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Main-chain benzoxazine oligomers: A new approach for resin transfer moldable neat benzoxazines for high performance applications

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ABSTRACT

A new approach has been developed to enhance the processability of main-chain benzoxazine polymers by synthesizing benzoxazine main-chain oligomers that are low in viscosity while maintaining the major part of the advantages of main-chain type polybenzoxazines. A series of main-chain benzoxazine oligomers have been synthesized using bisphenol-F isomers. The structure of the oligomers has been characterized by nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FT-IR). The molecular weight has been evaluated using size exclusion chromatography (SEC). For a viscosity study, a mixture of benzoxazine monomers derived from the same bisphenol-F isomers has been used as control and a reactive diluent to control the viscosity.

1. Introduction

Resin transfer molding (RTM) is widely used in the manufacturing of polymer matrix composites. The advantages of RTM include low investment in processing facility, lack of flash, and ability to mold large yet precision part with minimum void content. The desirable characteristics for RTM resins are: i) the resin has sufficiently low viscosity so as to infiltrate the preform with the applied pressure and sometimes with additional assisting evacuation; ii) the low viscosity is maintained at least during the infiltration period; iii) upon infiltration of the preform, efficient polymerization takes place without void formation; iv) the resin does not shrink excessively; and v) the resultant composite exhibits physical and mechanical properties to satisfy the requirement of a particular application [1–3]. Resins used for RTM are unsaturated polyesters, vinyl esters, urethanes, epoxies, cyanate ester, and bismaleimides. However, it is difficult to achieve good processability without sacrificing heat-resistance and mechanical properties for these resins. Moreover, they usually exhibit shrinkage upon polymerization, which may affect the dimensional stability of part. Therefore, it is desired to develop new RTM resins with dimensional stability and better physical and mechanical properties.

Polybenzoxazine (PBZ) has attracted much attention because of its excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing [4–26]. The polymerization of benzoxazines can be achieved through the cationic ring-opening of oxazine ring with or without an added initiator and/or catalyst. Another unique characteristic is that polybenzoxazines have a greater molecular design flexibility than any other polymers. They release no reaction by-product during polymerization reactions. No strong acid or alkaline catalysts are required for the synthesis of monomers or polymerization; however, some acids, such as phenols and carboxylic acids, will accelerate the rate of polymerization. Furthermore, no volatiles are released and nearly zero shrinkage is achieved upon polymerization.

Resin transfer molding (RTM) based on benzoxazine has been reported [27–29]. These resins are monofunctional benzoxazines or resin mixtures based on bisphenol-A/aniline and phenol/aniline benzoxazines. Although low viscosity can be obtained for these resins, their heat-resistance and mechanical properties are not sufficient to be used as matrices for high performance composites.

Recently, a new class of benzoxazines where oxazine rings are part of the polymer main-chain has been developed [30–41]. The thermal and mechanical performance of polybenzoxazine thermosets derived from main-chain benzoxazine polymers proved to be excellent in comparison to those derived from monomers. However, the synthesis of main-chain benzoxazine polymers through Mannich base polycondensation is associated with shortcomings, such as poor solubility of the products due to molecular rigidity, resulting in a low molecular weight and broad polydispersity, although the choice of solvent has not been rigorously optimized to date [2]. As an attempt to overcome this difficulty by using a flexible and thus more soluble segment,

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synthesis for short chain oligomers using isomer mixture of bisphenol-F and aromatic diamines will be attempted in this work. We have synthesized main-chain benzoxazine oligomers of excellent mechanical and physical properties, as well as ease in processing. Mixed isomers of bisphenol-F are commercially available in large quantity and could be an attractive alternative to bisphenol-A for which environmental concern is raised. Benzoxazine monomers made from formaldehyde, bisphenol-F isomers, and monofunctional aromatic amine were used as reactive diluents. The structure of these new polybenzoxazine precursors has been characterized, and the thermal, rheological and mechanical properties will be discussed.

2. Experimental

2.1. Materials

Mixed isomers of bisphenol-F were kindly supplied from Hexion Specialty Chemicals. Aniline (99%), Para-formaldehyde (96%), and 4,4′-Diamino-diphenylmethane (DDM) (>99%) were purchased from Aldrich Chemical Company. N,N′-dimethylformamide (DMF), toluene, hexanes (a mixture of isomers, tetrahydrofuran, methanol and ethanol) were obtained from Fisher Scientific Company. All the other chemicals were used as received.

2.2. Preparation of bisphenol-F benzoxazine monomer

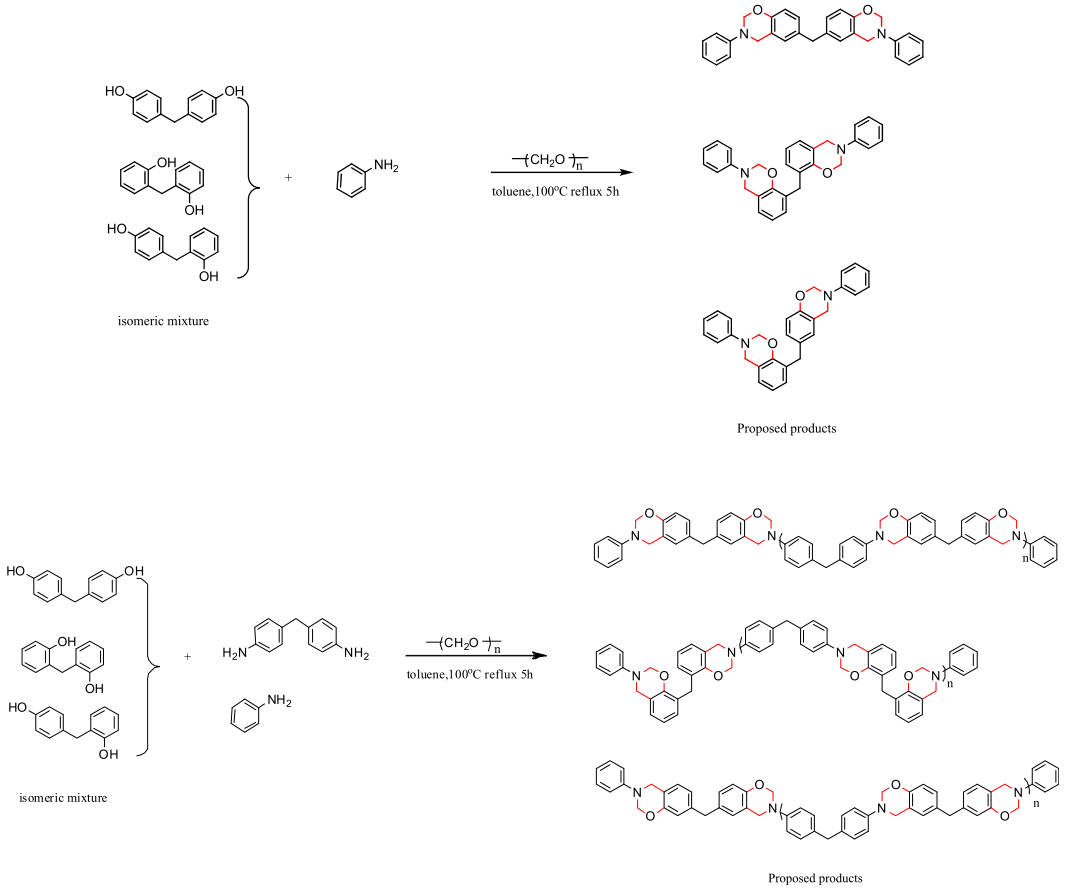
Bisphenol-F isomers (80 mmol, 16.02 g), and aniline (160 mmol, 14.90 g) in 100 mL toluene were dissolved in a 250 mL round bottom flask. Para-formaldehyde (320 mmol, 9.60 g) was added to the solution followed by heating the mixture at 90 °C in a preheated oil bath. By following the reaction using ^{1}H NMR, it was found that the best conversation to benzoxazine structure was achieved after ca.5 h. The solution was cooled and precipitated in hexanes to obtain a yellow powder. The powder was finally placed in a vacuum oven at 40 °C for 72 h to completely dry (Yield: 32 g, 81%).

2.3. Preparation of main-chain benzoxazine oligomers

A mixture of bisphenol-F isomers (100 mmol, 20.02 g), aniline (100 mmol,9.13 g) DDM (50 mmol.9.90 g) and para-formaldehyde (400 mmol,12 g) was added in a 250 mL round bottom flask with 150 mL toluene as solvent. The milky mixture was heated gradually and was kept stirring at 90 °C for 5 h. The formation of a gel that is caused by formation of triaza structure by condensation of primary amine and formaldehyde [11] was observed after ca.15 min. After 3 h, the insoluble white colored gel disappeared and transformed into a yellow solution. The reaction mixture was stirred for another 3 h at the same condition. It was cooled to room temperature and poured into hexane to obtain a yellow powder. The powder was redissolved in tetrahydrofuran and reprecipitated in methanol to yield a pale yellow powder (Yield: 36 g, 71%).

2.4. Polymerization of benzoxazine oligomers

A solution method was used to prepare samples in a film. A solution of 30% solid content of the monomers in DMF was prepared. Then, a film was cast over dichlorodimethylsilane-pretreated glass plates. The film was dried in an air circulating oven at 60 °C for 24 h to remove the solvent. The film as fixed on glass plates was heated stepwise at 110, 130, 160, 200, and 220 °C for 2 h



Scheme 1. Synthesis of bisphenol-F isomer-based benzoxazine monomer and oligomers.

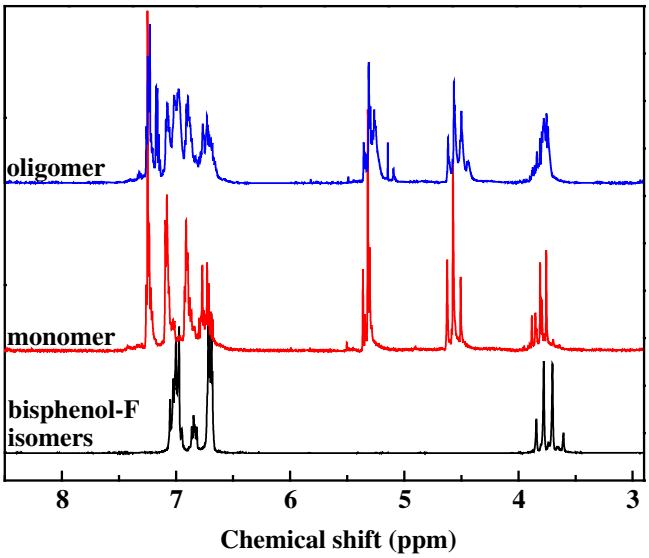


Fig. 1. ^{1}H NMR spectrum of bisphenol-F isomer-based benzoxazine monomer and oligomers.

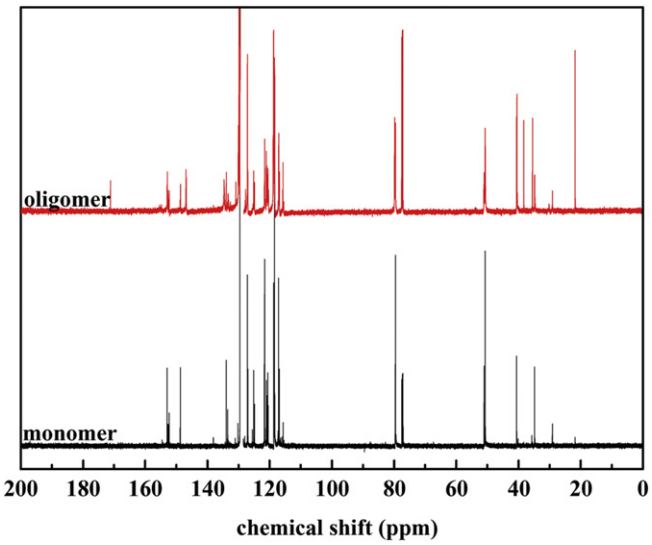


Fig. 3. ^{13}C NMR spectrum of bisphenol-F isomer-based benzoxazine monomer and oligomer.

each, and then slowly cooled to room temperature. The resulting film was brown in color. The thickness of the samples prepared according to the above procedures ranged from 0.1 to 0.8 mm.

2.5. Preparation of benzoxazine blends for viscosity measurements

Homogeneous blends of monomer and oligomers were made at the monomer content of 10%, 30%, and 50% with respect to the oligomer weight in chloroform and then placed in a vacuum oven for 72 h at 40 °C to completely remove the solvent. The dried samples were examined by ^{1}H NMR to evaluate the dryness of the sample, and only the ones that showed negligible solvent contents were used for the viscosity tests.

2.6. Measurements

^{1}H NMR spectra were acquired in deuterated dimethylsulfoxide with tetramethylsilane as an internal standard on a Varian Oxford AS300 at a proton frequency of 300 MHz. The average number of transients for ^{1}H NMR is 64. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra.

TA Instruments DSC model 2920 was used with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests of differential scanning calorimetric (DSC) study. All samples were crimped in hermetic aluminum pans with lids. Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with an amplitude of 10 μm and a temperature ramp rate of 3 °C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 40 mL/min. Viscosity was measured using Anton Paar MCR501 Rheometer with constant shear rate at 100 s^{-1} at different elevated temperatures. The sample was spread in a parallel plate fixture with a diameter of 50 mm. Polymer molecular weight was determined by size exclusion chromatography (SEC) using a Waters GPC system equipped with an LDC/Milton Roy max N series UV detector. The measurements were taken at 25 °C with HPLC-grade THF as a mobile phase on two Phenomenex Phenogel columns (100 and 10 nm). Molecular weight was calculated using a calibration based

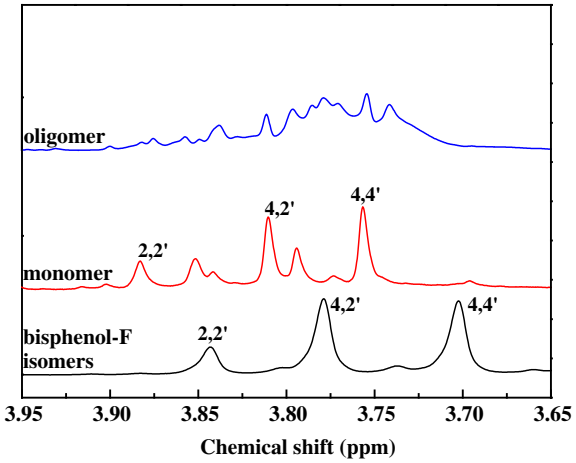


Fig. 2. Expanded region of ^{1}H NMR spectrum for the CH_2 group between two benzene rings for the bisphenol-F isomer mixture, benzoxazine monomer derived from bisphenol-F isomer mixture, and the main-chain type oligomers from bisphenol-F isomer mixture and DDM.

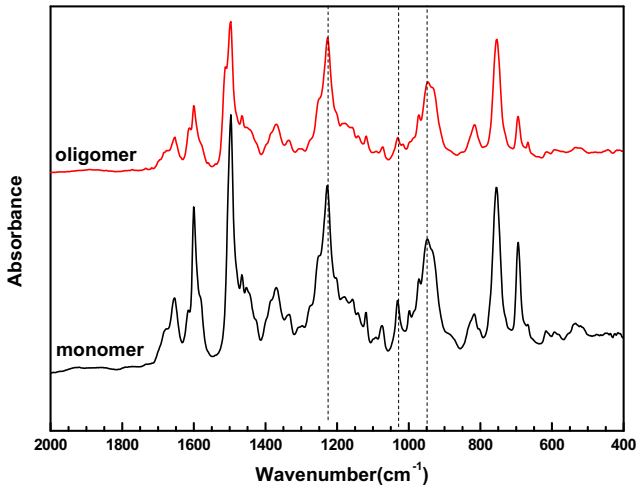


Fig. 4. IR spectra of bisphenol-F isomer-based benzoxazine monomer and oligomers.

Table 1
SEC data for synthesized oligomer.

	M_n (Daltons)	M_w (Daltons)	PDI
Oligomer	1527	2590	1.70

on monodisperse polystyrene standards. For DSC measurement, the sample size was 3.2 mg for benzoxazine monomer and 3.1 mg for benzoxazine oligomer. For DMA measurement, the sample size was 10.79 × 6.21 × 0.83 (length, width, and thickness) for polybenzoxazine film derived from the monomers and 10.61 mm × 6.87 × 0.63 mm (length, width, and thickness) for polybenzoxazine film derived from the oligomers. For TGA measurement, the sample weight was 12.7 mg for benzoxazine monomers and 12.8 mg for benzoxazine oligomers.

3. Results and discussion

3.1. Preparation of bisphenol-F isomers-based benzoxazine monomers

Monomers and oligomers of bisphenol-F isomers-based benzoxazines have been prepared from bisphenol-F isomers, aniline and para-formaldehyde, following Scheme 1.

The chemical structures of benzoxazine monomer and oligomers were confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR. Fig. 1 shows the ^{1}H NMR spectra of benzoxazines. Typically, benzoxazine monomers have two equal intensity singlet peaks in ^{1}H NMR spectra due to the CH_2S in the oxazine ring. These peaks, however, become broader in case of main-chain benzoxazine polymers due to the reduced molecular mobility. In the case of current bisphenol-F study, each characteristic CH_2 resonance of oxazine ring appears as multiplets due to the isomeric nature of bisphenol-F as starting material for benzoxazine synthesis. Two multiplets are observed at 4.51, 4.57, and 4.62 for the monomer mixture and 5.30, 5.32, and 5.36 ppm for the oligomer mixture, which are assigned to Ar–CH_2–N– and –O–CH_2–N–, respectively. The multiplet in the range of 6.58–7.48 ppm is assigned to the protons of the aromatic ring. The multiplet near 3.8 ppm in the monomer and 3.7 ppm in the oligomers correspond to the CH_2 between the benzene rings in bisphenol-F isomers.

As shown in Fig. 2, by expanding and comparing the region from 3.6 ppm to 3.9 ppm, we can assign the characteristic peak of different isomers in bisphenol-F [44]. By integrating the area of each peak, the isomeric ratio of bisphenol-F isomers as starting material can be determined, which is 16% 2,2′-methylenediphenol, 41% 2-(4-hydroxybenzyl) phenol and 43% 4,4′- methylenediphenol. Upon synthesizing benzoxazine isomers, these bisphenol-F isomer resonances shift to 3.75 ppm, 3.82 ppm, and 3.88 ppm for 2,2′-, 2,4′-, and 4,4′-isomer benzoxazines, respectively. These are expected to be the terminal bisphenol-F unit which has different structure from the ones in the middle of the chain. Expectedly, these peaks reduce in relative intensity in the oligomer spectrum. There are many resonances between these terminal group frequencies in the oligomer spectrum. Due to the complexity of those in the middle of the chain, further detailed study is needed to assign many resonances reliably. The relative intensities of the benzoxazine isomers are expectedly different from those of the bisphenol-F raw material due to the difference in reactivity and steric hindrance. The composition seems complex, and further detailed study is needed before quantitative determination of the concentration of different species can be made.

Table 2
Viscosityof benzoxazine precursors.

	Monomer/ Pa.s	Oligomer/ Pa.s	10% mixture Pa s	30% mixture/ Pa.s	50% mixture/ Pa.s
60	1190	–	–	–	–
70	–	58850	5525	5525	1059
80	14.4	3390	1115	804	105
100	0.947	67.6	49.1	31.5	8
120	0.175	5.50	5.61	2.89	1

Fig. 3 shows the ^{13}C NMR spectra of bisphenol-F benzoxazine monomer and oligomer. The characteristic carbon resonances of the oxazine ring show in the range of 49.36–50.01 ppm for Ar–CH_2–N– and 78.52–79.84 ppm for N–CH_2–O–. The peaks in the range of 36.32–37.86 ppm are assigned to the bridging methylene carbons in bisphenol-F structure. 2,2′-Methylene carbons appears around 31 ppm, 2,4′-methylene carbons around 36 ppm, and 4,4′-methylene carbons around 41 ppm [45]. Peaks in the range of 154.20–155.83 ppm correspond to carbon resonance of the C–N group in benzoxazine ring.

The structure of the benzoxazine monomer and main-chain oligomer was further confirmed by FT-IR. There are a number of infrared bands in the spectra highlighted by dotted lines in Fig. 4, which can be used as characteristic bands of benzoxazine structure.

The presence of the cyclic ether of benzoxazine structure is supported by the absorbance peaks at 1228 and 1035 cm^{-1} due to the C–O–C asymmetric and symmetric stretching modes, respectively. The characteristic mode of benzene with an attached oxazine ring is

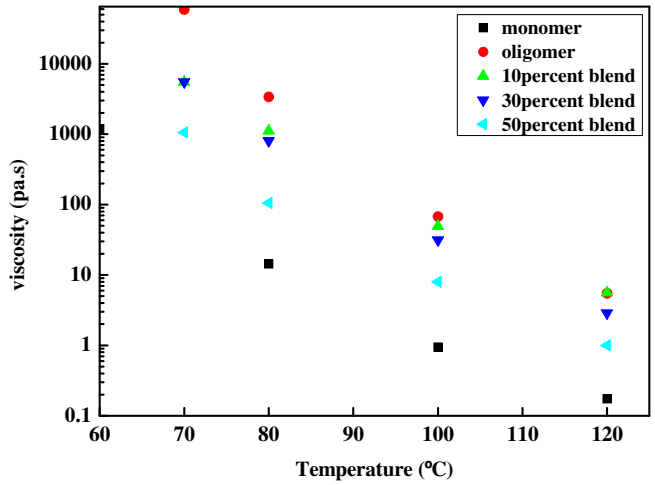


Fig. 5. Viscosity of benzoxazine resins.

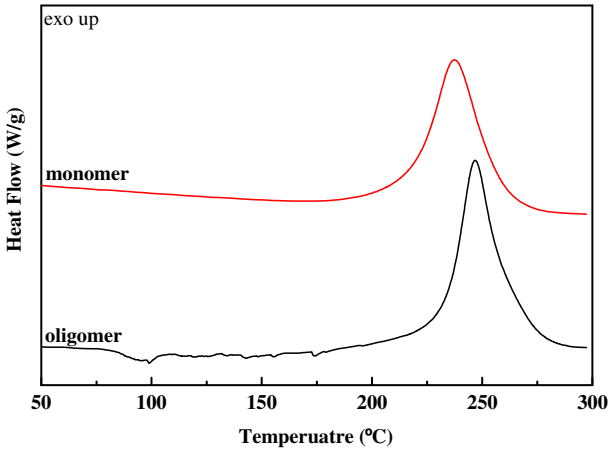


Fig. 6. DSC thermograms of benzoxazine monomer and oligomers.

Table 3
Thermal properties of main-chain benzoxazine monomer and oligomers.

	Onset (°C)	Max (°C)	Heat of polymerization	
			(J/g)	(kJ/mol/oxazine ring)
Monomer	177	238	190	41.3
Oligomer	176	247	238	53.1

located at 949 cm^{-1}. The two peaks around 750 cm^{-1} and 690 cm^{-1} indicate monosubstituted benzene ring, which corresponds to the terminal benzene ring that originates from the aniline group. Two bands at 1650 and 1600 cm^{-1} which correspond to the in-plane carbon–carbon stretching of the trisubstituted benzene ring are also observed.

The molecular weight of the oligomers was evaluated using SEC and the results are summarized in Table 1. The number average molecular weight (M_n) of the oligomers was estimated to be 1527, with a polydispersity index (PDI) equals to 1.70. This indicates that the synthesized oligomers are a series of short chain mixture with low molecular weight.

3.2. Viscosity of oligomers

Viscosity of the resin is a key factor for developing a new material for RTM. The required viscosity for such processing technique is roughly below 1 Pa s at the processing temperature. Therefore, the dynamic viscosities for the benzoxazines, including the neat oligomers, monomers, and oligomer/monomer blend have been studied as shown in Fig. 5. A low viscosity benzoxazine monomer can be used as a reactive diluent [2]. In the mixture of benzoxazine monomers and oligomers, both the benzoxazines can polymerize through ring-opening reaction yielding a crosslinked product. Furthermore, by mixing benzoxazine monomers with benzoxazine oligomers, one can control the viscosity of the mixture through varying the ratios of the two benzoxazines in the mixture. For the weight ratio of the benzoxazine monomers to benzoxazine oligomers of 1:9, 3:7 and 5:5, the viscosities of the mixture were measured.

Table 2 shows the viscosity change with temperature and the monomer/oligomer mixture ratio. For the benzoxazine monomers, 60 °C was the lowest temperature for the instrument with the current set-up to obtain a reliable viscosity value. On the other hand, for the oligomers and reactive diluent mixtures, temperatures above 70 °C were needed to obtain the viscosity value. For the 50% mixture, the viscosity can reach as low as 1 Pa s at 120 °C which is at the borderline of the viscosity suitable for RTM.

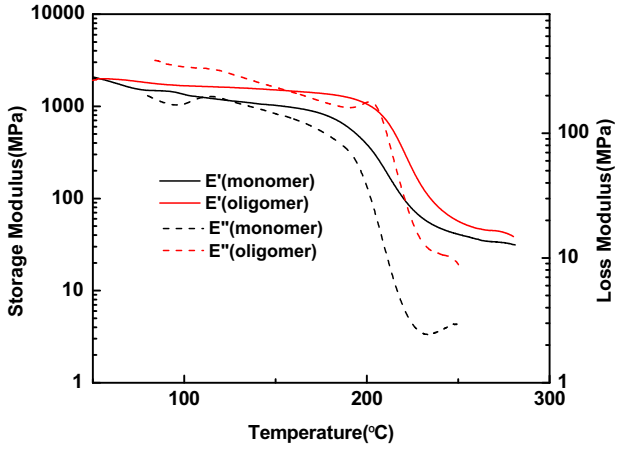


Fig. 7. Storage moduli and loss moduli of the benzoxazine monomer and oligomers.

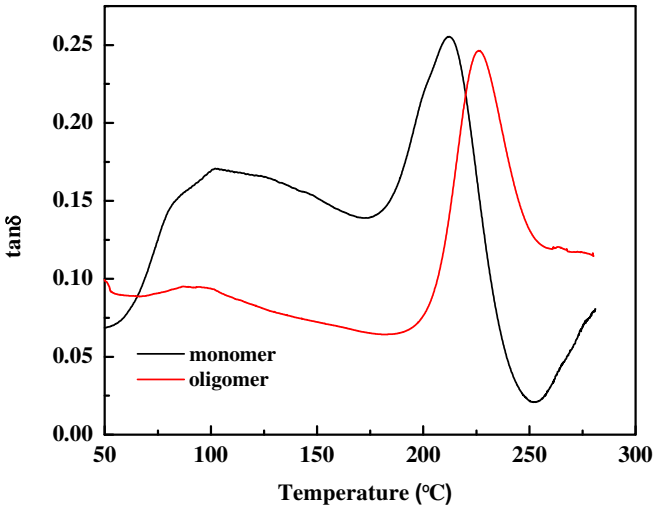


Fig. 8. Tan δ of bisphenol-F isomer-based benzoxazine monomers and oligomers.

3.3. Polymerization behavior of benzoxazine monomer and oligomers

The polymerization behavior of the monomer and oligomers was studied by DSC by stepwise heating at 110 °C, 160 °C, 200 °C, and 220 °C for 2 h each. The final polymerization temperature was restricted to 220 °C in order to prevent possible degradation. DSC thermograms are shown in Fig. 6, and the thermal properties are summarized in Table 3. The DSC trace of the monomers has an exotherm with the onset at 177 °C and maximum at 238 °C. The heat of polymerization is 190 J/g. For the oligomers, one exotherm was observed with the onset at 176 °C and maximum at 247 °C. The heat of polymerization is 238 J/g which is due to a higher concentration of the oxazine rings per unit weight in the benzoxazine oligomers.

3.4. Dynamic mechanical analysis (DMA) of crosslinked polybenzoxazines

The viscoelastic properties for the crosslinked polybenzoxazines were studied by DMA. Fig. 7 shows the temperature dependence of the storage moduli and loss moduli for the polybenzoxazine films. For the thermoset polymerized from benzoxazine monomers, the storage modulus is maintained at approximately the same value for a wide temperature range up to 150 °C. Since the peak positions were not well defined in the E″ spectra, tan δ was used for the T_g study. As shown in Fig. 8, the glass transition temperature (T_g) determined as the peak temperature of tan δ curve is around 154 °C. On the other hand, the crosslinked polybenzoxazine which is derived from benzoxazine oligomers has T_g of 213 °C. The significant increase in T_g by about 60 °C of the crosslinked polymers from oligomers is due to the presence of the difunctional amine linkage,

Table 4
Weight loss and Char yield of polybenzoxazines.

	5% weight loss temperature (°C)	10% weight loss temperature (°C)	Char yield (%)
Monomer	332	378	52
Oligomers	346	411	55

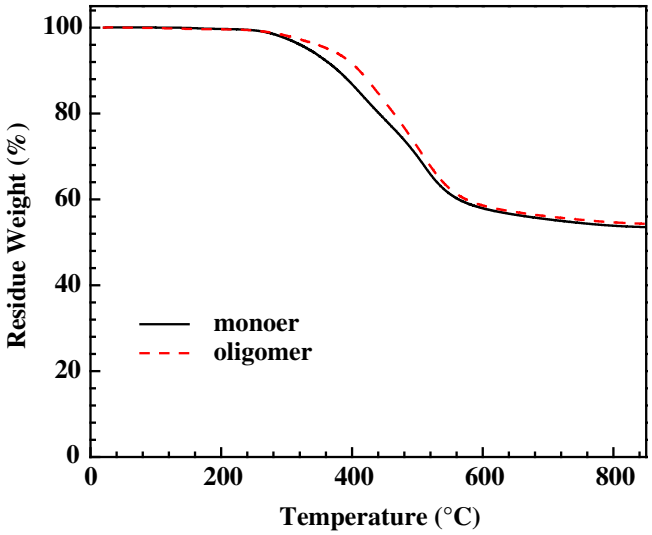


Fig. 9. TGA thermograms of the benzoxazine monomer and oligomers.

which helps to anchor the amine portion into the network and increases the chain rigidity. Typical glass transition temperature of the fully polymerized bisphenol-A and aniline (abbreviated as BA-a) polymer is about 170 °C and char yield at 800 °C under nitrogen environment is about 30% [42].

3.5. Thermal stability of crosslinked polybenzoxazines

The results of the thermogravimetric analyses of the crosslinked polybenzoxazine derived from the benzoxazine monomers and oligomers are summarized in Table 4, while the weight loss and derivative weight loss curves are presented in Fig. 9. The thermal degradation of polybenzoxazines has three stages: degradation of the chain ends, evaporation of the amine, and the simultaneous breakage of the phenolic linkage and degradation of the Mannich base [42,43]. These three events show peaks in the derivative weight loss thermograms around 300, 410 and 520 °C, respectively. The pendant benzene ring in bisphenol-F/aniline based benzoxazine monomers is relatively easy to degrade in comparison to the DDM-based benzoxazine oligomers. Hence, the polybenzoxazines derived from the oligomers show an increase in 5% weight loss temperature, T_{d5}, compared with polybenzoxazines derived from the monomers (from 332 °C to 364 °C) as a result of the reduced evaporation rate around 300 °C. This observation is consistent with the assignment that the derivative weight loss peak around 300 °C is due to the chain ends and/or branches, and the concentration of such groups in the main-chain polybenzoxazine is less than that of the polymer derived from the monomeric benzoxazines. Expectedly, a peak is still observed in this temperature range due to the use of small oligomers where the concentration of the chain ends is still appreciable. This peak for a large molecular weight main-chain polybenzoxazine will nearly completely disappears due to the negligible chain end groups present [31].

The char yield is defined in this work as the residual weight of the material at 800 °C under N_2. For the crosslinked polybenzoxazines, the char yield for the monomers and oligomers is 53% and 55%, respectively, which is much higher than that of the phenol-DDM-based polybenzoxazine at 46%. The crosslinked polybenzoxazine derived from the oligomers has higher char yield than the reference benzoxazine monomers as the degradation of the monomer at higher temperature around 500 °C is more intensive compared with the oligomers. While the char yield of the monomer and oligomers do not show significant difference, the intermediate temperature stability in the range of 300 °C and 500 °C is significantly higher in the oligomer-derived polybenzoxazine than the monomer derived.

4. Conclusion

We have synthesized a novel class of benzoxazine oligomers as a high performance, low viscosity thermosetting resin from bisphenol-F isomers, para-formaldehyde, and different types of aromatic amines, including 4,4′-diamino-diphenylmethane and aniline. The commercially available mixture of bisphenol-F isomers is used as a more environmentally friendly phenol than extensively used bisphenol-A. The crosslinked polymers under current study show excellent thermal stability and high T_g with easy processability, which are the properties ideally suited for high performance composites.

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