A New Sight into Bio-Based Polybenzoxazine: From Tunable Thermal and Mechanical Properties to Excellent Marine Antifouling Performance

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ABSTRACT: With the rapid development of bio-based polymers, polybenzoxazine derived from renewable resources has been widely investigated. However, there are few reports on the functional application of bio-based polybenzoxazine based on the special chemical structures of renewable compounds. In this work, an easy approach to prepare the polybenzoxazines with varied thermomechanical properties and excellent marine antifouling performance from renewable resources is presented. After a variety of main-chain-type benzoxazine polymers (MCBPs) were synthesized from the renewable daidzein, furfurylamine, polyetheramine, and paraformaldehyde, their chemical structures were identified by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy (^1H NMR). Then, their curing behaviors were monitored by differential scanning calorimetry and rheological tests. Results revealed that the cross-linked MCBPs with varied thermomechanical properties could be easily prepared by adjusting the molar ratio of polyetheramine and furfurylamine. Notably, these cured MCBP films demonstrated excellent antibacterial and algacidal properties due to the presence of daidzein and furan units. This work first presents the new application prospect of bio-based MCBPs, for example, in marine antifouling coatings.

INTRODUCTION

Polybenzoxazine, a relatively new phenolic-type thermoset with excellent properties, has attracted enormous interest from both academia and industry.^{1,2} It is well known that the most outstanding properties of polybenzoxazines stem from the Mannich bridges $[-\text{CH}_2-\text{N}(\text{R})-\text{CH}_2-]$ and hydrogen bonds.^{3–5} However, the existence of strong hydrogen bonding restricts the movement of molecular chains, which in turn results in the relatively low cross-linking density and high brittleness.⁶ To overcome this drawback, the molecular design flexibility of benzoxazine monomers was fully utilized, and thus a variety of main-chain-type benzoxazine polymers (MCBPs) that contain repeated benzoxazine units in the main chain were developed.^{7–11} MCBPs not only perform like ordinary thermoplastics, which have good processability, but also can form a three-dimensionally cross-linked network via ring-opening polymerization (ROP) of the oxazine ring in the main chain by heat treatment.

For the preparation of most MCBPs, bisphenol A is usually used as the starting material due to its abundant availability.^{7–10} However, the endocrine disruptor toxicity of bisphenol A has been well ascertained,¹² and the United States as well as other developed countries have banned the usage of bisphenol A in baby bottles.¹³ Therefore, it is highly desirable to look for the healthy alternative to bisphenol A. In addition,

synthesis of polymers from renewable feedstock has received extensive attention because of the increasing concern on petroleum resources and environmental issues.¹⁴ Benzoxazine resins are also on the same course and researchers have been making efforts to replace the petroleum-based phenols and amines by the bio-based ones.¹⁵ Up to now, varieties of benzoxazine monomers have already been synthesized from the renewable sesamol,¹⁶ diphenolic acid,¹⁷ thymol,¹⁸ cardanol,¹⁹ lignin derivatives (guaiacol, vanillin, eugenol),^{20–26} coumaric,^{27,28} chavicol,²⁹ umbelliferone,³⁰ furfurylamine,^{31,32} stearylamine,³³ and so on. However, compared with the benzoxazine monomers derived from renewable feedstock, research on bio-based MCBPs is seldom reported. Yagci et al. prepared a novel bio-based MCBPs from coumarin, and the obtained polybenzoxazine demonstrated satisfied thermal and mechanical properties.³⁴ The eugenol-based MCBPs showing excellent processing performance was also reported.³⁵ What should be pointed out here is that almost all the previous works are focused on the thermal, mechanical, or processing

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Scheme 1. Synthesis of MCBPs from Daidzein, Furfurylamine, Polyetheramine, and Paraformaldehyde

properties of bio-based MCBPs. Yet, there is little research on the unique chemical structure of renewable compounds, which sometimes endows polymers with special functionality.

Daidzein is a naturally occurring phenolic compound that can be isolated from soybeans and other legumes. Its derivatives have been widely used in cosmetics, drugs, and food supplements with excellent antioxidant and antimicrobial activities.^{37–39} Furfurylamine is another well-known bio-based platform chemical that can be industrially produced from agricultural byproducts. In addition, the furan ring can provide additional cross-linking points for the benzoxazine, thereby enhancing the performance of corresponding polybenzoxazines. More importantly, furan and its analogues have been proven to have excellent antifouling properties.^{40,41}

Based on the above information and analysis, besides the satisfied thermal and mechanical properties, we expect to design and synthesize MCBPs demonstrating some special functionalities, taking advantage of the unique structure of bio-based compounds. Both the antibacterial activity of daidzein³⁹ and the antifouling performance of furan analogues^{40,41} lead us to believe that the incorporation of daidzein and furfurylamine units will give polybenzoxazine some functional properties, for example, antibacterial and algacidal properties. Consequently, a series of MCBPs were synthesized from the renewable daidzein, furfurylamine, polyetheramine, and paraformaldehyde (Scheme 1). Also, furfurylamine also acted as the monoamine to regulate the molecular weight of MCBPs. The structure features, curing behaviors, and processability of these oligomers as well as the properties of cured resins, including thermodynamic properties, thermal stability, and antibacterial and anti-algae performance were systemically investigated. In summary, besides thermal and mechanical properties, the special functional properties of bio-based MCBPs caused by the unique structure of bio-based compounds were concerned in this work.

RESULTS AND DISCUSSION

Synthesis and Characterization of MCBPs. MCBPs with different compositions were synthesized from daidzein, amines (D-600 and furfurylamine), and formaldehyde. Their

chemical structures were determined by ¹H NMR and FT-IR. As shown in Figure 1, the characteristic peaks at 3.83 and 4.77

Figure 1. ¹H NMR spectra of (a) Dz-0.9d600-0.2f, (b) Dz-0.7d600-0.6f, (c) Dz-0.5d600-1.0f, and (d) Dz-0.3d600-1.4f.

ppm corresponded to the Ph-CH₂-N (H1-H4) and O-CH₂-N (H1'-H4') protons in the oxazine ring. The furan ring was strongly suggested by the signals at 6.0–6.5 ppm (H5, H6, H5', H6'), and their intensities displayed an increasing trend with the increase of furfurylamine content in amines. Besides, the presence of a furfuryl difunctional bisbenzoxazine monomer (Dz-f) was observed, as indicated in Figure 1. Based on the integrated area ratios of different peaks of Ph-CH₂-N (H1-H4), the ratio of MCBPs to Dz-f varied from 1:0.09 to 1:0.51. Figure S1 shows the FT-IR spectra of MCBPs. The absorbance peaks centered at 1233 and 914 cm⁻¹ were assigned to C–O–C asymmetric stretching and C–H out-of-plane bending in the benzene ring fused to the oxazine ring, attesting to the formation of oxazine ring. The band at

Table 1. Feed Composition, Yield, and Molecular Weight of Synthesized MCBPs

sample	D-600/furfurylamine molar ratio	yield (%)	M_n (g/mol)	M_w (g/mol)	$\bar{D}$
Dz-0.9d600-0.2f	9:2	71	5.5×10^3	11.6×10^3	2.1
Dz-0.7d600-0.6f	7:6	68	3.0×10^3	5.3×10^3	1.7
Dz-0.5d600-1.0f	5:10	73	2.3×10^3	3.3×10^3	1.4
Dz-0.3d600-1.4f	3:14	75	1.8×10^3	2.2×10^3	1.2

Figure 2. (a) DSC thermograms for the synthesized MCBPs; (b) DSC thermograms of Dz-0.5d600-1.0f at each curing stage; (c) viscosity as a function of temperature with the heating rate of 3 °C min⁻¹; and (d) viscosity as a function of time at 150 °C.

1497 cm⁻¹ was associated with the trisubstituted benzene ring. The strong band at 1630 cm⁻¹ was attributed to the C=O attached to daidzein units.³⁸ The successful incorporation of the furan ring was confirmed by the bands at 1578 and 744 cm⁻¹.⁴² In addition, the formation of MCBPs was also verified by gel permeation chromatography (GPC) (Figure S2). In Table 1, the number-average molecular weight (M_n) was in the range of 1.8×10^3 to 5.5×10^3 g/mol, corresponding to a degree of polymerization (DP) of ~2 to 6. As expected, the molecular weight increased with the reduction of furfurylamine content in amines. Also, the obtained MCBPs all showed narrow molecular weight distributions with a dispersity ($\bar{D}$) of 1.2–2.1.

Curing Behaviors of MCBPs. Differential scanning calorimetry (DSC) analysis was used to investigate the curing behaviors of obtained MCBPs. As shown in Figure 2a, all the MCBPs exhibited similar DSC profiles with one exothermic peak, which was related to the ROP of oxazine rings. Obviously, the ROP temperature of these MCBPs polymers was relatively low. The reason might be due to the existence of primary amine end groups in the molecular chain, which could catalyze the curing reaction and then decrease the starting curing temperature.⁴³ After more careful analysis, it was found that the peak temperature increased slightly from 191.0 to 197.1 °C with the increasing content of D-600 in amine mixtures, while the enthalpy value was decreased from 205.5 J/g for Dz-0.3d600-1.4f to 136.5 J/g for Dz-0.9d600-0.2f, which might be associated with the dilution effect. As reported in

previous work,^{10,35,36} the lower concentration of oxazine rings per unit weight would result in lower polymerization reactivity and enthalpy. To have further insight into the curing process, Dz-0.5d600-1.0f was taken as an example, and its non-isothermal DSC thermograms at each curing stage are presented in Figure 2b. It could be seen that the exothermic enthalpy gradually decreased along with the curing process, suggesting the increment in curing degree. Simultaneously, the exothermic peak shifted to a higher temperature due to certain structural rearrangement occurring and facilitating the diffusion-controlled reaction at high temperature.⁴⁴ After the sample was cured at 200 °C for 2 h, the exothermic peak disappeared, indicating the complete curing reaction. Therefore, the curing procedure for MCBPs described in the Experimental Section could ensure the full polymerization.

Processability of MCBPs. In this work, all the MCBPs were viscous liquids at room temperature, which is advantageous to processing. To carefully evaluate the processability, dynamic viscosity analysis was performed. As depicted in Figure 2c, the viscosity of all the MCBPs remained low and fairly constant at the temperature range from 100 to 150 °C. Meanwhile, when the temperature was over 150 °C, the viscosity was observed to increase rapidly, indicating the gelation of MCBPs at higher temperature. Usually, the maximum temperature at which the viscosity was greatly increased up to 10³ Pa·s was taken as the gelation temperature of thermosetting resins.³⁵ Thus, the gelation temperatures of Dz-0.9d600-0.2f, Dz-0.7d600-0.6f, Dz-0.5d600-1.0f, and Dz-

Table 2. Mechanical and Thermal Properties of Cross-Linked MCBPs

codes	σ^a (MPa)	E^b (MPa)	ϵ^c (%)	σ^d (MPa)	E^e (Mpa)	ϵ^f (%)
poly(Dz-0.9d600-0.2f)	16.3 $\pm$ 2.1	360 $\pm$ 10	8.8 $\pm$ 0.2	24.8 $\pm$ 1.5	420 $\pm$ 22	9.4 $\pm$ 0.3
poly(Dz-0.7d600-0.6f)	24.4 $\pm$ 1.1	540 $\pm$ 21	6.2 $\pm$ 0.6	38.5 $\pm$ 3.0	700 $\pm$ 26	6.9 $\pm$ 1.0
poly(Dz-0.5d600-1.0f)	41.6 $\pm$ 4.2	950 $\pm$ 45	6.2 $\pm$ 1.2	60.0 $\pm$ 5.4	970 $\pm$ 37	7.6 $\pm$ 0.5
poly(Dz-0.3d600-1.4f)	54.7 $\pm$ 5.1	1620 $\pm$ 32	3.9 $\pm$ 0.5	93.1 $\pm$ 7.1	1580 $\pm$ 41	6.4 $\pm$ 0.8

^aTensile strength. ^bYoung's modulus. ^cTensile strain (%). ^dFlexural strength. ^eFlexural modulus. ^fStrain at break for flexural (%).

Figure 3. (a, b) DMA and (c, d) TGA curves for poly(Dz-0.9d600-0.2f), poly(Dz-0.7d600-0.6f), poly(Dz-0.5d600-1.0f), and poly(Dz-0.3d600-1.4f).

0.3d600-1.4f were determined to be 167, 176, 175, and 176 °C, respectively.

The curing reactivity of synthesized MCBPs was also evaluated during isothermal curing at 150 °C. As shown in Figure 2d, the gel points for isothermal curing of these bio-based MCBPs at 150 °C were observed after 12.8, 21.2, 28.2, and 37.6 min, respectively, which also indicated that the curing reactivity of MCBPs increased gradually with the increasing content of furfurylamine in amine mixtures. This was consistent with the above DSC results.

Thermal and Mechanical Properties of Cross-Linked MCBPs. Figure S2 shows the stress–strain curves for all the cross-linked MCBPs, and the detailed data is collected in Table 2. As depicted in Figure S3a, when the ratio of D-600/furfurylamine varied from 9:2 to 3:14, Young's modulus was increased from 360 MPa for poly(Dz-0.9d600-0.2f) to 1620 MPa for poly(Dz-0.3d600-1.4f), and the related tensile strength was increased from 16.3 to 54.7 MPa. Meanwhile, their tensile strain at break decreased from 8.8 to 3.9%. As for the flexural stress–strain curves shown in Figure S3b, the same trend was observed. It is well known that a higher cross-linking density usually leads to an increased strength, modulus, and brittleness. In this work, the end-capped furan ring could participate in the polymerization and significantly increase the cross-linking density and rigidity of resulted resins.³⁰ As

described in the Experimental Section, the mole ratio between D-600 and furfurylamine could be manipulated freely; therefore, the cross-linked MCBPs with varied mechanical properties could be easily prepared.

The dynamic mechanical properties of cross-linked MCBPs were evaluated by DMA. The DMA curves are shown in Figure 3a,b, and the relevant data, including storage modulus, T_g , and crosslinking density, are collected in Table 3. As noticed, the storage moduli of cross-linked MCBPs at room temperature were found to be in the range of 0.6–2.7 GPa. Also, the T_g values defined by the tan δ peak for poly(Dz-0.9d600-0.2f), poly(Dz-0.7d600-0.6f), poly(Dz-0.5d600-1.0f), and poly(Dz-0.3d600-1.4f) were 92.9, 166.8, 212.8, and 268.5 °C, respectively. Obviously, both the storage modulus and T_g were significantly increased with the increasing content of furan moiety, which was mainly attributed to the formation of additional cross-linking points caused by the reaction between the furan ring and oxazine groups.⁴⁵ Compared with literature results, the T_g values of cross-linked MCBPs in this work were much higher. For example, Ishida et al.¹⁰ synthesized several poly(ether diamine)-based MCBPs showing excellent flexibility. However, even their highest T_g was lower than the room temperature.

Table 3. Dynamic Mechanical Properties and Thermal Stabilities of Cured MCBPs

codes	T_g^a (°C)	E'^b (GPa)	$\nu_c^c/10^3$ (mol m ⁻³)	N ₂		air	
				$T_{d10\%}$ (°C)	R_{800} (%)	$T_{d10\%}$ (°C)	R_{800} (%)
Poly(Dz-0.9d600-0.2f)	92.9	0.6	2.7	366	35.3	353	0.6
Poly(Dz-0.7d600-0.6f)	166.8	1.6	4.2	368	38.2	354	0.0
Poly(Dz-0.5d600-1.0f)	212.8	1.8	6.5	378	44.5	387	0.1
Poly(Dz-0.3d600-1.4f)	268.5	2.7	6.8	398	54.0	399	0.9

^aGlass transition temperature by DMA. ^bStorage modulus at 25 °C. ^cCross-linking density.

Figure 4. (a) Splitting FT-IR spectra between 2650 and 3700 cm⁻¹ of Poly(Dz-0.5d600-1.0f) under 25 (upper) and 250 °C (lower); (b) comparison of split peaks' integrated areas in Poly(Dz-0.5d600-1.0f) at 25 and 250 °C; (c) idealized chemical structure of cured MCBPs.

The cross-linking density of a polymer is defined as the number of cross-linking points per unit volume in the network. It could be calculated using the following equation:

$$\nu_c = E'/3RT \quad (1)$$

where E' is the storage modulus in the rubbery plateau region (E' at the temperature of 300 °C was chosen in this work), R is the gas constant, and T is the absolute temperature. The obtained ν_c values are listed in Table 3, and they also increased with the furan moiety content in MCBPs, which was in line with the above results.

The thermal stability of cross-linked MCBPs was investigated by TGA under N₂ (Figure 3c) and air (Figure 3d) atmospheres. The temperature for 10% weight loss ($T_{d10\%}$) and the residue at 800 °C (R_{800}) were selected for their thermal stability evaluation. In Figure 3c, the $T_{d10\%}$ was increased from 366 °C for poly(Dz-0.9d600-0.2f) to 398 °C for poly(Dz-0.3d600-1.4f) with the increasing content of furan moiety, much higher than those of similar MCBPs reported in the literature.^{8,10,34} In addition, the R_{800} values were also increased accordingly, from 35.3 to 54.0%. As for their thermal degradation in the air atmosphere (Figure 3d), the same trend was observed. According to a previous study,³⁸ the monomer-type polybenzoxazine based on daidzein and

furfurylamine also showed excellent thermal stability both in nitrogen and air atmospheres. The reason was attributed to the special benzopyrone structure of daidzein and the presence of the furan moiety. In this work, the increasing thermal stability of cross-linked MCBPs was also attributed to the fact that the furan moiety could participate in the polymerization at high temperatures and then increase the cross-linking density, which slows down the degradation and promotes the char formation. In addition, the presence of residual Dz-f monomers in different systems might be another reason for the relatively higher T_g and better thermal stability for the cured resins.

As we know, due to their intrinsic brittleness, the static mechanical properties of monomer-type polybenzoxazines, such as tensile strength and modulus, are seldom reported. Also, the MCBPs, which contain repeated benzoxazine units in the main chain, usually demonstrate higher toughness. In order to further enhance the toughness of cured MCBPs, the long flexible units are often incorporated. However, the long soft chain will seriously sacrifice their thermal properties and mechanical strength. Based on the literature survey,^{2,9,10} it was a proven fact that the cross-linked MCBPs usually show relatively low T_g and strength, except the excellent flexibility. Unlike the previously reported results, in this work, the MCBPs based on daidzein and furfurylamine showed satisfied

Table 4. Coating Performances of Cross-Linked MCBPs

codes	thickness	pencil hardness	flexibility	adhesion	MEK resistance	ethanol resistance
Poly(Dz-0.9d600-0.2f)	50 μm	B	0T	5B	>400	>400
Poly(Dz-0.7d600-0.6f)	50 μm	1H	0T	5B	>400	>400
Poly(Dz-0.5d600-1.0f)	50 μm	3H	1T	5B	>400	>400
Poly(Dz-0.3d600-1.4f)	50 μm	4H	2T	5B	>400	>400

mechanical and thermal properties as shown in Tables 2 and 3. Besides the varied cross-linking density caused by the well-known crosslinking reaction involved with the end-capped furan ring as well as the residual Dz-f monomer, the daidzein unit, which could participate in the formation of extra hydrogen bonding and then improve the performance of cured resin, might be another reason for their good mechanical and thermal properties.⁴⁶

In order to study the hydrogen bonding interactions in the cured MCBPs in detail, poly(Dz-0.5d600-1.0f) was taken as an example and the normalized FT-IR spectra at different temperatures (25 and 250 °C) were recorded for investigation (Figure 4a). As we know, the hydrogen bonds, such as O–H $\cdots$ O, O–H $\cdots\pi$, O–H $\cdots$ N, and O $\cdots$ H $\cdots$ N, generally exist in polybenzoxazine.⁴⁷ Based on the literature, they could be divided into O $\cdots$ H $\cdots$ N ($\sim$ 2800 cm^{-1}), O–H $\cdots$ N ($\sim$ 3150 cm^{-1}), O–H $\cdots$ O ($\sim$ 3440 cm^{-1}), and O–H $\cdots\pi$ ($\sim$ 3580 cm^{-1}) intramolecular hydrogen bonding interaction as well as O–H $\cdots$ O ($\sim$ 3350 cm^{-1}) and O–H $\cdots$ N ($\sim$ 3300 cm^{-1}) intermolecular hydrogen bonding for the sake of figuring out which part of them made the main contribution to thermal performance.⁴⁸ The splitting FT-IR spectra of poly(Dz-0.5d600-1.0f) under 25 °C (Figure 4a, upper) and 250 °C (Figure 4a, lower) were displayed. It was clear that the hydrogen bonding with different features possessed the uneven ability of withstanding high temperature, especially for the intramolecular O–H $\cdots\pi$, which was completely disappeared when the temperature was increased to 250 °C.

The integrated areas of splitting peaks at different temperatures for poly(Dz-0.5d600-1.0f) were calculated, and their ratios are illustrated in Figure 3b. As noticed, when the temperature was increased to 250 °C, the intensity of absorption bonds was decreased accordingly, which should be related to the decreased hydrogen bonding strength. Other than the several intramolecular hydrogen bonds with high strength retained more or less, to our surprise, the generally weak intermolecular O–H $\cdots$ O hydrogen bonding was majorly retained. As we know, hydrogen bonding is a kind of electrostatic force; usually, the higher the negativity of the receptor, the higher the strength of the hydrogen bonding.⁴⁹ In this work, one of the significant features of the daidzein unit was that they contained an alkaline oxygen atom with high negativity and a carbonyl group, which could not only increase the probability of constructing more intermolecular O–H $\cdots$ O hydrogen bonding but also enhance their strength and then increase their durability at higher temperature. With these results and deductions, for easy identification, we only put forward the intermolecular O–H $\cdots$ O hydrogen bonding involved in daidzein units in Figure 4c (marked by red circles). Although it might be a preliminary investigation on the hydrogen bonding interactions here, the contribution of the hydrogen bonding involved in the alkaline oxygen atom and carbonyl group in daidzein units to the satisfied thermal and mechanical properties of cured MCBPs should not be ignored. In the following work, more information about the

formation and characteristic of hydrogen bonding interactions in daidzein-based polybenzoxazines will be provided.

Coating Performance of Cross-Linked MCBPs. Considering the excellent film-forming and processing properties of MCBPs, it has been extensively used for the preparation of solvent-free coatings. The coating performances of cross-linked MCBPs in terms of adhesion, pencil hardness, flexibility, and solvent resistance were investigated, and the results are tabulated in Table 4. The adhesion of organic coatings is closely related to its polar group content, which can significantly enhance the interaction between the coatings and substrate.⁵⁰ As shown in Table 4, the adhesion of all the cured MCBPs on tinplate was as high as 5B (the highest level). That should be attributed to the presence of numerous aromatic rings and phenolic hydroxyl groups in the cross-linked networks.⁵¹ The pencil hardness of coatings shows highly correlation with their T_g . Higher T_g results in higher hardness values, from B to 4H. In the contrary, the flexibility of these coatings was decreased with the increasing T_g . When the D-600 content was 0.9–0.7, the flexibility of the film was 0T, which was the highest grade of flexibility according to the ASTM D4145-10. When the content of furan unit was increased to be higher than 0.6, the rigidity and cross-linking density of cured networks were both increased, which would lead to the decreased flexibility. The solvent resistance of coatings is another important factor in determining their end use. As could be seen from Table 4, all the coatings showed excellent solvent resistance without any defect after 400 double rubs with ethanol and methyl ethyl ketone.

Antibacterial Assay of Cross-Linked MCBPs. Marine biofouling is a worldwide problem in marine systems. It is mainly caused by the adhesion of barnacles, macroalgae, and microbial slimes. According to the mainstream view of biofouling formation mechanism, preventing the surface from colonization of bacteria is the key to inhabit the biofouling.⁵² Therefore, the suspension assays were carried out by measuring both bacteria's colonies in solution with and without treatment to assess the bacterial killing efficiency of cured MCBPs. Figure 5 shows the elimination ratio of both *Escherichia coli* ATCC 25922 and *Bacillus cereus* ATCC6538 after contact with the cured MCBPs films, and the images of these two bacterium colonies that survived on the nutrient agar plates are exhibited in Figure S4. On the whole, the killing effect of these polybenzoxazine films on *E. coli* was stronger than that on *B. cereus*. The highest elimination ratio of *E. coli* was 99.9%, and it was 70.6% for *B. cereus*. Their different cell wall structures should be responsible for this result. The toxicity of the same antibacterial substance to different bacteria depends on the degree of contact with the cells, and Gram-positive *Bacillus* species have a much thicker cell wall that could prevent the passage of antibacterial substances through the cell wall. Additionally, the elimination effect of these cured MCBP films on the bacteria increased with the furan content. As the molar ratio of D-600 to furfurylamine increased from 0.2 to 1.4, the elimination ratio against the two bacteria

Figure 5. Antimicrobial activity of cured MCBPs films.

increased from 27.1% (*E. coli*) and 31.2% (*B. cereus*) to 99.9% (*E. coli*) and 70.6% (*B. cereus*). This result indicated that it might be the functional groups, such as the furan ring, responsible for the antifouling activities of cured MCBP films. In fact, the intrinsic antifouling properties of the furan ring and its derivatives have already attracted much attention. For example, the halogenated furanones extracted from the red alga *Ahnfeltiopsis flabelliformis*⁵³ and other furanones⁵⁴ are typical quorum-sensing blockers. They are able to accelerate the degradation of transcriptional activator LuxR and inhibit the acylated homoserine lactone regulatory system of bacteria, resulting in an inhibition of biofilm formation. Other furan analogues, including 14-hydroxycembra-1,3,7,11-tetraene, 15-hydroxycembra-1,3,7,11-tetraene, 13 α -acetoxypukalide, and (9*E*)-4-(6,10-dimethylocta-9,11-dienyl)furan-2-carboxylic acid

also had excellent antibacterial activity.^{55,56} Of course, the other variable factor here, that is, the content of D-600 moiety, might be another reason for the satisfied antifouling property of cured films, which should be confirmed in the near future.

Anti-Algae Performance of Cured MCBPs. The settlement behavior of algae like *Phaeodactylum tricornutum* and *Navicula* sp. on the surface of these bio-based polybenzoxazine films was also studied. As shown in Figure 6, the confocal laser scanning microscope photograph showed the distribution of fluorescence. The state of the two diatoms on the surface of the silicon wafer and these polybenzoxazine films was highly similar. However, the fluorescence distribution on the surface of cured MCBPs films was diffused and filled the whole view rather than being dense but having a strict distinction from the background in the control group. This might be due to the toxic effect of the polybenzoxazine films on the two algae cells, which resulted in the breakage of the algae cells, causing the chlorophyll efflux cells to be evenly distributed on the surface of the samples. The SEM photos in Figure 6 demonstrated the above hypothesis. Large amounts of algae with complete cell morphology attached to the surface of the silicon wafer, and almost no algal cells with ruptured cell morphology were observed. However, on the surface of the polybenzoxazine films, algae cells showed a state of accumulation, with a large number of flocculent cell debris around, indicating that these polybenzoxazine films had a toxic effect on both algae and had good algae resistance. As previously stated, the daidzein derivatives have shown excellent antioxidant and antimicrobial activities when used as drugs and food supplements.^{37,38} In this work, the amazing anti-algae performance of cured MCBP films should also be attributed to the presence of daidzein units.

Figure 6. Confocal laser scanning microscope photograph of (A) *Navicula* sp. and (B) *P. tricornutum* adhering onto (1) poly(Dz-0.9d600-0.2f), (2) poly(Dz-0.7d600-0.6f), (3) poly(Dz-0.5d600-1.0f), and (4) poly(Dz-0.3d600-1.4f) after 1 day; SEM images for *Navicula* sp. (C0) before and (C1) after adhering onto the polybenzoxazines films after 1 day; *P. tricornutum* (C2) before and (C3) after adhering onto the polybenzoxazines films after 1 day.

■ CONCLUSIONS

A variety of bio-based main-chain-type benzoxazine polymers (MCBPs) were synthesized from the renewable daidzein, furfurylamine, polyetheramine, and paraformaldehyde. Their microstructures were identified by FT-IR, NMR, and GPC before the curing behaviors were investigated by DSC and dynamic rheological analysis. Prior to the curing reaction, the synthesized MCBPs showed excellent processability, and after heat treatment, the cross-linked MCBPs exhibited varied thermal and mechanical properties, depending on the molar ratio of polyetheramine and furfurylamine. Their T_g was in the range of 92.9–268.5 °C, their tensile strength varied from 16.3 to 54.7 MPa, and their flexural strength ranged from 24.8 to 93.1 MPa. Some of them were even higher than the monomer-type polybenzoxazines. These results were totally different from the literature results where the cured MCBPs usually showed relatively low T_g and strength, except the excellent flexibility. Notably, the MCBP-based coatings demonstrated very good antibacterial properties and excellent algae-killing ability, which had huge potential application in the field of marine antifouling coatings, and the reason was attributed to the unique structure of daidzein and furan units. In this work, the functional application of polybenzoxazine based on the special structures of renewable compounds was first demonstrated, which might be a remarkable step toward the functionalization of bio-based materials, besides the high thermal and mechanical properties.

■ EXPERIMENTAL SECTION

Materials. Daidzein (98%) was obtained from SHANXI HAICHEN Bio-Technology Co., Ltd. Poly(propylene glycol) bis(2-aminopropyl ether) (D-600, 98%), furfurylamine (99%), paraformaldehyde (96%), and toluene (99%) were acquired from Aladdin Reagent, China. Petroleum ether (60–90 °C) and methanol (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received.

Synthesis of MCBPs. The synthesis of MCBPs was simply illustrated in Scheme 1. Toluene (200 mL), a predetermined mixture of D-600 and furfurylamine (the total amino group content of D-600 and furfurylamine was 1 mol with varied molar ratio), and paraformaldehyde (2 mol) were added into a 500 mL round-bottom flask and stirred at room temperature for 30 min. Then, 0.5 mol of daidzein dissolved in 50 mL of toluene was added into the above mixture. After being heated at 90 °C for 12 h, the solution was cooled down to room temperature and concentrated under reduced pressure. The obtained crude product was washed several times with petroleum ether and then precipitated in methanol. Finally, the residual solvent was evaporated under vacuum to yield the target product. The nomination, feed composition, yield, and molecular weight of resulting MCBPs are shown in Table 1.

Curing Procedure for MCBPs. The curing reaction for MCBPs was conducted in a stainless steel mold according to the following procedure: MCBPs in a stainless steel mold were degassed under vacuum oven at 100 °C for 20 min and then step-cured in a convection oven for 2 h at 140 °C, 2 h at 160 °C, 2 h at 180 °C, and 2 h at 200 °C. Once they were completely cured, the samples were allowed to slowly cool to room temperature, and the brown films were obtained. For coating performance evaluation, the degassed fluid MCBPs were sprayed on polished tin plates to form a resin film with a

thickness of $\sim 50 \mu\text{m}$. Then, the coatings were cured according to the same curing procedures.

Measurements. Fourier transform infrared spectra (FT-IR) were acquired on a NICOLET 6700 (NICOLET, America) spectrometer at room temperature. Samples were prepared by blending with KBr powder and then being compressed into a pellet. The spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . The chemical structure of MCBPs was verified by ^1H nuclear magnetic resonance (NMR) spectra recorded on a 400 MHz AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) at 25 °C using CDCl_3 as the solvent. The molecular weight determination of MCBPs was conducted on an HLC-8320 (TOSOH ECOSEC, Japan) gel permeation chromatography (GPC) system using monodisperse polystyrene as the calibrant and THF as the eluent at a flow rate of 1 mL/min. The curing behavior of MCBPs was analyzed by differential scanning calorimetric (DSC) measurement conducted on a DSC (METTLER TOLEDO, Switzerland) from 25 to 300 °C under a high-purity nitrogen atmosphere at a flow rate of 20 mL/min. The thermal stability of cured samples was evaluated with a Mettler-Toledo TGA/DSC1 (METTLER TOLEDO, Switzerland) from 50 to 800 °C at a heating rate of 20 °C/min. A universal mechanical testing machine (Instron 5569A) was used to measure the tensile (100 mm $\times$ 8 mm $\times$ 0.5 mm) and flexural (100 mm $\times$ 8 mm $\times$ 3 mm) properties with a crosshead speed of 10 and 2 mm min^{-1} . Five tests were carried out for each sample.

Dynamic mechanical analysis (DMA) was performed on a TA Instrument (TA Q800, USA) in tension mode with a heating rate of 3 °C/min in the temperature range of 25 to 350 °C using a frequency of 1 Hz. The dimensions were 20 mm $\times$ 5 mm $\times$ 0.5 mm, and the amplitude was set as 10 mm. To evaluate the melt processability of MCBPs, a dynamic rheological analyzer (Anton Paar Physica MCR-301, Austria) was utilized. The test was performed between parallel plates in steady shear mode with a heating rate of 3 °C/min and shear rate of 1 s^{-1} . The pencil hardness was evaluated using a pencil hardness tester (Tianjin Kexin Test machinery factory, China) according to ASTM D3363-00. The flexibility of the film was measured according to ASTM D4145-10. The adhesion was determined by a crosshatch adhesion method according to ASTM D3359-09. The solvent resistance of coating films was determined by the double rub method according to the ASTM D5402-06. These films were wiped with a cotton gauze using ethanol or methyl ethyl ketone as the solvent. The results were reported as the minimum number of double rubs at which a significant change on the surfaces was observed or it was reported as “>400” if no change was observed after 400 double rubs, which was the maximum number of double rubs in the test. The antifouling property of cured films was assessed by examining the formation of a bacterial biofilm and settlements of algae on their surfaces. *E. coli* (ATCC 25922, Gram-negative) and *B. cereus* (ATCC6538, Gram-positive) were chosen as the model bacteria (ASTME2149-01): the bacterium was incubated in a fluid medium (0.5 wt % yeast extract powder, 1 wt % fish meal peptone, 1 wt % NaCl) with a shake speed of 120 rpm at 30 °C for 24 h. Then, the bacteria-containing medium was centrifuged at 2500 rpm for 10 min. After the supernatant was removed and washed three times with sterile 9 wt % saline solution, the concentration of bacterium solution was determined using a microplate reader (SpectraMax 190, Molecular Devices) until an OD 600 of 0.1

A (10^8 CFU/mL) was reached. Further appropriate dilution with the sterile 9 wt % saline solution led to a final concentration of 10^5 CFU/mL. Each film was added into a flask, which contains 50 mL of bacterium solution with the concentration of 10^5 CFU/mL, and was placed on a shaker at 37 °C (120 rpm). After cultivation for 36 h, 100 μ L of solution was extracted and diluted (10^{-1} , 10^{-2}) and 100 μ L of diluted solution was placed on nutrient agar plates in triplicate and incubated at 37 °C for 24 h. The number of bacterial colonies on each plate was counted. The killing ratio (R) was calculated by $R = (N_0 - N_t)/N_0 \times 100\%$. N_0 and N_t are the bacterium concentrations of control and experiments, respectively. Diatoms *P. tricornutum* (NMBguh001, from Ningbo University, China) and *Navicula* sp. (NMBguh006–8, from Ningbo University, China) were selected to further investigate the antifouling performances. The diatoms were cultured in sea water until the concentration was close to 10^5 cells/mL. The MCBP films were incubated in a biochemical incubator with the above diatom suspension. Adhesion of algae on the surface of MCBP films for 24 h was performed, and then they were observed using a 3100v laser scanning confocal microscope (LSCM, TCS SP5, Leica, Germany) analysis system and a scanning electron microscope (SEM, EVO18, ZEISS, Germany). Each sample was randomly selected at 10 fields of vision, and the amount of attached algae was calculated. At least three experiments were repeated for each sample.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c00025>.

FT-IR spectra and GPC curves of Dz-0.9d600-0.2f, Dz-0.7d600-0.6f, Dz-0.5d600-1.0f, and Dz-0.3d600-1.4f; tensile stress–strain curves and flexural stress–strain curves for cured MCBPs; images of two bacterium colonies that survived on the nutrient agar plates after treatment with control and cured MCBPs (PDF)

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Notes

The authors declare no competing financial interest.

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