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Processable Main-chain Benzoxazine Resin Derived from Daidzein with Intrinsic Flame Retardancy

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Electronic Supplementary Information

Abstract The development of intrinsically flame-retardant, low-smoke, low-toxicity, and halogen-free polymers represents a critical challenge. In this study, bio-based daidzein was employed as a partial phenolic source, and a series of main-chain benzoxazine resins (Dz-Ph-ddm) was synthesized *via* Mannich condensation with phenol, 4,4′-diaminodiphenylmethane, and paraformaldehyde. The effects of daidzein content on the thermal stability, flame retardancy, mechanical properties, and char-forming behavior of cured resins were investigated. The results indicate that the rigid aromatic structure and benzopyranone unit of daidzein significantly promoted the formation of a dense and continuous char layer, achieving gas- and condensed-phase synergistic flame retardancy. With 20 mol% of daidzein addition, the resin exhibited a glass transition temperature (T_g) of 259.6 °C, the char yield at 800 °C increased by 42.5% compared to the control group, a UL-94 V-0 rating, and a 30.9% reduction in total heat release (THR) in cone calorimetry tests. The glass fiber-reinforced composite prepared using this resin as the matrix showed a 100.6% improvement in impact strength, with flexural and compressive strengths reaching 748.4 and 340.8 MPa, respectively. Moreover, it demonstrated good fire safety performance even in an 80 kPa low-pressure combustion environment. This work provides a facile strategy for the preparation of high-performance eco-friendly flame-retardant composites.

Keywords Benzoxazine; Daidzein; Intrinsic flame retardancy; Bio-based resin

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INTRODUCTION

Polybenzoxazine resins, a new class of high-performance thermosetting resins prepared *via* Mannich condensation of phenols, primary amines, and paraformaldehyde, have become ideal candidates to replace traditional epoxy and phenolic resins in aerospace, high-end electronic packaging, and rail transportation.[1–4] This is because of their near-zero curing shrinkage, low moisture absorption, high char yield, excellent mechanical properties, thermal stability, and outstanding molecular design flexibility.[5–7]

Although the aromatic structure of the benzoxazine skeleton confers a certain degree of intrinsic flame retardancy, the limiting oxygen index (LOI) is typically limited. Pristine resins often only achieve a UL-94 V-1 rating, and the heat release rate is relatively high, making it difficult to meet the stringent requirements for material fire safety in applications such as aircraft interiors and enclosed electronic equipment. To enhance their flame retardancy, early research widely used additives or reactive halogen-based flame retardants.[8,9] However, halogenated flame retardants tend to release corrosive and toxic gases during combustion, potentially causing significant secondary hazards in enclosed spaces, and their use is increasingly restricted by stringent environmental regulations.[10] Halogen-free flame retardant strategies have emerged, among which phosphorus-containing flame retardants (such as DOPO and its derivatives) have attracted much attention because of their high efficiency.[11–14] However, phosphorus-based flame retardants often exacerbate smoke and toxic gas release during combustion and may reduce the thermal stability and long-term aging performance of the matrix.[15,16] Similarly, although silicon-based flame retardants help promote char formation,[17,18] their compatibility with the resin, impact on mechanical properties, and cost issues remain unresolved.[19] Therefore, the development of halogen-free and phosphorus-free intrinsically flame-retardant benzoxazines to construct efficient and environmentally friendly flame-retardant structures within polymer networks through molecular design has become the focus of cutting-edge research.[20,21]

The core of intrinsic flame retardancy is to promote the for-

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mation of a dense, stable, and continuous high-quality char layer during combustion through chemical structure design[22,23] thereby exerting multiple effects such as heat and mass insulation in the condensed phase.[24] In recent years, researchers have successfully designed a series of high-performance intrinsically flame-retardant benzoxazines by introducing bio-based phenolic sources with high aromatic density and multiple functional groups[25] (such as deoxybenzoin,[26] resveratrol,[27] and magnolol). For example, Zhang[28] and Teng[29] synthesized resins with ultra-high glass transition temperatures and thermal decomposition stabilities using resveratrol and magnolol derivatives, respectively. These achievements demonstrate the great potential of bio-based aromatic structures for improving char formation efficiency and thermal performance.[30,31] However, these high-performance monomers often rely on natural products with limited sources and complex extraction processes, leading to high synthesis costs.[32] Moreover, their extremely high crosslinking density is often accompanied by increased processing viscosity,[33] reduced fluidity, and increased material brittleness, posing severe challenges in balancing economy, processability, and comprehensive performance.[34]

To address these challenges, this study proposes a synergistic molecular design strategy that balances high performance, environmental friendliness, and economic feasibility by selecting the abundant natural product daidzein as a partial phenolic source for copolymerization modification with the industrially widely usedphenol/4,4′-diaminodiphenylmethane (DDM) system.[9] Daidzein (7-hydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one) is a typical flavonoid compound with a distinct structural advantage:[35] it is abundant in rigid aromatic rings and benzopyranone units,[36] which can act as efficient char-forming precursors during pyrolysis, remarkably increasing the char yield and promoting the formation of a more graphitized and denser protective char layer, thus greatly enhancing the condensed-phase flame-retardant efficiency.[37,38]

Based on the above molecular design, we successfully synthesized a series of phenol/DDM-based benzoxazine resins (Dz-Ph-ddm) with different daidzein contents. The expected structures were confirmed by proton nuclear magnetic resonance (^{1}H-NMR) and Fourier transform infrared spectroscopy (FTIR) spectroscopy. The influence of daidzein content on the thermal stability of the resin, dynamic thermomechanical properties, flame-retardant behavior, and char microstructure were systematically studied. Furthermore, a glass fiber-reinforced composite based on this resin was prepared, and its properties, especially its fire safety, even under low-pressure combustion conditions were investigated. This work provides a facile strategy for the preparation of high-performance eco-friendly flame-retardant composites.

EXPERIMENTAL

Materials

Daidzein (Dz, 98%) was purchased from Shaanxi Liangxu Biotechnology Co., Ltd. Phenol (Ph, 99%), 4,4′-diaminodiphenylmethane (DDM, 98%), and paraformaldehyde (>95%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 1,4-Dioxane and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. An alkali-free glass fiber cloth (04 style, 200 g/m^2) was purchased from Hongxing Composite Material Co., Ltd. All the chemicals were used as received without further purification.

Synthesis of Dz-Ph-ddm Benzoxazine Precursors

A series of main-chain-type benzoxazine precursors with different daidzein contents was synthesized *via* a one-pot Mannich condensation reaction. Taking the synthesis of 0.05Dz-1.9Ph-ddm as an example: DDM (25.0 g, 0.126 mol) was dissolved in a mixed solvent of 1,4-dioxane and anhydrous ethanol (2/1, *V*/*V*) in a 500 mL three-necked flask equipped with a magnetic stirrer and a condenser. After stirring at room temperature, paraformaldehyde (15.15 g, 0.504 mol) was slowly added. The temperature was increased to 50 °C and maintained for 1 h until the mixture turned milky white. Then, a mixture of daidzein (1.6 g, 0.0063 mol), phenol (22.53 g, 0.2394 mol), and an additional portion of the mixed solvent was added dropwise *via* a funnel. The reaction temperature was increased to 100 °C (oil bath) and maintained for 12 h under continuous stirring. After cooling to room temperature, most of the solvent was removed *via* rotary evaporation. The crude product was washed repeatedly with deionized water for at least three times and then dried in a vacuum oven at 60 °C to obtain a yellow amber-like solid product (0.05Dz-1.9Ph-ddm). The product yield was approximately 74%. 0.1Dz-1.8Ph-ddm, 0.15Dz-1.7Ph-ddm and 0.2Dz-1.6Ph-ddm) were synthesized following a similar procedure by adjusting the molar ratios of Dz, Ph, and DDM (Table S1 in the electronic supplementary information, ESI). The unmodified reference monomer, Ph-ddm, was also synthesized using an equivalent molar ratio of Ph to DDM.

Preparation of Poly(Dz-Ph-ddm) Thermosets

The synthesized benzoxazine precursors were placed in silicone molds and melted/degassed in a vacuum oven at 130 °C for 1 h to remove residual solvent. The curing process was carried out in an air-circulating oven using a stepwise heating procedure: 160 °C/2 h, 180 °C/2 h, 200 °C/2 h, 220 °C/2 h, and finally 240 °C/2 h. The resulting thermosets are denoted as poly(Ph-ddm), poly(0.05Dz-1.9Ph-ddm), poly(0.1Dz-1.8Ph-ddm), poly(0.15Dz-1.7Ph-ddm), and poly(0.2Dz-1.6Ph-ddm), respectively. All the cured samples were conditioned at room temperature for 24 h before testing.

Preparation of Glass Fiber Reinforced Composites (GF/PBz)

The composites were fabricated using a hot pressing technique. The glass fiber cloth and benzoxazine resin precursor (*e.g.*, poly(0.2Dz-1.6Ph-ddm)) were stacked alternately in a mold with a fiber-to-resin mass ratio of 2:1. The molding process involved an initial stage at lower temperature and contact pressure to allow resin flow and fiber impregnation, followed by a stepwise temperature increase to the curing range (160–240 °C) under higher pressure. A final post-curing cycle was applied to ensure complete cross-linking. The composites based on the different resins were labeled as GF/PBz-1 (poly(Ph-ddm)), GF/PBz-2 (poly(0.05Dz-1.9Ph-ddm)), GF/PBz-3 (poly(0.1Dz-1.8Ph-ddm)), GF/PBz-4 (poly(0.15Dz-1.7Ph-ddm)), and GF/PBz-5 (poly(0.2Dz-1.6Ph-ddm)).

Characterizations

Fourier transform infrared spectroscopy (FTIR): performed on an

Agilent Cary 660+620 spectrometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} (32 scans). Nuclear magnetic resonance (NMR): ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Differential scanning calorimetry (DSC): conducted on a Mettler Toledo MET DSC instrument under N_2 atmosphere from 25 °C to 300 °C at a heating rate of 10 °C/min. Rheological analysis: performed on a TA HR-3 rotational rheometer to determine viscosity and gelation behavior. Thermogravimetric analysis (TGA): carried out on a NETZSCH TG209F1 instrument under N_2 atmosphere from 25 °C to 800 °C at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA): measured on a TA Q800 instrument in single cantilever mode from 25 °C to 300 °C at a heating rate of 3 °C/min and a frequency of 1 Hz. Mechanical testing:tensile, flexural, and compressive tests were performed on a Zwick/Roell Z030 universal testing machine at a speed of 2 mm/min. The impact strength was determined using an Izod impact tester with a 150° notch angle, and the limiting oxygen index (LOI) was determined according to the ASTM D2863 standard using specimens with dimensions of 80 mm × 10 mm × 4 mm, with a group of 15 specimens. The vertical burning test (UL 94) was conducted according to the ASTM D3801 standard using specimens with dimensions of 125 mm × 13 mm × 3.2 mm, with a group of 5 specimens. Cone calorimetry tests were performed on an FTT Cone Calorimeter according to ISO 5660-1 at an incident heat flux of 35 kW/m^2 (resin) or 50 kW/m^2 (composite), with sample dimensions of 100 mm × 100 mm × 4 mm. Low-pressure (80 kPa) cone calorimetry tests were conducted in a specially modified chamber. Smoke and toxicity analysis:gas concentrations (CO_2, CO, HCN, NO_x, *etc.*) were monitored during cone calorimetry tests according to EN ISO 5659-2. Morphological and structural analyses: scanning electron microscopy (SEM) was performed on the fracture surfaces and residual chars. Raman spectroscopy of chars was conducted on a Renishaw in*via* Reflex spectrometer (700–2000 cm^{-1}). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS SUPRA spectrometer. Thermogravimetry-Fourier transform infrared (TG-FTIR) analysis was carried out on a PerkinElmer TGA 8000-Spectrum Two-Clarus SQ8T system.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The synthesis route for the main-chain-type Dz-Ph-ddm precursors and the chemical structures of the cured resin are illustrated in Fig. 1(a). FTIR spectra (Fig. 1b) of all precursors showed characteristic absorption bands at 935 cm^{-1} (oxazine ring), 1234 and 1043 cm^{-1} (C—O—C stretching of oxazine), and 1627 cm^{-1} (C=O stretching of daidzein)[37,38]. In the ^1H-NMR spectra (Fig. 1c), the signals at 5.42 and 4.76 ppm were assigned to the —O—CH_2—N— and —Ar—CH_2—N— protons of the oxazine ring, respectively. The characteristic proton signals of the daidzein unit appeared around 7.86 and 8.03 ppm, and their in-

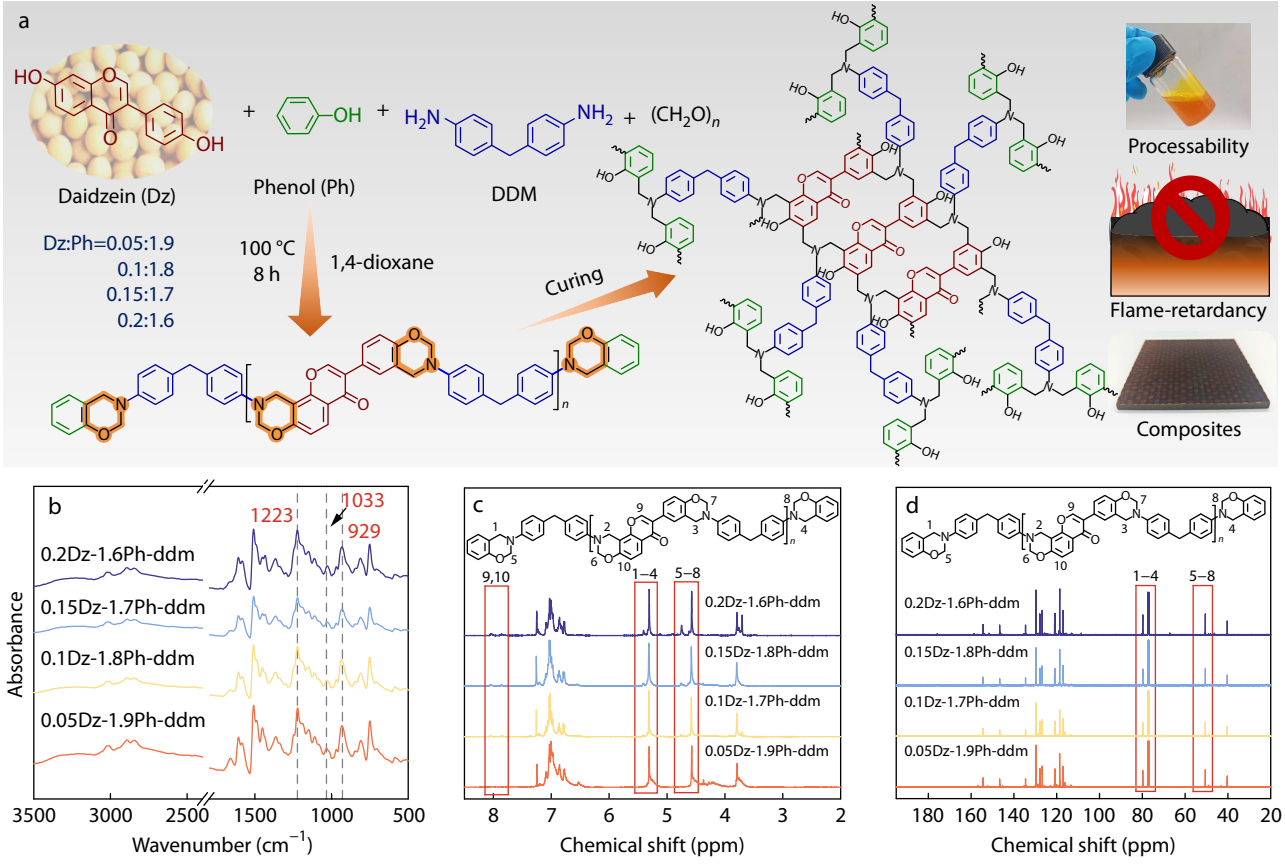

Fig. 1 (a) Schematic illustration for the preparation of poly(Dz-Ph-ddm) using bio-based daidzein as a modifier; (b) FTIR spectra, (c) ^1H-NMR spectra, and (d) ^{13}C-NMR spectra of the Dz-Ph-ddm precursors.

tensity increased with higher Dz content. ^{13}C-NMR spectra (Fig. 1d) further confirmed the formation of the oxazine ring with signals at 79.78 and 50.57 ppm. These results collectively verify the successful synthesis of the target precursors.

Processability and Curing Behavior

As shown in Fig. 2(a), the Dz-Ph-ddm precursors exhibited lower complex viscosity and a significantly broader processing window (100–170 °C) compared to the Ph-ddm precursor. This confirms the improved processability achieved by introducing a main-chain structure. The gelation temperatures (defined as the temperature the viscosity reaches 10^3 Pa·s) of Dz-Ph-ddm resins were in the range of 176–185 °C, lower than that of Ph-ddm (198 °C), indicating enhanced reactivity. DSC analysis (Fig. S1 in ESI) showed that Dz-Ph-ddm had lower curing onset and peak temperatures[28] and broader exothermic peaks compared to Ph-ddm, suggesting an autocatalytic curing process facilitated by the free phenolic —OH group retained on the daidzein unit.[39] The total curing enthalpy decreased from 327.1 J/g for Ph-ddm to 274.9 J/g for Dz-Ph-ddm with 20 mol% Dz content, attributed to the "dilution effect" of the non-exothermic rigid daidzein skeleton on the reactive oxazine ring density per unit mass. FTIR monitoring of staged curing of 0.2Dz-1.6Ph-ddm (Fig. S2 in ESI) confirmed the gradual disappearance of the oxazine characteristic bands (929, 1223 cm^{-1}) upon heating, indicating complete ring-opening polymerization.

Thermal and Thermomechanical Properties

The thermal stability of poly(Dz-Ph-ddm) was investigated using thermogravimetric analysis (TGA) under a nitrogen atmosphere. As shown in Fig. 2(b) and Table 1, the char yield at 800 °C gradually increased as the Dz content, rising from 44.0% for poly(Ph-ddm) to 62.7% for poly(0.2Dz-1.6Ph-ddm)—an improvement of 42.5%. The high carbon content indicates that the polymer can retain its dimensional stability and maintain its performance at elevated temperatures.[40] Furthermore, the thermal degradation temperature exhibited a clear upward trend with increasing Dz content. Poly(0.2Dz-1.6Ph-ddm) displayed a $T_{d5\%}$ of 423.3 °C, which is higher than that of most intrinsic flame-retardant benzoxazines and 59.1 °C above the $T_{d5\%}$ of poly(Ph-ddm). Its $T_{d10\%}$ reached 445.4 °C, exceeding that of poly(Ph-ddm) by 56.9 °C. According to a previous study, a monomer-type polybenzoxazine based on daidzein and furfurylamine also exhibits excellent thermal stability in nitrogen.

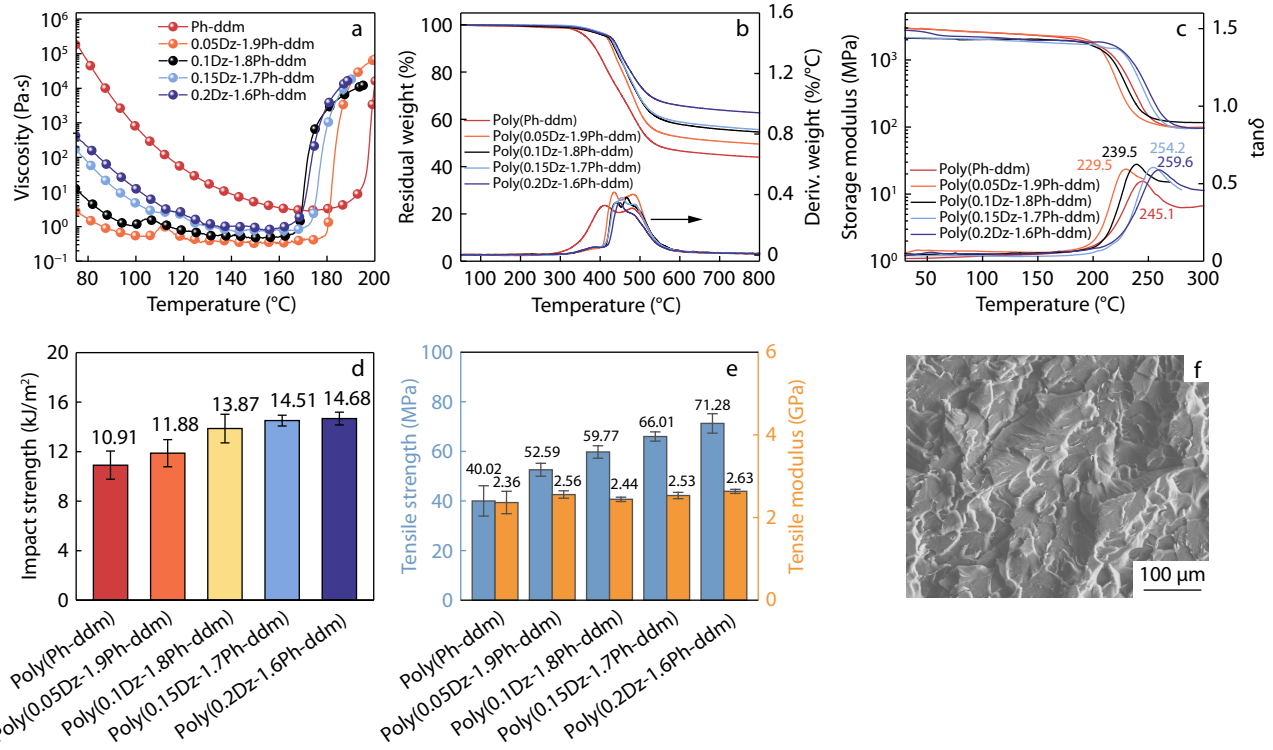

Fig. 2 (a) Complex viscosity as a function of temperature for the precursors at a heating rate of 3 °C/min; (b) TGA and DTG curves; (c) Storage modulus (E') and tanδ curves; (d) Impact strength of poly(Dz-Ph-ddm) resins; (e) Comparison of tensile strength and tensile modulus for poly(Dz-Ph-ddm) resins; (f) SEM image of the impact-fractured surface morphology for poly(0.2Dz-1.6Ph-ddm).

Table 1 TGA and DMA parameters of poly(Dz-Ph-ddm).

Sample	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	Char yield (%)	E' (MPa)	T_g (°C)	ν_e (mol/m^3)
Poly(Ph-ddm)	364.2	388.5	44.0	2965	245.1	7295
Poly(0.05Dz-1.9Ph-ddm)	415.1	430.5	49.6	3219	229.5	8075
Poly(0.1Dz-1.8Ph-ddm)	417.6	437.3	54.6	2118	239.5	8943
Poly(0.15Dz-1.7Ph-ddm)	422.7	439.8	55.6	2166	254.2	6809
Poly(0.2Dz-1.6Ph-ddm)	423.3	445.4	62.7	2795	259.6	6877

This can be attributed to the unique benzopyranone structure of Dz, which possesses good thermal stability and a high char-forming capability.[27] The above results demonstrate that the introduction of daidzein endows poly(Dz-Ph-ddm) with considerably enhanced heat resistance, underscoring its outstanding thermal stability.

The DMA results (Fig. 2c, Table 1) showed that all cured resins possessed a high storage modulus (2–3.2 GPa at room temperature) and good modulus retention upon heating. The glass transition temperature (T_g, taken from the tanδ peak) first decreased slightly for poly(0.05Dz-1.9Ph-ddm) (229.5 °C) compared to poly(Ph-ddm) (245.1 °C), likely due to initial disruption of network homogeneity. However, with further increase in Dz content, T_g increased significantly, reaching 259.6 °C for poly(0.2Dz-1.6Ph-ddm). This high T_g surpasses that of common commercial benzoxazines (*e.g.*, 169 °C for bisphenol A-aniline type), demonstrating the effectiveness of the rigid daidzein unit in enhancing chain stiffness. The crosslinking density (v_e), calculated from the rubbery plateau modulus, showed a trend of first increased and then decreased with increasing Dz content (Table 1). The decrease at higher Dz loadings was likely due to steric hindrance from the bulky daidzein structure, which impeded the formation of a highly crosslinked network. Nevertheless, the dominant contribution from the chain rigidity led to a continuous increase in T_g.

Properties of Poly(Dz-Ph-ddm) Resins

As shown in Figs. 2(d) and 2(e), both the tensile and impact strengths of polybenzoxazines increased with increasing daidzein content. poly(0.2Dz-1.6Ph-ddm) exhibited a tensile strength of 71.28 MPa and an impact strength of 14.68 kJ/m^2, representing increases of 78.1% and 34.6%, respectively, compared to poly(Ph-ddm). The elongation at break also improved slightly but remained below 4%, indicating the characteristic brittle fracture of the thermosets. This mechanical enhancement is attributed to the increased rigidity of the polymer chain and the strengthened intermolecular interactions (*e.g.*, hydrogen bonding) introduced by daidzein.[41] The SEM images of the impact-fractured surfaces (Fig. 2f and Fig. S4 in ESI) clearly show that the fracture morphology changed from a smooth surface for poly(Ph-ddm) to a rough, river-line-patterned surface with microcracks and pits for poly(0.2Dz-1.6Ph-ddm). This evolution suggests that the daidzein units promote crack deflection, branching, and energy dissipation during fracture, leading to improved toughness.

The flame-retardant properties were evaluated using cone calorimetry and UL-94 and LOI tests. The key cone calorimetry data are listed in Table 2. As the daidzein content increased, the time to ignition (TTI) continuously increased, indicating improved resistance to ignition. The peak heat release rate (pHRR) and the total heat release (THR) decreased significantly. Notably, poly(0.2Dz-1.6Ph-ddm) showed reductions of 21.8% in pHRR and 30.9% in THR compared with poly(Ph-ddm). The average effective heat of combustion (Av-EHC) also systematically decreased, suggesting a less efficient combustion of volatiles. Furthermore, the total smoke production (TSP) was drastically reduced by 67.9% for poly(0.2Dz-1.6Ph-ddm) (4.3 m^2) compared to poly(Ph-ddm) (13.4 m^2).[42] Real-time gas analysis (Fig. 3f and Fig. S6 in ESI) confirmed that the concentrations of toxic gases such as CO, HCN, and NOx were significantly lower, and their release peaks appeared earlier for Dz-containing samples, demonstrating effective smoke and toxicity suppression.[43]

In the UL-94 test (Fig. 3d and Fig. S7 in ESI), poly(Ph-ddm) continued to burn for nearly 30 s after the second ignition and failed to self-extinguish rapidly. In contrast, poly(0.2Dz-1.6Ph-ddm) exhibited a significantly shortened self-extinguishing time and achieved a V-0 rating. The limiting oxygen index (LOI) values (Fig. 3e) increased with increasing Dz content, with poly(0.2Dz-1.6Ph-ddm) reaching an LOI as high as 40.2%. This far exceeds that of the traditional bisphenol A-aniline-based benzoxazine (about 26%), classifying it as a self-extinguishing material. Notably, this superior flame retardancy was achieved by introducing only 11.1 mol% daidzein into the total phenolic feedstock, which fully demonstrates its high efficiency.

The thermal performances and flame retardancies of the five poly(Dz-Ph-ddm) samples are compared in Fig. 3(g). A clear trend was observed: both the overall thermal stability and flame-retardant properties improved progressively with increasing Dz content. Among them, poly(0.2Dz-1.6Ph-ddm) with the highest Dz loading exhibited the most balanced and superior comprehensive performance, meeting the requirements for benzoxazine resins in applications that require both high heat resistance and excellent flame retardancy.

Digital photographs of the residues after the cone tests (Fig. S8 in ESI) showed that poly(Ph-ddm) left a fragmented, discontinuous char, whereas the chars from the Dz-containing resins were more intact, expanded, and coherent. SEM images of the char residues (Fig. 4a and Fig. S9 in ESI) revealed that poly(Ph-ddm) char had large cracks and holes, making it difficult to form an effective physical barrier, whereas poly(0.2Dz-1.6Ph-ddm) char exhibited a dense and continuous outer surface and a uniform honeycomb-like internal structure.[44] This "dense outer layer and honeycomb-like inner layer" structure is a hallmark of highly efficient flame-retardant char layers, which act as a barrier against heat and

Table 2 Characteristic data of different samples in the cone calorimetry.

Sample	TTI (s)	pHRR (kW/m^2)	THR (MJ/m^2)	SPR (m^2/s)	TSP (m^2)	Av-EHC (MJ/kg)	Char yield (%)
Poly(Ph-ddm)	81	351.1	100.4	0.074	13.4	32.6	49.0
Poly(0.05Dz-1.9Ph-ddm)	96	251.7	82.7	0.042	8.9	30.3	57.3
Poly(0.1Dz-1.8Ph-ddm)	109	271.4	77.1	0.049	8.7	29.8	57.5
Poly(0.15Dz-1.7Ph-ddm)	104	261.8	73.7	0.042	7.1	29.9	59.6
Poly(0.2Dz-1.6Ph-ddm)	110	274.6	69.4	0.044	4.3	28.0	64.7

TTI, time to ignition; pHRR, peak heat release rate; THR, total heat release; SPR: Smoke production rate; TSP, total smoke production; Av-EHC, average effective heat of combustion of volatiles.

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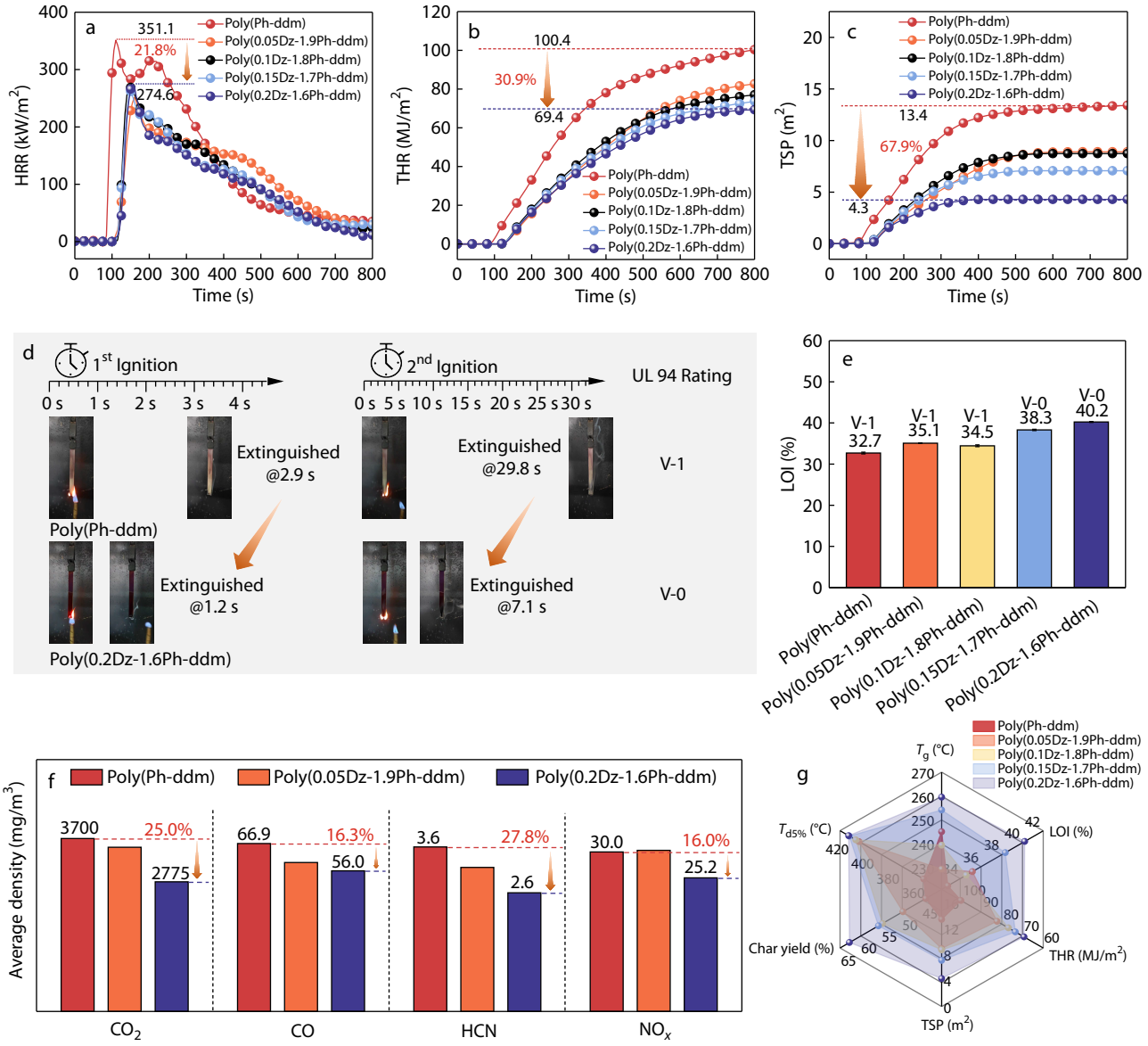

Fig. 3 (a) Heat release rate (HRR) curves, (b) total heat release (THR) curves, and (c) total smoke production (TSP) profiles; (d) UL-94 vertical burning test results; (e) Limiting oxygen index (LOI) values; (f) Average concentrations of CO_2, CO, HCN and NO_x; (g) Comparison of the integrated thermal and flame-retardant performance for poly(Dz-Ph-ddm) resins.

oxygen, whereas the cellular interior delays heat conduction. Raman spectroscopy (Fig. 4b) showed that the intensity ratio of D band to G band (I_D/I_G) for the chars decreased from 2.83 (poly(Ph-ddm)) to 2.59 (poly(0.2Dz-1.6Ph-ddm)), indicating a higher graphitization degree and thus better thermal stability of the char.[45] The XPS analysis (Fig. 4c, Fig. S10 and Table S2 in ESI) further corroborated this conclusion: the char layer of poly(0.2Dz-1.6Ph-ddm) exhibited the lowest relative contents of C—O and C=O species. This indicated that daidzein promoted more efficient dehydration and carbonization reactions, thereby enhancing the oxidation resistance of the char layer and resulting in the formation of a carbon network with superior thermal stability.[46] TG-FTIR analysis (Fig. 4d, Figs. S11 and S12 in ESI) further elucidates the gas-phase behavior during thermal pyrolysis. Compared to poly(Ph-ddm), poly(0.2Dz-1.6Ph-ddm) released significantly fewer combustible volatiles, whereas the proportion of non-flammable gases (such as CO_2) released was higher, with their release peaks occurring earlier. This gas-phase dilution effect effectively reduces the concentration of flammable gases in the flame zone, thereby further inhibiting the combustion process.[47]

Based on the aforementioned multi-dimensional characterization analysis, the flame-retardant mechanism is proposed to be a dual-phase synergistic action dominated by the condensed phase and supplemented by the gas phase (Fig. 4e). In the condensed phase, the benzopyranone unit within the daidzein molecule acts as an efficient char-forming center. During the initial stage of combustion, this structure catalyses the rapid crosslinking and aromatization of the resin matrix, leading to the formation of a dense, continuous, and highly graphitized intumescent char layer.[38,48] SEM observa-

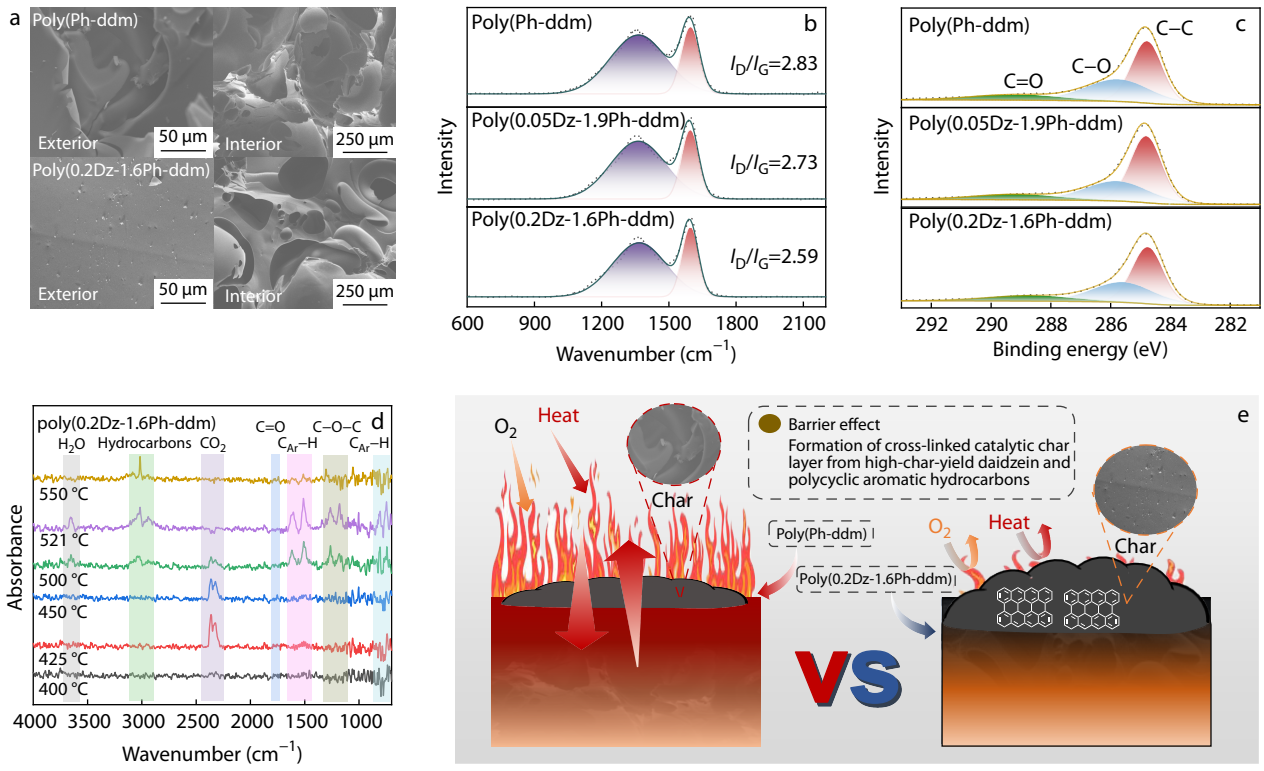

Fig. 4 (a) SEM micrographs of the residual chars for poly(Ph-ddm) and poly(0.2Dz-1.6Ph-ddm) (surface: left; interior: right); (b) Raman spectra of the char layers for poly(Ph-ddm), poly(0.05Dz-1.9Ph-ddm), and poly(0.2Dz-1.6Ph-ddm); (c) Fine scans of the XPS spectra for the char residues; (d) FTIR spectra of the pyrolysis products of poly(0.2Dz-1.6Ph-ddm) at different temperatures; (e) Schematic diagram and mechanism analysis of the flame-retardant process for poly(Dz-Ph-ddm).

tions revealed a "dense outer layer and honeycomb-like inner layer" structure, which effectively blocked the inward transfer of oxygen and heat, while the cellular interior delayed heat conduction through its porous structure. The decrease in the I_D/I_G ratio observed in Raman spectroscopy (indicating an increased degree of graphitization), along with the reduced content of oxygen-containing carbon species (C—O/C=O) revealed by XPS analysis, collectively confirms that the char layer possesses excellent thermal stability and oxidation resistance. This char layer acted as a physical barrier, suppressing the release of internal combustible volatile components.[49] In the gas phase, TG-FTIR analysis indicated that the modified resin released a greater amount of non-flammable gases (such as CO_2) during pyrolysis, with their release peaks occurring significantly earlier. These gases dilute the concentration of oxygen and combustible gases in the flame zone, exerting a supplementary dilution effect that inhibits the combustion reaction.In summary, the efficient, dense, and stable char layer barrier in the condensed phase is the dominant factor in enhancing flame retardancy, while the dilution effect of non-flammable gases in the gas phase serves as a secondary factor. Their synergistic action enables poly(0.2Dz-1.6Ph-ddm) to achieve a 30.9% reduction in total heat release (THR), along with a substantial 67.9% decrease in total smoke production (TSP), realizing efficient, low-smoke, and low-toxicity intrinsic flame-retardant characteristics.[20,36]

Fabrication and Properties of GF/PBz Composites

Glass-fiber-reinforced benzoxazine composites (GF/PBz-1 to GF/PBz-5) were successfully prepared by compression molding (Fig. 5a). All composites displayed dense defect-free microstructures with excellent fiber wetting. As the Dz content increased, the interfacial bonding between the resin matrix and fibers was markedly enhanced, with uniformly coated fiber surfaces and no evidence of debonding. This strong interfacial adhesion is ascribed to physical adsorption and hydrogen bonding between the aromatic groups of daidzein and the silanol groups on the fiber surface, which ensures efficient stress transfer. To systematically evaluate the impact of daidzein modification on the macroscopic mechanical behavior of the composites, a comprehensive set of mechanical tests, including flexural, impact, and compressive tests, was performed on a series of glass-fiber-reinforced benzoxazine composites. The results were compared to those of an unmodified commercial Ph-ddm resin-based composite.

As shown in Figs. 5(b)–5(d), the test results clearly reveal a significant trend: the flexural, impact, and compressive strengths of the composites all increased regularly with increasing daidzein (Dz) content in the resin matrix.[50] This trend is highly consistent with the variation in mechanical properties observed for the pure resin castings, confirming the multiscale reinforcing effect of daidzein modification from the bulk resin to the fiber-reinforced composite. A performance peak was achieved with the GF/PBz-5 composite. With a Dz content of 20%, it exhibited a flexural strength of 748.4 MPa, an impact strength of 329.8 kJ/m^2, and a compressive strength of 340.8 MPa. These values represent increases of 27.4%, 100.6%, and 93.6%, respectively, compared to those of the GF/PBz-1 composite, indicating a remarkable enhance-

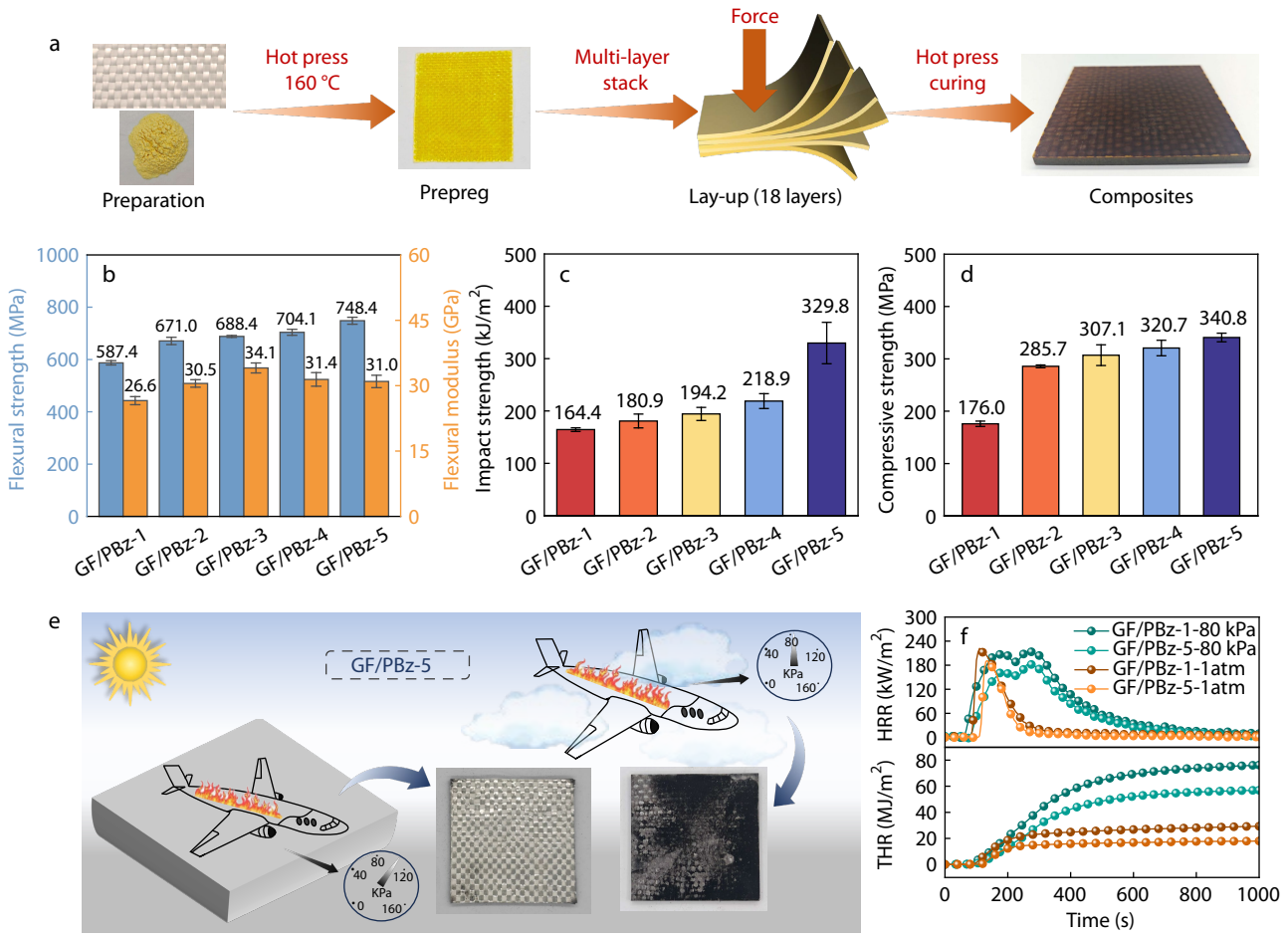

Fig. 5 (a) Fabrication process of the glass fiber reinforced benzoxazine composites; (b) Flexural properties; (c) Impact properties; (d) Compressive properties; (e) Comparison of the combustion behaviors for GF/PBz-5 under low pressure (80 kPa) and normal pressure; (f) Heat release rate (HRR) and total heat release (THR) curves.

ment. Meanwhile, compared with other glass fiber-reinforced benzoxazine composites, the impact strength of polyester ether nitrile, phthalonitrile resin, and fiber-reinforced composite systems only reaches 105.62 kJ/m^2, which fully demonstrates the significant advantages of the daidzein-modified composite.[51] The improvement in the mechanical properties of these glass-fiber-reinforced composites stems from the enhanced interfacial interactions, highlighting the exceptional synergistic effect between the glass fiber reinforcement and the modified resin matrix. In summary, the introduction of daidzein successfully led to the preparation of high-performance benzoxazine composites possessing both ultrahigh strength and excellent toughness.[52] This was achieved by strengthening the resin matrix and forming a robust interfacial bond with the glass fibers, demonstrating significant potential for application in the field of advanced composite materials.[53]

To assess the combustion behavior of Dz-Ph-ddm/glass fiber composites in realistic fire scenarios and to further simulate their fire safety performance in low-pressure environments, such as aerospace applications,[54] combustion tests were conducted on GF/PBz-1 and GF/PBz-5 under both normal atmospheric pressure and a reduced pressure of 80 kPa. As shown in Fig. 5(f), compared with its combustion under normal pressure, GF/PBz-5 exhibited a lower peak heat release rate (HRR) under low pressure. However, the combustion process became less stable and prolonged, delaying the rapid formation of a stable and dense char layer during the initial stage. Consequently, the flame temperature increased, promoting more thorough pyrolysis and surface oxidation, which led to a slight increase in total heat release (THR). Fig. 5(e) shows that under low pressure, the sample surface did not undergo rapid charring to form an effective protective barrier to halt further combustion. Nevertheless, GF/PBz-5 ultimately maintained a high degree of char structural integrity and barrier performance even under 80 kPa, demonstrating the good pressure-adaptive performance of the material.

Critically, GF/PBz-5 consistently exhibited lower HRR and THR values than GF/PBz-1 under both normal- and low-pressure conditions, and the THR was reduced by 25.3% and 38.9%, respectively, indicating enhanced flame retardancy. This confirms that the flame-retardant enhancement provided by daidzein is effective under reduced pressure. The underlying mechanism lies in the fact that the dense char layer promoted by the high char-forming capability of Dz can still effectively inhibit the escape of pyrolysis gases and diffusion of oxygen, even in a low-pressure atmosphere. This characteristic helps improve the flame-retardant performance of com-

mercial benzoxazine/glass fiber systems across varying pressure environments, underscoring the material's significant application potential under special operating conditions.

CONCLUSIONS

In summary, a main-chain-type benzoxazine resin (Dz-Ph-ddm) with excellent intrinsic flame retardancy, high heat resistance, and good processability was designed and synthesized using bio-based daidzein. The introduction of the benzopyranone structure from daidzein significantly enhanced the char-forming ability and thermal stability of the resin, yielding a char yield of 62.7% at 800 °C under N_2, a T_g of 259.6 °C, a UL-94 V-0 rating, and an LOI of 40.2%. The flame retardant mechanism involves the formation of a dense, continuous intumescent char layer in the condensed phase acting as a barrier, coupled with the release of non-flammable gases (*e.g.*, CO_2) in the gas phase that dilutes O_2, representing a synergistic dual-phase action.The corresponding glass fiber-reinforced composite exhibited outstanding comprehensive properties, including an impact strength of 329.8 kJ/m^2, a flexural strength of 748.4 MPa, and a compressive strength of 340.8 MPa, superior to most reported intrinsically flame-retardant benzoxazine composites. It also maintained high char stability and fire safety under low-pressure (80 kPa) combustion, indicating its suitability for applications such as aerospace, and a systematic study on the combustion behavior of the material under low-pressure conditions represents a promising avenue for future research. This work innovatively utilizes abundant bio-based daidzein to synergistically improve the flame retardancy, mechanical properties, and processability of benzoxazine resins without relying on halogens or phosphorus, providing a valuable molecular design paradigm and experimental basis for developing next-generation green, high-performance flame-retardant composite materials.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request. Contact information: daijinyue@nimte.ac.cn (Jinyue Dai) and krista9150@sina.com (Hui Zhang).

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Graphical Abstract

Processable Main-chain Benzoxazine Resin Derived from Daidzein with Intrinsic Flame Retardancy

Chao-Fan Hu, Jin-Yue Dai, Jing-Kai Liu, Shuai-Peng Wang, Li Jia, Hui Zhang, and Xiao-Qing Liu

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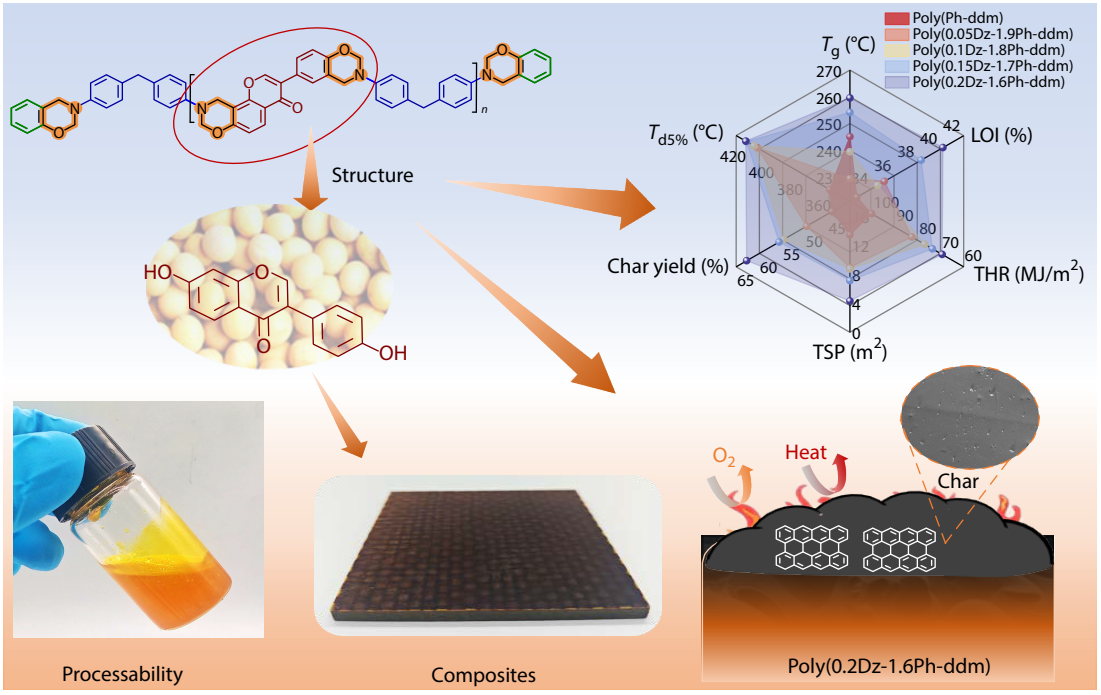
A daidzein-based benzoxazine resin achieved a UL-94 V-0 rating (LOI 40.2%) and 62.7% char yield *via* condensed/gas-phase synergy. Its glass fiber composite exhibited a flexural strength of 748.4 MPa and impact strength of 329.8 kJ/m^2.



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