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Synthesis of Eugenol-Based Silicon-Containing Benzoxazines and Their Applications as Bio-Based Organic Coatings

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Abstract: In this work, several bio-based main-chain type benzoxazine oligomers (MCBO) were synthesized from eugenol derivatives via polycondensation reaction with paraformaldehyde and different diamine. Afterwards, their chemical structures were confirmed by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR). The curing reaction was monitored by Differential Scanning Calorimetry (DSC) and FT-IR. The polybenzoxazine films were prepared via thermal ring-opening reaction of benzoxazine groups without solvent, and their thermodynamic properties, thermal stability, and coating properties were investigated in detail. Results indicated that the cured films exhibited good thermal stability and mechanical properties, showing 10% thermal weight loss ($T_{d10\%}$) temperature as high as 408 °C and modulus at a room temperature of 2100 MPa as well as the glass transition temperature of 123 °C. In addition, the related coatings exhibited high hardness, excellent adhesion, good flexibility, low moisture absorption, and outstanding solvent resistance.

Keywords: bio-based; benzoxazine; eugenol; coatings

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1. Introduction

Polybenzoxazines play an indispensable role in the thermosets market. They are widely applied in the areas of coatings, adhesives, microelectronics, and aerospace due to their exceedingly good properties, such as excellent chemical resistance, good thermal stability, minimal water absorption, nearly zero shrinkage, and good electronic properties [1–6]. As we know, the currently predominant raw materials for the synthesis of polybenzoxazine resins are almost always derived from fossil resources. With the fast consumption of petroleum oil and increasingly serious environmental pollution, utilization of bio-based feedstock to prepare green polymeric materials has attracted more and more attention in both academic and industrial communities [7–9]. A variety of bio-based benzoxazines have been prepared from renewable phenolic resources, such as arbutin [10], cardanol [11,12], cellulose derivative (diphenolic acid) [13–15], and lignin derivatives (vanillin, guaiacol, eugenol) [16–22]. The most widely used bio-based amines are furfurylamine and stearylamine [16,19,23–25]. Besides that, 1,4-butanediamine could also be regarded as a bio-based amine resource, which is called putrescine. Undoubtedly, the employment of phenols or amines derived from biomass to prepare benzoxazine has certain advantages. However, the promising structure design and chemical modification are still the most important subjects for the synthesis of bio-based benzoxazine. For instance, similar to the petroleum-based benzoxazine, it is still a challenge for us to further improve their thermal and mechanical properties, lower the curing temperature, and increase their toughness [26]. Eugenol (4-allyl-2-methoxyphenol) is a relatively cheap (ca. \$5 kg^{-1}) bio-based compound with multi-reactive groups, which can be prepared via the pyrolysis [27,28] or depolymerization [29,30] of lignin. It has great potential to be widely used in polymer science due to its unique structure, abundant availability, and low cost. Up to now, several benzoxazine resins derived from eugenol have been reported. It was noted that the cross-link density of eugenol-based benzoxazines without extra polymerizable sites was a little low due to the occupied ortho and para position, with respect to the phenolic hydroxyl group [20,31,32]. In addition, its high brittleness is also a problem that need to be resolved [33]. Much effort has been made to increase the toughness of polybenzoxazine resin, and the strategies reported already could be divided into two categories. One is blending the flexible or soft polymers, include rubber [34], polyurethane [35,36], polysiloxanes [37–39], and chitosan [40] with the cured resins. For instance, Jang and Yang [34] prepared a polybenzoxazine composite with good toughness by blending with rubber. In Hosta's work [38], a series of poly(B-a)-P(DMS/DPS) hybrids films were successfully prepared and the hybrid films showed higher tensile strength and elongation upon breaking than the pristine poly(B-a). The second approach is the incorporation of long soft chains into benzoxazine architecture. For example, the main-chain type benzoxazine polymers (MCBP) with high-molecular-weight prepared from difunctional phenols and diamines were widely reported [41–45]. Before the curing reaction, these main-chain type polybenzoxazines could behave like the thermoplastic, which demonstrated good solubility in most common organic solvents and satisfied processability as well as excellent film-forming properties [42–45].

To the best of our knowledge, the eugenol-based main-chain type benzoxazine polymer (MCBP) has never been reported previously. In this study, the silicon-containing eugenol derivative, 4,4′-(1,3-dipropyl-tetramethyldisiloxane)bis-2-methoxyphenol (SIE) was synthesized at first. Then it was reacted with different diamines and paraformaldehyde to obtain different oligomers. The chemical structures and curing reaction of synthesized oligomers as well as the properties of cured resins—in terms of thermodynamic properties, thermal stability, and coating properties—were investigated. The objective of this work is to develop bio-based benzoxazine precursors with good processability and film-forming properties at room temperature, then to prepare high performance organic coatings derived from eugenol.

2. Materials and Methods

2.1. Materials

The following were all purchased from Aladdin Reagent (Shanghai, China): 1,1,3,3-tetramethyl disiloxane (99%), chloroplatinic acid hexahydrate (99%), toluene (99%), petroleum ether (99%), and isopropyl alcohol (99.5%). The following were obtained from Zhejiang Guoguang Biochemistry Co., Ltd. (Hangzhou, China): 1,2-ethylenediamine (99%), 1,4-butanediamine (99%), 1,6-hexanediamine (99%), paraformaldehyde (95%), and dioxane (99.5%). All the chemicals were used as received without any purification. According to the procedures described previously, 4,4′-(1,3-dipropyl-tetramethyldisiloxane) bis-2-methoxyphenol (SIE) (Figure 1) was synthesized by the hydrosilylation of eugenol with 1,1,3,3-tetramethyldisiloxane [44]. Before the following reaction with amines, its chemical structure was identified in detail.

SIE: ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 6.97 (s, 1H), 6.86 (s, 1H), 6.67–6.69 (m, 4H), 3.85 (s, 6H), 2.58 (m, 4H), 1.64 (m, 4H), 0.59 (m, 4H), 0.08 (s, 12H).

^{13}C-NMR (400 MHz, $CDCl_3$, δ, ppm): 146.91 (s), 143.70 (s), 134.59 (s), 121.00 (s), 114.40 (s), 111.21 (s), 55.79 (s), 39.36 (s), 25.75 (s), 18.18 (s), 1.07 (s).

FT-IR (KBr, cm^{-1}): 3456 (–OH); 2955 ($-CH_3$); 2924, 2857 ($-CH_2-$); 1612, 1514 (Benzene: –C=C–); 1055 (–Si–O–Si–).

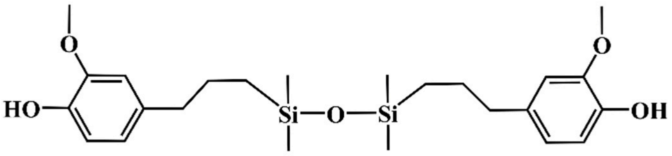

Figure 1. Structure of 4,4′-(1,3-dipropyl-tetramethyldisiloxane)bis-2-methoxyphenol (SIE).

2.2. Measurements

The ^{1}H NMR spectra was recorded with a Bruker AVANCE III 400MHz NMR spectrometer (Bruker, Billerica, Switzerland). It was conducted at room temperature and deuterated chloroform was used as a solvent. TMS was used as an internal standard and the average transient number was 64.

The infrared spectrum (FT-IR) was collected with NICOLET 6700 FTIR (NICOLET, Thermo Fisher Scientific, Waltham, MA, USA) using the KBr pellet method. The spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans were collected for each sample. The samples were prepared by dissolving a small amount of compounds in chloroform, then smearing the solution onto a KBr crystal plate and evaporating the solvent at the higher temperature (40 °C) completely.

The molecular weight and dispersity of benzoxazine oligomers were measured by a HLC-8320 Gel Permeation Chromatograph (GPC, Tosoh Corporation, Tokyo, Japan). The standard sample was monodisperse polystyrene with the molecular weight in the range of 2500 to 1110,000 g/mol. The mobile phase was THF and the flow rate was 1 mL/min.

The viscosities of synthesized oligomers were obtained by the isothermal rheological analyzer (Anton Paar Physica MCR-301, Anton Paar GmbH, Graz, Austria) with a parallel plate. The diameter of the plate was 25.0 mm and the gap between the two plates was set to be 0.30 mm. The test was performed at 30 °C with a shear rate of 5 s^{-1}.

The non-isothermal curing reactions were monitored by a Mettler-Toledo MET DSC (METTLER TOLEDO, Greifensee, Switzerland) in a high purity nitrogen atmosphere with a flowing rate of 60 mL/min. The heating rate was 10 °C/min.

Mechanical properties of the free polybenzoxazine films were measured using a Universal Mechanical Testing Machine (Instron 5569A, Instron Limited, High Wycombe, UK). The crosshead speed was 5 mm/min. Before testing, all the films were conditioned at room temperature for 24 h with a humidity of 50%. The tensile properties of each film were reported as the average of five specimens.

Dynamic Mechanical Analysis (DMA) tests were performed on a TA Instrument (TA Q800, New Castle, DE, USA) in a tension fixture mode. The free polymer films with the dimension of 20 mm × 5 mm × 0.5 mm were tested from 0 °C to 200 °C at a heating rate of 3 °C/min and a frequency of 1 Hz. For accuracy, five specimens were tested for each polymer film.

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC1 (METTLER TOLEDO, Greifensee, Switzerland). The purge gas was high purity nitrogen. All the polymer films were heated from 50 to 800 °C with a heating rate of 20 °C/min.

The pencil hardness of coatings with a thickness of about 50 μm on the tinplate were measured according to ASTM D3363-00 [46]. The flexibility of the coatings was measured by T-Bend Test according to ASTM D4145-10 [47]. The adhesion on tinplate was evaluated using the ASTM D3359-09 crosshatch adhesion method [48]. Water absorption properties of free polybenzoxazine films were measured by immersing them in the water at room temperature for 48 h. Then the soaked specimens were taken out and both surfaces were dried with dust-free paper before weighing. Water absorption was calculated by the weight differences between the swollen and dry samples. Solvent resistance was determined by the double rub method according to ASTM D5402-06 [49]. The coatings on substrate were rubbed with a cotton gauze using ethanol as the solvent. The results were reported as the minimum number of double rubs at which obvious change on the surfaces were observed, or reported as ">400", if no change was observed after 400 double rubs, which was the maximum number of double rubs in this method.

2.3. Synthesis of Different Benzoxazine Oligomers

Three kinds of benzoxazine oligomers were prepared from SIE, 1,2-ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine, and paraformaldehyde according to the following procedure. Into a 500 mL round flask equipped with a condenser and magnetic stirrer, 3.0 g 1,2-ethylenediamine (0.05 mol) and 6.0 g paraformaldehyde (0.2 mol), together with 100 mL toluene, were added. After the mixture was stirred at room temperature for 30 min, 23.1 g SIE (0.05 mol) was added. Then, the mixture was heated to 90 °C and maintained at this temperature for 12 h before the toluene was stilled out of the system. The product was washed by petroleum ether several times before the residual solvent was removed by vacuum oven and the final product (17.3 g) was obtained (yield of 56%). The synthetic route was shown in Figure 2 and in the following Table 1, the feeding composition for different oligomers were listed. Based on the used diamines, the benzoxazine oligomers were named as poly (SIE-e), poly (SIE-b), and poly (SIE-d), respectively. The synthesis procedures for poly (SIE-b) and poly (SIE-d) were the same as that of poly (SIE-e).

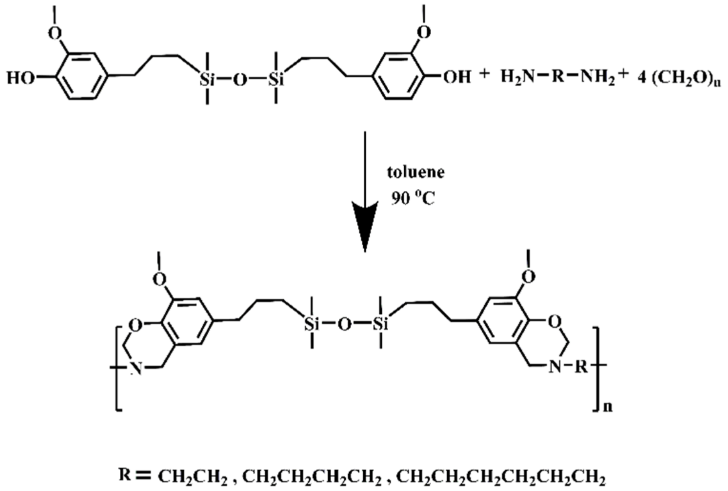

Figure 2. Illustration for the synthesis of poly (SIE-e), poly (SIE-b), and poly (SIE-d).

Table 1. Feed composition, Gel Permeation Chromatograph (GPC) data, and viscosities of the synthesized benzoxazines.

Sample	Diamine	M_n	M_w/M_n	Viscosity at 30 °C (Pa·s)	Bio-Based Content (%)	Yield
poly (SIE-e)	1,2-ethylenediamine	960	1.9	730	60	56%
poly (SIE-b)	1,4-butanediamine	1000	1.5	280	57	59%
poly (SIE-d)	1,6-hexanediamine	1260	1.7	30	55	71%

2.4. Curing of Poly (SIE-e), Poly (SIE-b), Poly (SIE-d), and Coating Preparation

Poly (SIE-e), poly (SIE-b) and poly (SIE-d) were degassed under vacuum oven at 50 °C for 30 min and then poured into a Teflon mold to prepare the films with the dimensions of 20 mm × 5 mm × 0.5 mm. The curing reaction was performed in an air-circulating oven at the temperatures of 120 °C, 160 °C, 200 °C, and 220 °C for 2 h each [50]. Finally, the cured samples were cooled down to room temperature and carefully removed from the mold. All of the cured samples were dark brown and the prepared sample was directly applied for properties evaluation.

For the preparation of coatings, the tinplates were cleaned with acetone to remove rust and degrease before coating, then the benzoxazines oligomers were spread on them without any solvent using an automatic spreader (Tian Jin Hong Ju Li Co., Ltd., Tianjin, China) to form thin wet films with the thickness of about 50 µm. The curing reaction was followed by the procedures as described above.

3. Results and Discussion

3.1. Characterization of Different Benzoxazine Oligomers

The FT-IR spectra of poly (SIE-e), poly (SIE-b), and poly (SIE-d) are shown in Figure 3. They showed quite similar absorption peaks. In Figure 3, the strong band shown at around 1060 cm^{-1} was due to the Si–O–Si stretching [51], and the peak at 1147 cm^{-1} indicated the presence of C–N–C. For the peak at 1256 cm^{-1}, it was assigned to the antisymmetric stretching of C–O–C in the oxazine ring [20] and the characteristic signal for C–H stretch of benzene was shown at 928 cm^{-1}. The absorption band centered at 1498 cm^{-1} corresponded to the trisubstituted benzene ring vibration. In order to make a further structure confirmation, the ^{1}H-NMR spectra of poly (SIE-e), poly (SIE-b), and poly (SIE-d) are shown in Figure 4. The characteristic peaks of benzoxazine corresponding to the methylene units in oxazine rings (O–CH_2–N and Ph–CH_2–N) were observed at 3.93–3.97 ppm and 4.89–4.94 ppm [41], respectively. The characteristic peaks for aromatic protons were shown in the range of 6.33–6.57 ppm. Based on the characteristic peak assignment and their integral shown in Figure 4, the formation of target products could be confirmed. As shown in Table 1, the number-average molecular weight (M_n) of all the oligomers were ranged from 955 to 1261 g/mol, which indicated the average number of repeating units was about 2. In addition, the viscosity is also an important factor determining the application of organic coating. As shown in Figure 5, the viscosity of poly (SIE-e,f), poly (SIE-b,f), and poly (SIE-d,f) were 727, 278 and 29 Pa·s, respectively. Due to the longest aliphatic units in poly (SIE-d,f), it exhibited the lowest viscosity. The relatively low viscosity at 30 °C ensured their good film-forming properties.

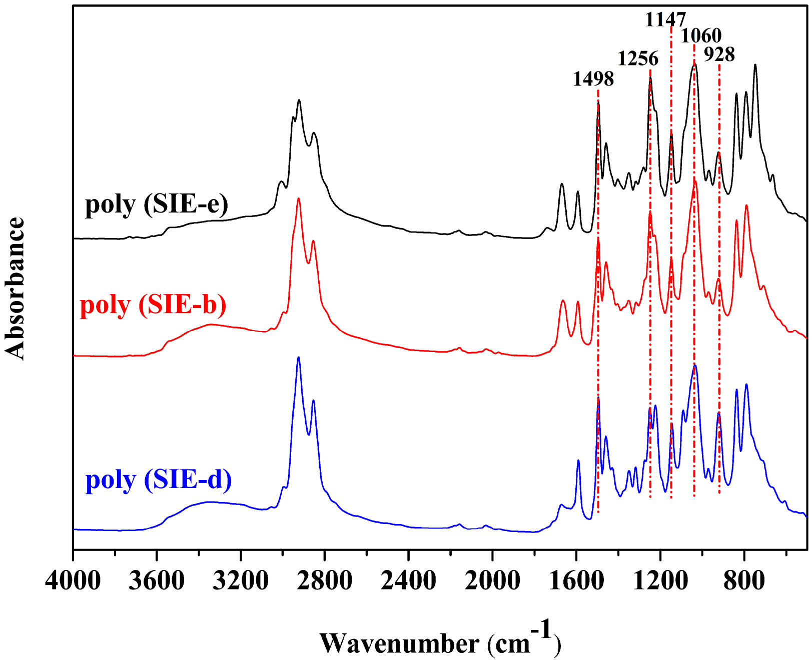

Figure 3. FT-IR spectra of different benzoxazine oligomers.

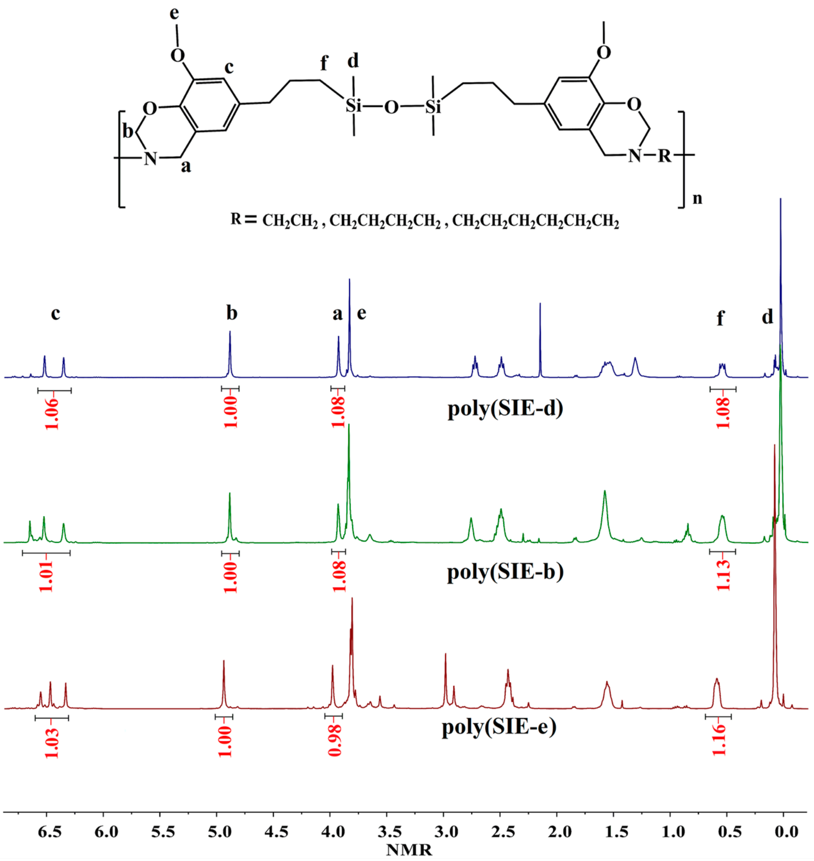

Figure 4. NMR spectra of different benzoxazine oligomers.

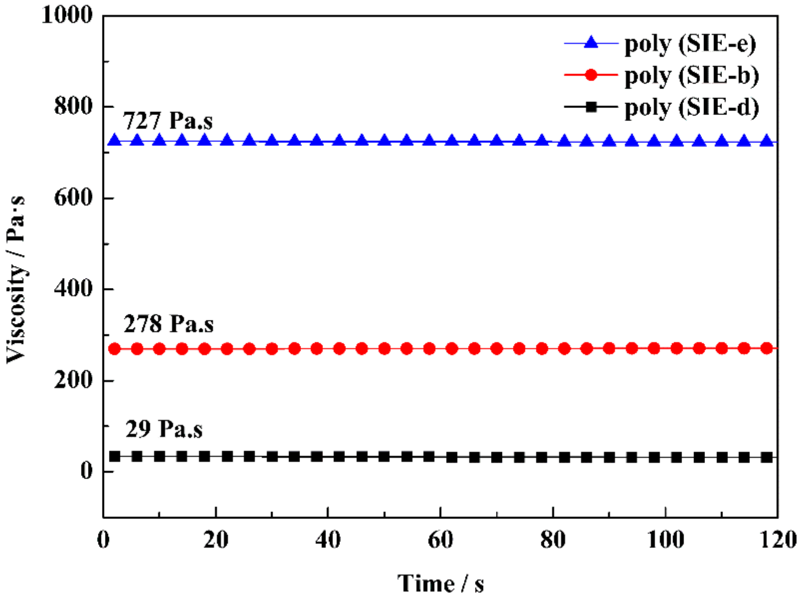

Figure 5. The viscosity of different benzoxazine oligomers at 30 °C.

In order to regulate and guide the development of bio-based polymers, some international standards for the determination of bio-based content have been established. For example, the bio-based content of a product was defined as "the amount of bio-based carbon in the product as a percentage of the weight of the total organic carbon in the product" by United States Department of Agriculture

(USDA) [52]. Based on above definition, the bio-based content (In Table 1) of poly (SIE-e), poly (SIE-b) and poly (SIE-d) was calculated to be 60%, 57% and 55%, respectively.

3.2. Curing Behavior of Poly (SIE-e), Poly (SIE-b), and Poly (SIE-d)

In order to explore the optimal curing conditions, the curing behaviors of poly (SIE-e), poly (SIE-b), and poly (SIE-d) were monitored by DSC. As shown in Figure 6a, the DSC curves for all the samples presented a single broad exothermic peak, which corresponded to the ring-opening polymerization of the oxazine ring. As a general rule, the peak temperature for DSC exothermic curves is usually taken as an indicator to evaluate the curing reactivity. The lower the temperature of the peak, the higher the reactivity of the component [53]. In Figure 6a, the onset curing temperatures for poly (SIE-e), poly (SIE-b), and poly (SIE-d) were as low as 134 °C, 135 °C, and 132 °C, and their peak curing temperature were 215 °C, 220 °C, and 224 °C, respectively. Compared with the conventional benzoxazines, the onset curing temperatures for these bio-based benzoxazine oligomers were much lower [54]. The reason might be due to the existence of phenol or primary amine end groups in the molecular chain, which could catalyze the curing reaction and then decrease the starting curing temperature [55]. And the trace impurity also might decrease curing temperature. As marked in Figure 6a, the exothermic enthalpy values of poly (SIE-e), poly (SIE-b), and poly (SIE-d) were about 70, 55, and 51 J/g respectively, corresponding to a ΔH of 56 kJ to 73 kJ per mole of benzoxazine ring, which was in good accordance with the widely accepted enthalpy value for the benzoxazine ring opening reaction. Figure 6b showed the DSC curves for poly (SIE-e), poly (SIE-b), and poly (SIE-d) after the curing reaction and no more exothermic peaks were observed in the range of 200–250 °C, which confirmed the full polymerization of oxazine rings. However, a deviation of the base line was observed for all the systems when the temperature was increased to higher than 270 °C, which might be caused by the post-curing or the thermal degradation of cured resins at higher temperature [32,56].

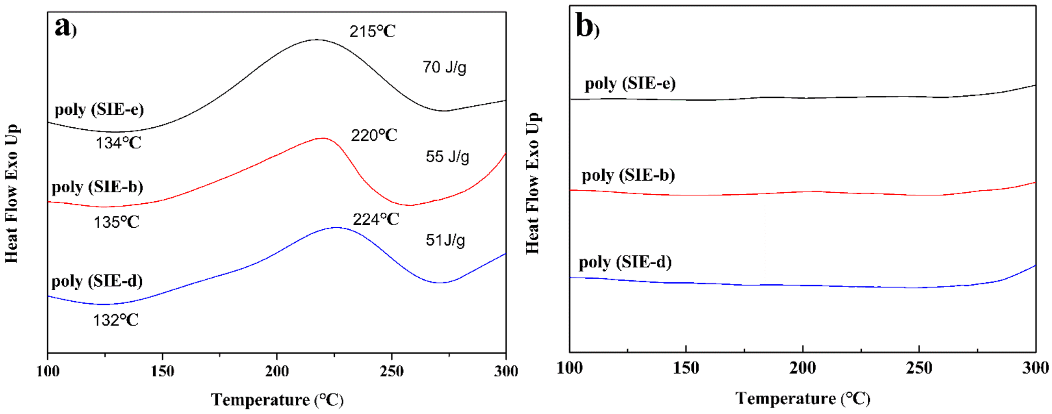

Figure 6. DSC heating curves for different benzoxazine oligomers (**a**); Non-isothermal DSC thermograms for the cured benzoxazine oligomers (**b**).

Although the assignments of FT-IR characteristic signals for polybenzoxazine were quite difficult due to their complex chemical structures, the FT-IR spectra of poly (SIE-b) at different curing stages were shown in Figure 7. It was noticed that the characteristic absorption bands attributed to the oxazine ring and trisubstituted benzene ring showing at 928, 1147, and 1498 cm^{-1} were gradually decreased along with the curing process and finally disappeared after the 220 °C cure stage, which was another indirect evidence for the fully curing reaction of the synthesized oligomers. Based on the above DSC and FT-IR analysis, the applied curing procedures was proven to be suitable for the curing reaction. According to the previously reported results [16], the proposed chemical structures of the final polybenzoxazine is shown in Figure 8.

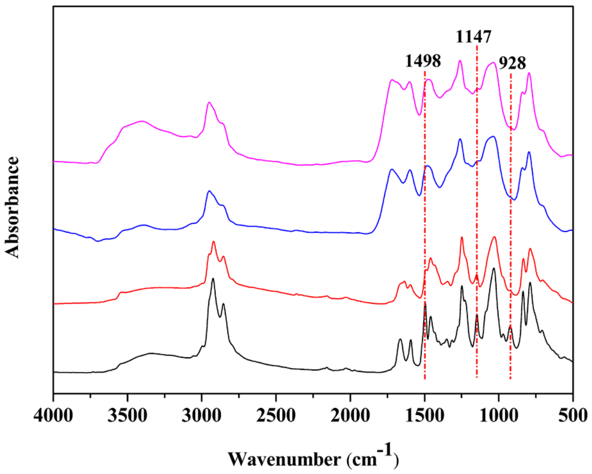

Figure 7. FT-IR spectra of poly (SIE-b) at different curing stages.

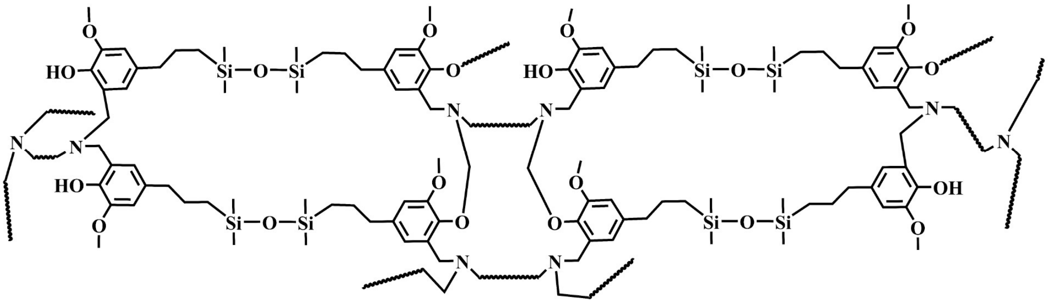

Figure 8. The possible chemical structures of final cured polybenzoxazine.

3.3. Mechanical Properties of the Cured Oligomers

Generally, the tensile properties of polybenzoxazine are difficult to measure, due to its inherent high brittleness. However, in this work the cured benzoxazine oligomers demonstrated high flexibility. As shown in Figure 9, all the polybenzoxazine films could be completely folded. The stress–strain curves of cured-poly (SIE-e), cured-poly (SIE-b), and cured-poly (SIE-d) are shown in Figure 10 and related values are collected in Table 2. The tensile strength of cured-poly (SIE-e), cured-poly (SIE-b), and cured-poly (SIE-d) were 24.7, 20.9, and 16.6 MPa, respectively, with an elongation upon breaking of 2.9%, 3.0%, and 3.9%. It was noted that when the length of diamine was increased, from 1,2-ethylenediamine to 1,6-hexanediamine, the tensile strength of cured benzoxazine resins was decreased accordingly, and their elongation upon breaking demonstrated the opposite tendency.

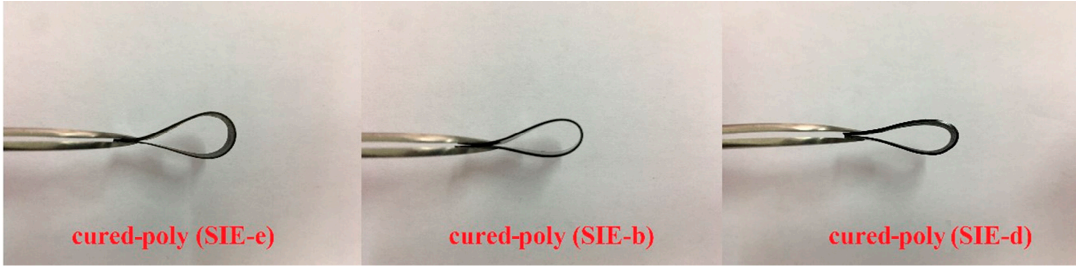

Figure 9. Thin film photographs for cured-poly (SIE-e), cured-poly (SIE-b), and cured-poly (SIE-d).

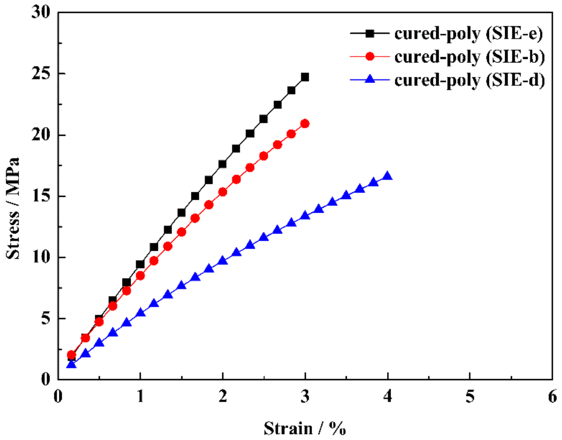

Figure 10. Stress-strain curves of different cured polymers.

Table 2. DMA and TGA data of the cured MCBPs.

Cured-Samples	**T_g [a] (°C)**	**E' [b] (MPa)**	**ν_e [c]/10^3 (mol·m^{-3})**	**σ [d] (MPa)**	**ε [e] (%)**	**$T_{d10\%}$ (°C)**	**T_{dmax} [f] (°C)**	**R_{800} (%)**
cured-poly (SIE-e)	123	2102	47.0	24.7 ± 1.5	2.9 ± 0.2	402	409	56
cured-poly (SIE-b)	96	1863	43.9	20.9 ± 0.9	3.0 ± 0.1	397	411	53
cured-poly (SIE-d)	89	1723	30.6	16.6 ± 1.1	3.9 ± 0.2	392	415	45

[a]: Glass transition temperature determined by DMA; [b]: Storage modulus at 25 °C; [c]: Caculated crosslink density; [d]: Tensile strength; [e]: Elongation at break; [f]: Temperatures for maximum degradation rate.

3.4. Dynamic Mechanical Properties and Thermal Stability of Cured Benzoxazine Oligomers

The dynamic mechanical analysis (DMA) was usually taken to study the viscoelastic properties of thermosets. In Figure 11, all the cured resins presented similar DMA curves and their modulus as well as glass transition temperature (T_g) are collected in Table 2. The storage modulus for the cured-poly (SIE-e), cured-poly (SIE-b), and cured-poly (SIE-d) at 25 °C were found to be 2102 MPa, 1863 MPa, and 1723 MPa, respectively. Their T_g ranged from 89 to 123 °C, which was lower than the conventional polybenzoxazine resins' T_g. However, when compared with the main-chain type polybenzoxazines reported in the literature [57,58], the T_g of 123 °C were higher than or comparable with them. For example, Zhang et al. prepared a bio-based main-chain type polybenzoxazine whose T_g was 113 °C. In Tuezuen's work, three kinds of MCBPs were prepared, and the highest T_g of cured product was only 87 °C. It was reasonable and easy to understand that the longer aliphatic chain (1,6-hexanediamine > 1,4-butanediamine > 1,2-ethylenediamine) would lead to decreased crosslink density and then lower the storage modulus and T_g of cured benzoxazine resins. Of course, the crosslink density should not be the only factor responsible for the mechanical and thermomechanical properties; the so-called comonomer effect (this could be seen as the different amine segment in this work) would be another reason [59].

The crosslink density (ν_e: the number of moles of network chains per unit volume of the cured systems) of the cured benzoxazine oligomers could be obtained by the following equation derived from the theory of rubber elasticity [53]:

$$\nu_e = \frac{E'}{3RT} \qquad (1)$$

where E' is the storage modulus of the cured samples in the rubbery plateau region at 190 °C (much higher than T_g), R is the gas constant, and T is the absolute temperature. The calculated crosslink density for the cured resin was listed in Table 2. As expected the crosslink density was decreased in the order: cured-poly (SIE-e) > cured-poly (SIE-b) > cured-poly (SIE-d). As we know, the height and width of tan δ peak provides valuable information. Usually, the broader peak of tan δ is associated with the inhomogeneous features and the lower tan δ peak reflects the weaker segment mobility of the network. In Figure 11a, the lowest tan δ peak was observed for cured-poly (SIE-e), which was in good accordance with its highest T_g. The relatively broader peaks of tan δ might be helpful for the flexibility of these cured systems.

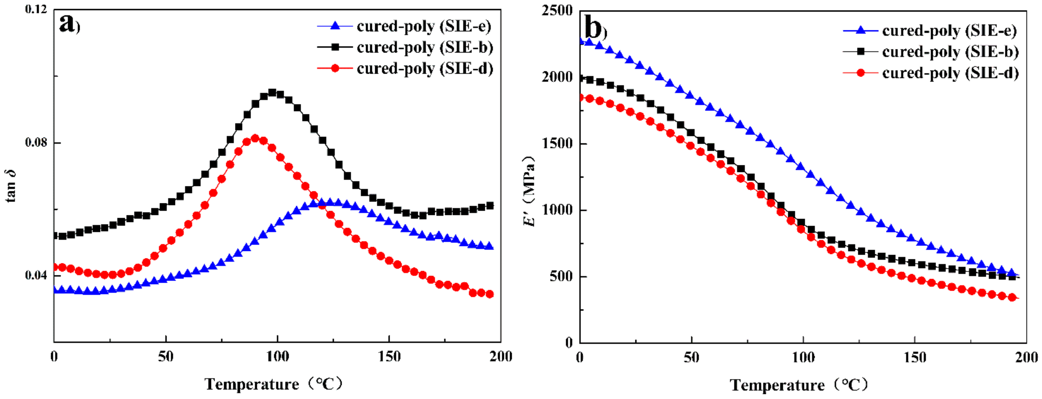

Figure 11. DMA curves for the cured benzoxazine oligomers: (**a**) tan δ of the bio-based cured benzoxazine polymers; (**b**) *E′* of the bio-based cured benzoxazine polymers.

TGA was performed to investigate the thermal stability of the cured oligomers and Figure 12 is the TGA curves under nitrogen atmosphere. It can be seen that all the cured samples remained stable before 350 °C and their degradation temperatures for 10% weight loss ($T_{d10\%}$) ranged from 392 °C to 402 °C, which indicated their good thermal stability. The char yields at 800 °C (R_{800}) for all the samples are also listed in Table 2. The value of R_{800} was varies from 45% to 56% and in the order of cured-poly (SIE-e) > cured-poly (SIE-b) > cured-poly (SIE-d). This was due to the fact that in the sample containing shorter aliphatic diamine units, the aromatic and siloxane segments contents were relatively higher, which could result in a higher char yield at elevated temperature [60].

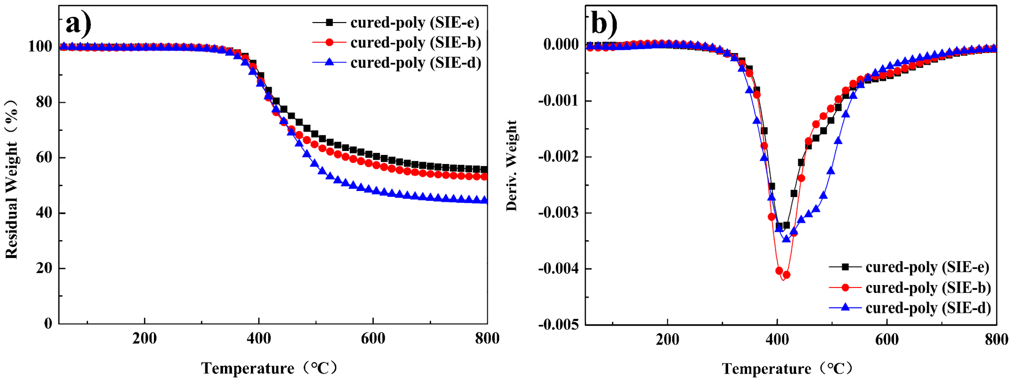

Figure 12. TGA curves for the bio-based cured benzoxazine polymers: (**a**) TG curves of the bio-based cured benzoxazine polymers; (**b**) DTG curves of the bio-based cured benzoxazine polymers.

3.5. Coating Properties of the Cured Oligomers

The characterization of coating properties such as pencil hardness, adhesion, water absorption, and solvent resistance were all investigated and the results were shown in Table 3. As seen from the digital photographs for coatings in Figure 13, all the benzoxazine oligomers could be coated well on the surface of tinplates using an automatic spreader. Due to low viscosity of oligomers, the thin films could be prepared without the addition of any solvent. After the curing reaction, the coatings showed a lower pencil hardness (3H) and better flexibility when compared with the conventional benzoxazine coatings; this was reasonable and might be attributed to several factors, including the soft silicone segments, broad T_g, aliphatic flexible segments, and low crosslink density. As we know, the polybenzoxazines is usually very brittle and we are eager to achieve higher flexibility [41]. In this work, the polybenzoxazine coatings demonstrating relatively higher flexibility were obtained by the incorporation of Si–O–Si units. As could be seen, the adhesion of cured resins to tinplate was as high as 5B, which was the highest grade of adhesion according to ASTM D3359-09. It should be the plentiful aromatic rings and phenolic hydroxyl groups in the cured benzoxazine that made contributions to the excellent adhesion [61]. The water absorption value of the coatings was extremely low. That was the intrinsic advantage of polybenzoxazine resins [5]. The solvent double rub test was performed for more than 400 cycles using ethanol and MEK (2-butanone) and no obvious defect such as loss of shine or brightness, or removal of coating on the coating surface was detected.

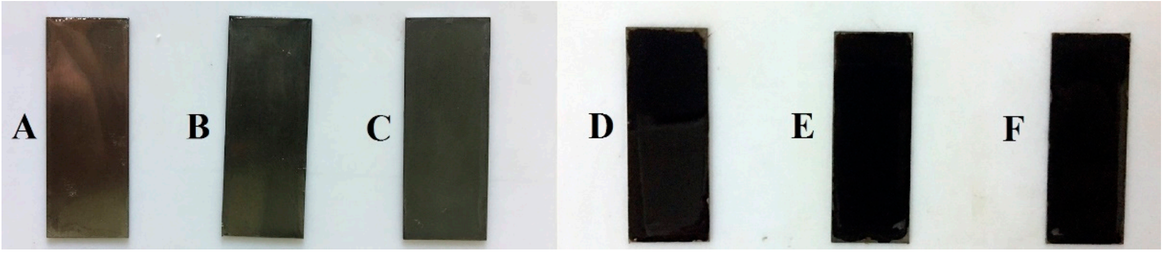

Figure 13. Digital photographs of benzoxazine coatings before and after curing reaction: (**A**) for poly (SIE-e); (**B**) for poly (SIE-b); (**C**) for poly (SIE-d); (**D**) for cured-poly (SIE-e); (**E**) for cured-poly (SIE-b); and (**F**) for cured-poly (SIE-d).

Table 3. Coating performance of cured benzoxazine oligomers.

Samples	Thickness (um)	Pencil Hardness	Flexibility	Adhesion	Water Sbsorption	MEK Resistance	Ethanol Resistance
cured-poly (SIE-e)	50	3H	1T	5B	1.2%	>400	>400
cured-poly (SIE-b)	50	3H	1T	5B	1.1%	>400	>400
cured-poly (SIE-d)	50	3H	1T	5B	0.7%	>400	>400

4. Conclusions

A series of bio-based benzoxazine oligomers were synthesized from eugenol derivatives, paraformaldehyde, and several different diamines. The oligomers showed good processability and film-forming properties at room temperature. The cured films were prepared via thermal ring-opening reaction of oxazine groups. According to the thermal and coating properties investigation, the cured benzoxazines demonstrated good thermal stability and mechanical properties. In particular, all the coatings exhibited high hardness, excellent adhesion, good flexibility, low moisture absorption, and outstanding solvent resistance. Starting from renewable eugenol, the synthesis of bio-based benzoxazine precursors with good processability and film-forming properties was demonstrated and its application potential in the field of high performance organic coatings was revealed.

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