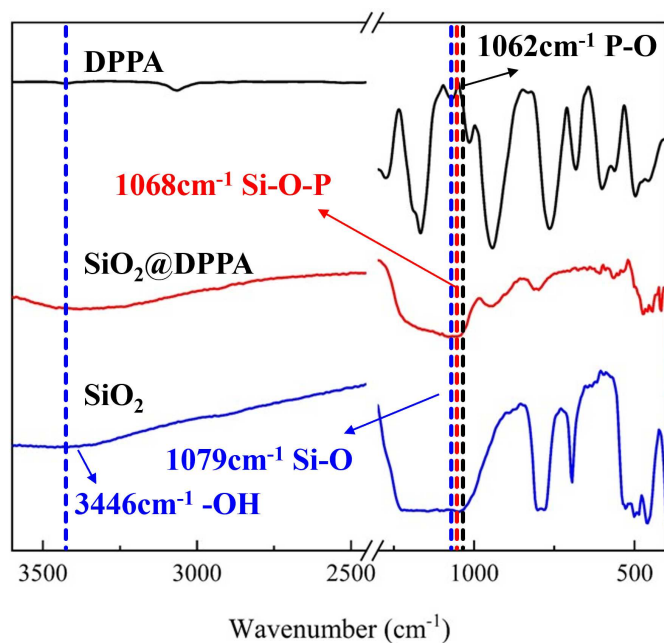


Fig. 2 FTIR spectra of DPPA, SiO₂, and SiO₂@DPPA composites.

The XPS spectra reflect the elemental species contained in SiO₂ and SiO₂@DPPA, as shown in Fig. 3. SiO₂ contains Si and O elements, while SiO₂@DPPA contains Si, O, C, and P elements. In Figure 3(b), the binding energy of 102.9 eV corresponds to the Si-O-Si bond of SiO₂. In Figure 3(d), the Si 2p peak of SiO₂@DPPA exists two peaks, corresponding to the Si-O-Si bond and the Si-O-P bond, respectively [105]. In Figure 3(e), the O 1s peak of SiO₂@DPPA exists two peaks, corresponding to the P-O bond and the Si-O bond, confirming the formation of the P-O-Si bond^[20] and the successful preparation of SiO₂@DPPA^[21].

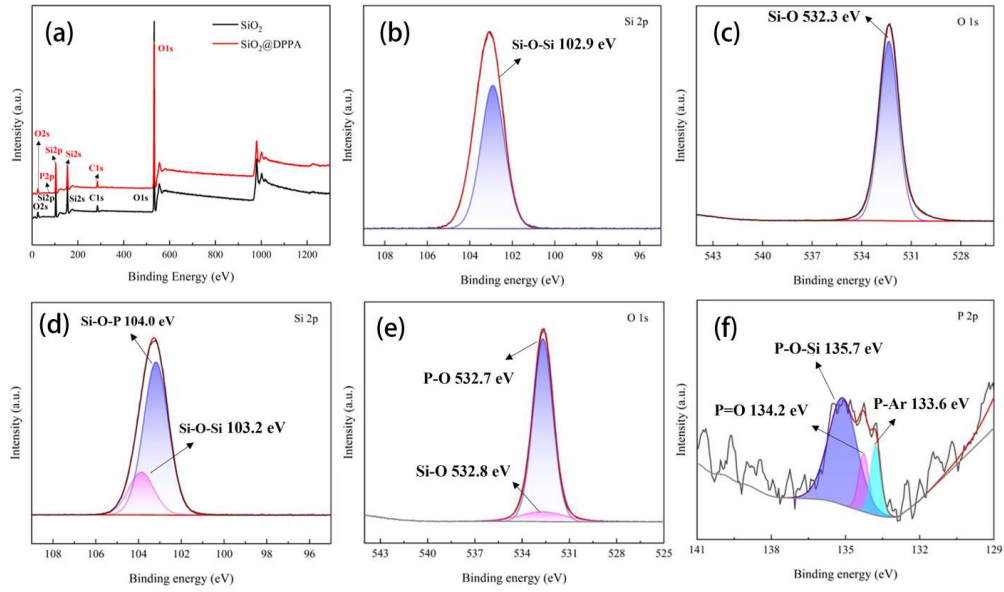


Fig. 3 XPS spectra of full spectra of (a) SiO_2 and $\text{SiO}_2@\text{DPPA}$, (b) Si 2p and (c) O 1s of SiO_2 ; (d) Si 2p, (e) O 1s, and (f) P 2p of $\text{SiO}_2@\text{DPPA}$.

3.2 Microstructure of EP/ $\text{SiO}_2@\text{DPPA}$ composite coatings

Fig. 4(a-d) shows the surface morphology and cross-sectional morphology of EP/ $\text{SiO}_2@\text{DPPA}$ composite coatings. Control the ratios of SA, OMMT, and $\text{SiO}_2@\text{DPPA}$, three contents of SA/OMMT/EP/ $\text{SiO}_2@\text{DPPA}$ composite coatings (abbreviated to EP/ $\text{SiO}_2@\text{DPPA}$ as follow) were prepared, with the content of 7wt% SA, 2wt% OMMT and 2wt% $\text{SiO}_2@\text{DPPA}$. As shown in Fig.4(a-b), the surface of the composite coating is dense and uniform. The addition of $\text{SiO}_2@\text{DPPA}$ would enhance the intermolecular crosslinking density, while the porous structure and surface protrusions increase the amount of air stored within the coating, forming a stable air layer inside.

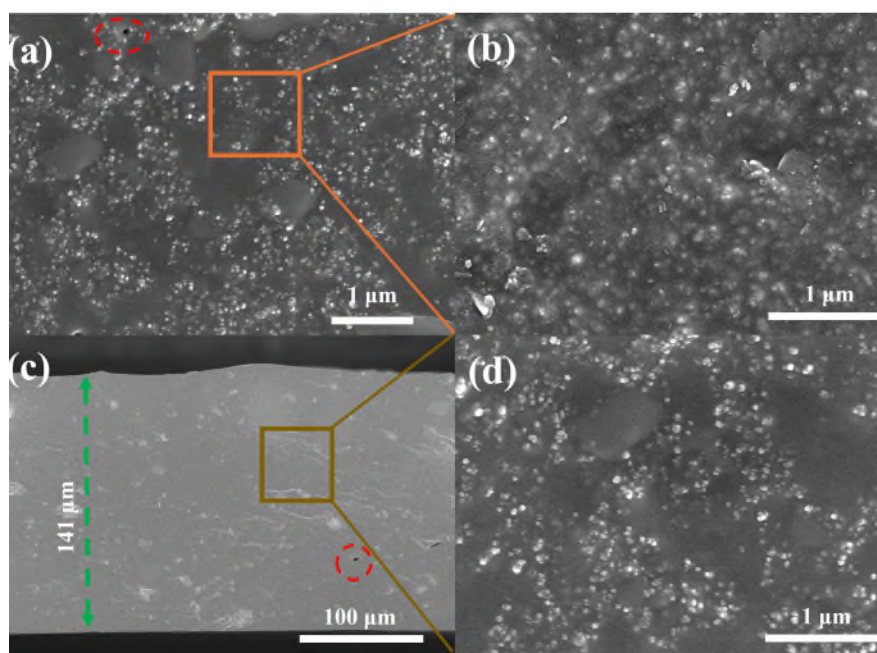


Fig. 4 SEM of EP/SiO₂@DPPA composite coatings. (a-b) surface morphology (c-d) cross-sectional morphology.

The reason for the generation of these characteristic peaks is the presence of Si elements and phosphorus-containing groups in the composite coating. Furthermore, the peaks at 1654 cm⁻¹, 1543 cm⁻¹, and 1425 cm⁻¹ indicate the formation of new aromatic hydrocarbons and polyaromatic hydrocarbons in the coating. The rapid cracking reaction of the aromatic ring indicates that the resin undergoes isomerization during the decomposition process. This reaction can improve the degree of crosslinking and form a char layer, which inhibits the generation of gaseous products in the later stage of decomposition. These results are all conducive to the application of flame retardants^[22]. The FTIR results further suggest that the presence of phosphorus-containing substance and SiO₂ in SiO₂@DPPA powder can promote the carbonization of the polymer matrix; The latter can further enhance the strength of the coating. The combination of the two effectively prevents the material beneath the coating from burning by forming a charlayer^[23], which is the main reason why 7-2-2 has better flame retardancy.

The FT-IR spectra of the EP/SiO₂@DPPA composite coatings are shown in Fig.5. In the EP/SiO₂@DPPA composite coating, the stretching vibration of Si-O-Si at 1056 cm⁻¹ and the peak of P-O-C at 1098 cm⁻¹ originates from the SiO₂@DPPA compound. The SiO₂@DPPA organic phosphorus compounds would promote the formation of char layer, which suppress flames and play a positive role in the gas phase^[24]. The peaks at 1654 cm⁻¹, 1543 cm⁻¹, and 1425 cm⁻¹ indicate the formation of new aromatic and

polyaromatic hydrocarbons in the composite coating. The rapid cleavage of aromatic rings implies that isomerization occurs during the decomposition of the resin, which improves the degree of crosslinking and facilitates the formation of a char layer. This inhibits the generation of gaseous products in the later stages of decomposition, contributing to the flame-retardant effect^[25].

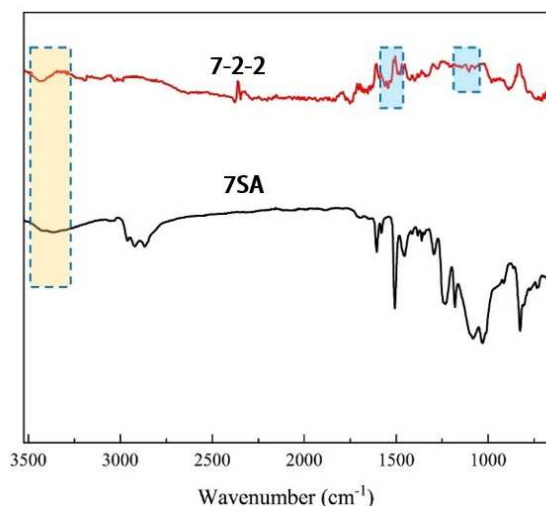


Fig. 5 FTIR spectra of EP/SiO₂@DPPA composite coatings.

3.3 Thermal insulation test

The EP/SiO₂@DPPA composite coatings were measured on pure tinplate as the metal substrate to evaluate their thermal insulation performance. Fig.6 shows the temperature difference of the EP/SiO₂@DPPA composite coatings with the different content of SiO₂@DPPA. In the EP/SiO₂@DPPA composite coatings, the content of SA is 7%, the content of OMMT is 2%, and the content of SiO₂@DPPA is 1%, 2%, and 3% by mass fraction, respectively. The heating rates of the EP/SiO₂@DPPA composite coatings were similar under 80 °C. When the temperature exceeded 80 °C. The heating rate of the pure EP increased, indicating a reduction in its thermal insulation capability. The surface temperature of EP/SiO₂@DPPA (2wt%SiO₂@DPPA) composite coatings reached only 100.2 °C when the heated side temperature reached 130 °C.

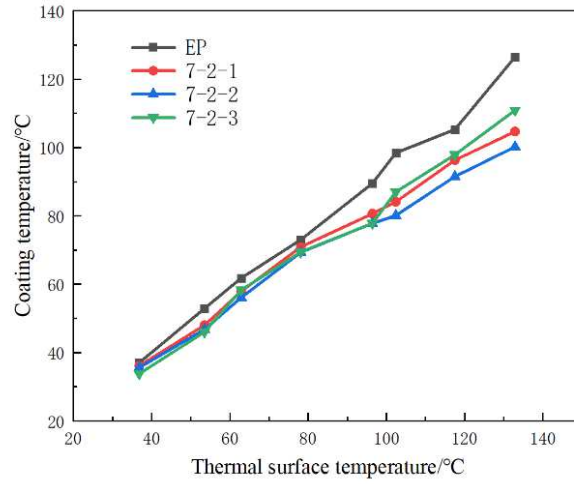


Fig. 6 Thermal insulation of EP and EP/SiO₂@DPPA composite coatings.

Fig.7 shows the flame retardancy test results of the EP/SiO₂@DPPA composite coatings under a heat flux of 35 kW/m², including the peak heat release rate (pHRR), total heat release (THR), smoke production rate (SPR), and total smoke production (TSP). The pure EP has a pHRR of 479.3 kW/m² and a THR of 8.4 MJ/m². Compared with the pure EP, EP/SiO₂@DPPA composite coatings show a reduction in pHRR. Among them, the EP/SiO₂@DPPA (2wt% SiO₂@DPPA) composite coating shows a pHRR value of 247.2 kW/m², a decrease of 48.4%, and a THR of 4.4 MJ/m², a reduction of 47.6%. After reaching the peak value, and the combustion time also prolonged, which indicates that the residues might have played a protective role during the combustion process. The TSP of EP coating is 2.7 m². The TSP value of EP/SiO₂@DPPA (2wt% SiO₂@DPPA) composite coating is 1.58 m², a reduction of approximately 41.5%. It indicates that SiO₂@DPPA would improve the flame retardancy of the composite coating.

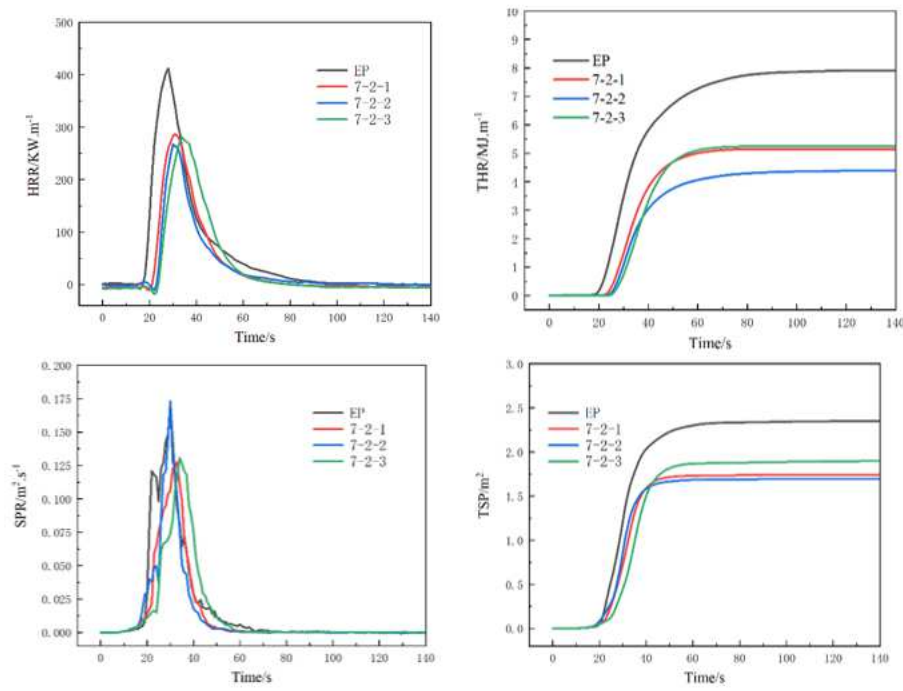


Fig. 7 Specific results of the flame retardancy test of EP and EP/SiO₂@DPPA composite coatings: (a) HRR, (b) THR, (c) SPR, (d) TSP.

Table 1 Comparison of the flame retardant properties of composite coatings with other reported [26-31].

Sample	pHRR (kW/m ²)	Ref
EP/SiO ₂ @DPPA	267.79	This work
EP/5Co-MOF-74&2DOPO	739.02	26
EP/5Ni-MOF-74&2DOPO	732.39	26
PVA/PNC-12.5	257.3	27
EP/Talc@FeHP	540.02	28
PLA/MXene-PAMn/CMSs	310.2	29
EP/5-LKD	366.8	30
PP/25wt%Si1.2PAP	350.8	31
WPU/PHID/Si	448.0	32

In conclusion, the flame-retardant performance of the EP/SiO₂@DPPA composite coatings was evaluated and compared with other reported retardant performance of the composite coating (as shown in Table 1). The results demonstrate that the EP/SiO₂@DPPA composite coatings exhibit the lower peak heat release rate (pHRR), relative to most counterparts. Notably, this advantage is achieved at a loading level within the common range while employing a simpler preparation method.

3.4 Chemical stability test

Fig.8 shows the potentiodynamic polarization curves of EP/SiO₂@DPPA composite coatings in a 3.5wt% NaCl solution at 30°C. Table 2 presents the potentiodynamic polarization parameters of the EP/SiO₂@DPPA composite coatings with the different content of SiO₂@DPPA. The corrosion current of sample EP/SiO₂@DPPA (2wt% SiO₂@DPPA) composite coatings is 1.79×10^{-11} A, which is six orders of magnitude lower than that of Q235 steel. It indicate that the EP/SiO₂@DPPA composite coatings would block water molecules and corrosive ions to enhance the the corrosion resistance.

Table 2 presents the corresponding strength and elongation of the EP/SiO₂@DPPA composite coatings. The tensile strength of the EP/SiO₂@DPPA composite coatings with 2wt% SiO₂@DPPA reached 11.1 MPa, which decrease 14.5% compared to the EP coating.

Table 2 Potentiodynamic polarization parameters and tensile strength of EP/SiO₂@DPPA composite coatings

Sample	Self-corrosion potential (V)	Self-corrosion current density (A·cm ⁻²)	Tensile strength (MPa)	Contract ion (%)
Q235	-0.72	2.31×10^{-5}		
EP			12.9	23.0
EP/1wt%SiO ₂ @DPPA	-0.17	7.73×10^{-11}	10.1	31.6
EP/2wt%SiO ₂ @DPPA	-0.14	1.79×10^{-11}	11.1	34.3
EP/3wt%SiO ₂ @DPPA	-0.18	1.72×10^{-10}	9.4	30.6

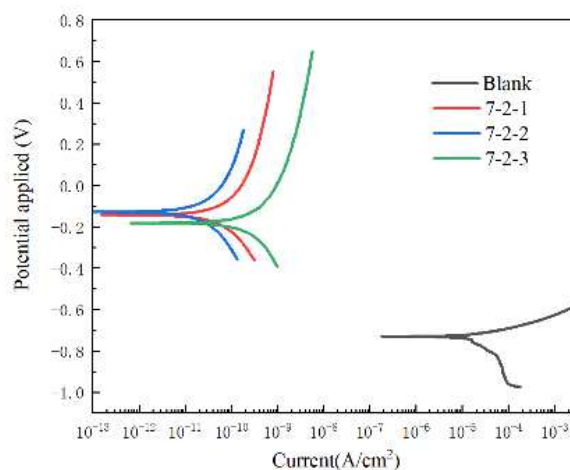


Fig. 8 The potentiodynamic polarization curves of composite coatings.

Fig.9 shows the XRD of EP/SiO₂@DPPA composite coatings after combustion. The P₂O₅ was produced by the decomposition of SiO₂@DPPA, corresponding to the characteristic peak of 20.8° and 31.1°. The SiO₂@DPPA retardants can catalyze the carbonization of the polymer matrix in the solid phase and capture H• and OH• radicals in the gas phase, thereby terminating the combustion reaction. The SiO₂@DPPA would promote the formation of the char layer by esterification and dehydration processes. The dense char layer would protect polymer materials, demonstrating excellent performance in reducing fire load and inhibiting flame spread.

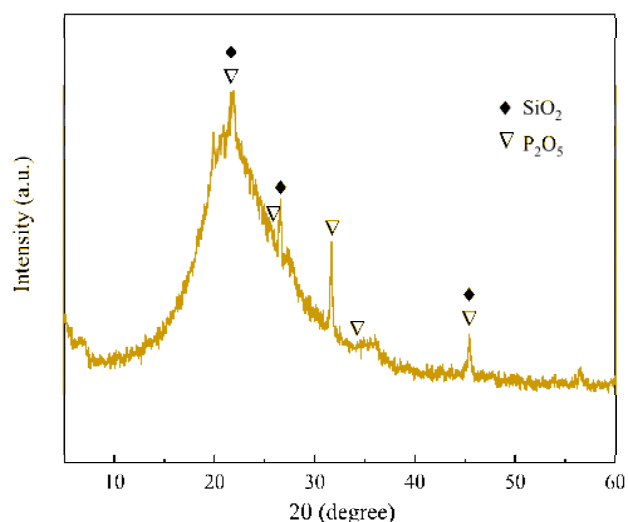


Fig. 9 XRD of EP/SiO₂@DPPA composite coatings after combustion.

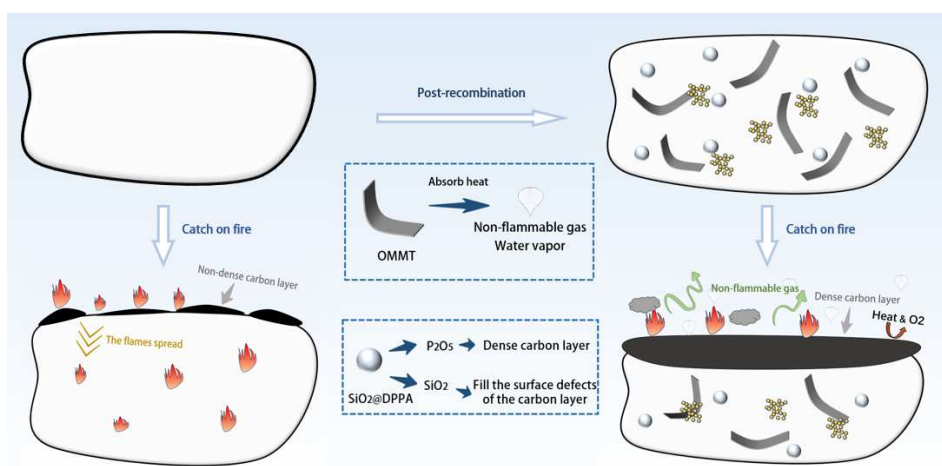


Fig.10 The flame-retardant mechanism for EP/SiO₂@DPPA composite coatings.

The above analyses support a comprehensive flame-retardant mechanism for the EP/SiO₂@DPPA composite coatings, illustrated in Fig.10. At the onset of combustion, SiO₂@DPPA phosphate groups decompose into polyphosphoric acid, catalyzing

polymer cross-linking/carbonization to form the initial char layer. Meanwhile, SiO₂@DPPA pyrolysis produced some P-containing compounds and non-combustible gases, which could dilute the concentration of combustible gases in the combustion zone of the gas phase. The results of XRD show that the P₂O₅ in the residual char, confirming that polyphosphoric acid forms a stable phosphoresidual char. In the condensed phase, phosphorus-containing compounds such as phosphoric acid generated by DPPA pyrolysis initiated carbonization, and SiO₂ was able to form a stable and dense char layer on the surface of EP. The multi-porous SiO₂ has an adsorption effect in the fire scene to suppress the smoke. SiO₂ migrates to the surface of the coating to fill the uneven holes and cracks in the coating. OMMT would decompose and release a large amount of crystalline water, which will evaporate and absorb a large amount of heat, reducing the surface temperature of the composite coating to cool the matrix. Above all, the EP/SiO₂@DPPA composite coatings have acted as a physical protective barrier to play the role of heat insulation and oxygen isolation, preventing the further spread and development of the fire.

4. Conclusion

In summary, the SiO₂@DPPA flame retardant was successfully developed. The incorporation of 7wt% SA, 2wt% OMMT together with 2wt% SiO₂@DPPA significantly reduced the fire hazards of epoxy resin, as evidenced by pronounced decreases in peak heat release rate and toxic gas production in cone calorimeter tests. Specifically, the pHRR values of the EP/SiO₂@DPPA composite coatings were reduced by 428.4%, while TSP was suppressed by 41.5% compared with neat EP. This is because phosphorus-containing flame retardants can catalyze the carbonization of the polymer matrix to form a char layer and simultaneously capture H• and OH• free radicals in the gas phase, thereby terminating the combustion reaction. This dense phosphorus-based carbonized layer can effectively protect the substrate and has good protective capabilities in terms of fire load and reducing flame spread. Thermal insulation tests show that EP/SiO₂@DPPA composite coatings has a temperature difference of 29.8 °C at 130°C. Polarization curve results show that the corrosion current density of EP/SiO₂@DPPA composite coatings is $1.79 \times 10^{-11} \text{ A} \cdot \text{cm}^{-2}$, which is six orders of magnitude higher than that of Q235 steel.

Authorship contribution statement

Tiannan Man: Methodology, Formal analysis, Data curation. **Le Fu:** Writing, Methodology, Investigation, Formal analysis. **Zhaolong Xiang:** Formal analysis, Methodology. **Zhisheng Nong:** Formal analysis, Funding acquisition, Conceptualization. **Shanshan Guo:** Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

Reference

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