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ARTICLE

Synthesis and Characterization of Thermoset (Epoxy-Benzoxazine)

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Abstract: A main chain benzoxazine oligomer MCBOs(PH-p.APH) containing phenolic hydroxyl end group based on phenol, 4-aminophenol and paraformaldehyde was synthesized using a solvent-free method. Epichlorohydrine was used for the epoxidation of the benzoxazine oligomer in the presence of tetra-butyl ammonium chloride (TBAC). The benzoxazine oligomer and its epoxidized product were then step cured in a stainless steel mold in an air-circulating oven according to a heating cycle from 140 to 250 °C. The benzoxazine oligomer MCBOs(PH-p.APH) was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, and number average molecular weight was measured using the cryscopic technique. The epoxy derivative of benzoxazine oligomer [E-MCBOs(PH-p.APH)] was characterized by FT-IR spectroscopy and ^{1}H-NMR. The polymerization process and the curing behavior were verified with DSC and FT-IR. The thermal stability of the cured product was investigated with TGA. The DSC analysis showed that the presence of phenolic hydroxyl in benzoxazine oligomer resulted in lowering the curing temperature compared to epoxy derivative of benzoxazine oligomer due to catalytic effect of phenolic hydroxyl and the retardation effect of epoxy group. The TGA analysis of the thermosets showed that the cross-linked structure of polybenzoxazine(PH-p.APH) has higher thermal stability than that of poly[E-MCBOs(PH-p.APH)].

Keywords: Thermoset, Main chain benzoxazine oligomer, Differential scanning calorimetry (DSC).

Introduction

Polybenzoxazines (PBZs) are a class of thermosetting resins having unusual material properties[1-4]. Their mechanical performance and thermal stability are distinctive and they have significant advantages when compared with other thermosets[5,6]. Especially, the molecular design flexibility of polybenzoxazines has gained increased interest in the field of high-performance polymers, because numerous benzoxazines can be synthesized using specially selected phenol derivatives and primary amines and desired material properties can be incorporated into the final polybenzoxazine resin[7-13]. However, the shortcoming of PBZs is an inherent brittleness as is common for thermosets, which limits their application. Various efforts, which can be classified into two types of strategies, have been made to overcome overcome this drawback. The first method is chemical modification *via* a molecular design of a benzoxazine monomer (BZ) achieved by using linear aliphatic BZ[14] and main-chain type polybenzoxazine precursors[15,16]. However, this approach is really arduous, owing to the difficulties in purifying the precursors. The second method is physical blending, which involves the incorporation of fillers, such as liquid rubber[17], core-shell particles [18], thermo-plastic resin[19,20] and nano-inorganic particles[21]. Those modifiers usually lead to phase-separated morphologies in the PBZ resin matrix. These composites often suffer a sacrifice of the glass transition temperature (T_g), storage modulus, mechanical strength or processability. Thus, the development of a new method for the enhancement of the comprehensive properties of BZ is desired.

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It has been reported that the copolymerization of benzoxazines and epoxy resins was an effective method to improve the properties of the polybenzoxazines[22-25]. This is because the phenolic hydroxyl group from the ring opening polymerization of benzoxazine can react with the epoxy resin at an elevated temperature to generate additional crosslinking points. The increase of crosslink densities can enhance the T_g and flexural properties of polybenzoxazines. Nevertheless, the retardation of the curing reaction of benzoxazine resin can be found with an addition of epoxy resins as a shift of curing reaction to higher temperature.

In the present article, benzoxazine oligomer is synthesized from 4-aminophenol, paraformaldehyde and phenol and the resulting oligomer is reacted with epichlorohydrine (ECH) precursors to synthesize epoxy-benzoxazine thermoset. The influence of epoxy group with end capped phenolic hydroxyl on the curing behavior of benzoxazine is tested using DSC.

Materials and Methods

Materials

Paraformaldehyde (95%) and dimethylsulfoxide (DMSO) (PROLABO), phenol (>99%) (PANREAC PRS), 4-aminophenol, Epichlorohydrine ECH (>99%) (Merck), tetra-butyl ammonium chloride (98%) (TBAC) (ALFA AESAR), Sodium hydroxide (>98%) (Sigma-aldrich), dimethylformamide (DMF) (POICHA), distilled water.

Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400-MHz NMR spectrometer in dimethylsulfoxide-D6 and chloroform-D1 as solvents with TMS as internal standard. The FTIR spectra were collected on an FTIR spectrometer (Jena Company). Differential scanning calorimetry (DSC) data was obtained on a DSC-SETARAM instrument at a heating rate of 10°C/min in an argon flow for all tests. Thermo-gravimetric analysis was used to study the thermal stability of the cured systems; approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 800°C at a heating rate of 10°C/min in an argon flow. All TGA experiments were performed by using SETARAM device from TA instruments.

Preparation of Main Chain Benzoxazine Oligomers MCBOs(PH-p.APH)

This procedure stems from the ones described by Ishida et al.[26] Phenol 4.7 g (0.05 mol) and 4-aminophenol 5.45 g (0.05 mol) were mixed by a mechanical agitator at 90°C in a long 250 ml beaker for ten minutes. Paraformaldehyde, in excess of 10%, 3.3 g (0.1 mol), was then rapidly introduced under vigorous stirring in order to limit the bubbling due to the decomposition of paraformaldehyde into formaldehyde. The mixture was then allowed to react for 15 min under continuous stirring and temperature was increased at a heating rate of 1°C/min. A red vitrified resin (10.68 g) was obtained. The precursor obtained from the above procedure is a mixture of benzoxazine compounds containing more than one benzoxazine ring. The vitrified resin was dissolved in DMSO and the solution was filtered to distilled water, which was then refiltered and dried in an air-circulating oven at 50°C. The precursors were readily soluble in many common organic solvents, such as acetone, dioxane, tetrahydrofuran and N,N-dimethylformamide and this suggests easy processability.

Preparation of Epoxy-Benzoxazine Precursors E-MCBOs(PH-p.APH)

A 100 ml two-necked flask equipped with a condenser, a septum cap and magnetic stirring bar was charged with 1.136 g of MCBOs(PH-p.APH) containing 5.089 mmol of hydroxyl (based on ^{1}H-NMR spectrum) and epichlorohydrin (10 M eq/OH, 50 mmol, 4.62 g). The suspension was heated at 60°C and tetrabutylammonium chloride (0.05 M eq/substrate, 0.254 mmol, 0.072 g) was added. After 1 h, the solution was cooled to 25ºC and an aqueous solution of NaOH 20 w% (2M eq/OH) with 0.05 M equiv. of phase transfer catalyst (TBAC) was added. The mixture was stirred vigorously for 30 min at room temperature. Water (30 ml) was added to the reaction mixture and the aqueous phase was extracted with 3*30 ml of ethyl acetate. The organic phase was washed with 40 ml of distilled water, then dried over $MgSO_4$ and vacuum concentrated. It was then precipitated into 40 ml hexane. A yellow fine powder was obtained after vacuum drying.

Curing of MCBOs(PH-p.APH) and E-MCBOs(PH-p.APH) Precursors

All the precursors were introduced in a stainless-steel mold, molten and then step cured in an air-circulating oven according to the following cycle: 1 h at 140°C, 2 h at 180°C, 2 h at 200°C, 1 h at 220°C and 30 min at 250°C. Thereafter, the samples were allowed to slowly cool down to room temperature before their unmolding.

MCBOs(PH-p.APH) Number Average Molecular Weight Measurement

Number average molecular weight of MCBOs(PH-p.APH) was evaluated using cryoscopic (freezing point depression) measurements. A series of dilute solutions of MCBOs(Ph-p.APh) in 1,4-dioxane were prepared. A thermometer sensitive to 0.001°C temperature change and the apparatus illustrated in Fig. 1 are used for the freezing point depression measurements.

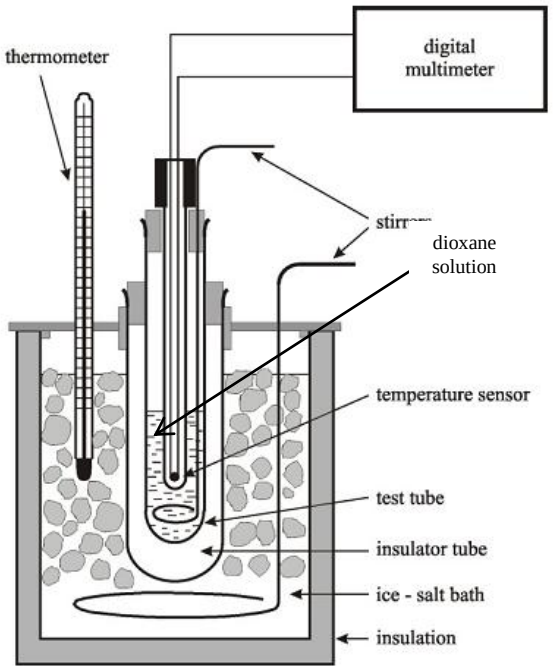


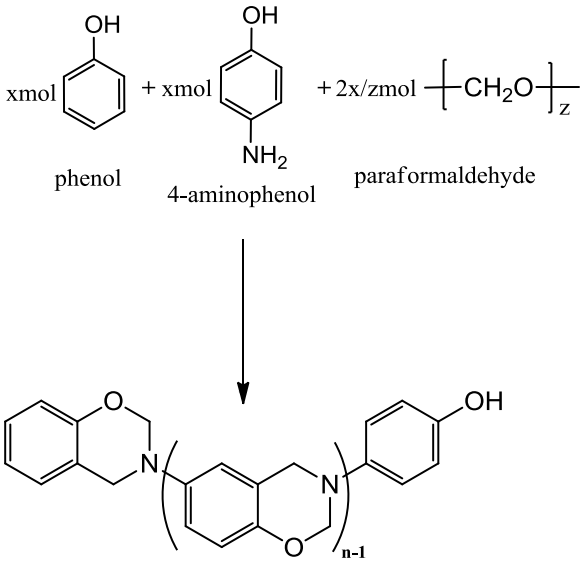
Figure 1. Apparatus for freezing point determination.

Results and Discussion

Preparation of Precursors

Main chain benzoxazine oligomers MCBOs(PH-p.APH) were successfully prepared by a solvent-free method from phenol, 4-aminophenol and paraformaldehyde, with a straight and scalable procedure according to the reactions depicted in Scheme 1.

Scheme 1. Synthesis of MCBOs(PH-p.APH).



MCBOs(PH-$_p$.APH)

The structure of the new MCBOs(PH-p.APH) was investigated by ^{1}H-NMR as shown in Fig. 2. Signal assignments were achieved with the help of ACD ^{1}H-NMR simulation. Typically, benzoxazine monomers have two singlet peaks of equal intensity in ^{1}H-NMR spectra due to the CH_2s in the oxazine ring. These peaks, however, become broader in the case of MCBOs(PH-p.APH) due to reduced molecular mobility. The peaks around 4.36 ppm and 5.22 ppm may be attributed to the Ph-CH_2-N and O-CH_2-N of oxazine ring, respectively, thus verifying the formation of benzoxazine. Additional peak, labeled c, with resonance at 9.15 ppm refers to the formation of the desired benzoxazine structure containing the phenolic hydroxyl moiety. An additional information supporting the absence of polymerized structure is provided by the absence of resonance signal that could be assigned to Mannich-type linkage in the methylene proton area.[27] Thus, the synthesis procedure is clearly robust enough to produce MCBOs(PH-p.APH) without leading to ring opening of the reactive oligomers.

The number average molecular weight $\bar{M}_n$ was evaluated using the cryoscopic method. A series of dilute solutions of MCBOs(PH-p.APH) in 1,4-dioxane were prepared as shown in Table 1.

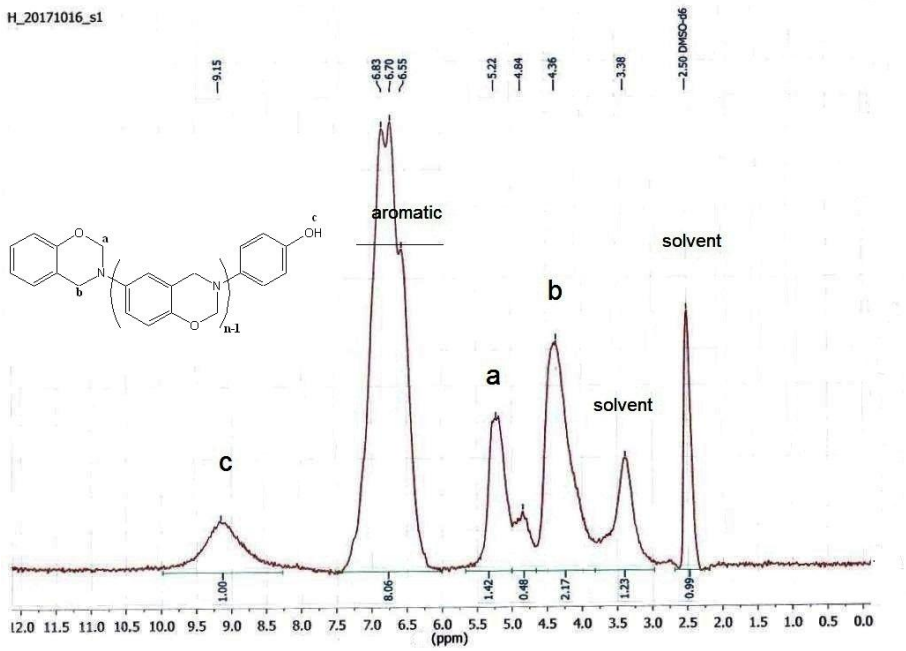


Figure 2. ^{1}H NMR spectra of MCBOs(PH-p.APH).

The freezing point depressions of solutions are illustrated in Figure 3. The working equation for the cryoscopic method is as follows:

$$\lim_{c\to 0}\frac{\Delta T}{c} = \frac{M_S \times R \times T_S^2}{\rho \times \Delta H_f \times \overline{M}_n} + A_2 c$$

c: oligomer solution concentration g/cm^3, ΔT: freezing point depression K, M_s: molecular weight of pure solvent (88.11 g/mol), R: 8.314 J/K.mol, ρ: solvent density 1.033 g/cm^3, ΔH_f: enthalpy of fusion 12.84 KJ/mol, T_S: freezing point of pure solvent k, A_2: second virial coefficient.

$\Delta T/c$ must be graphically plotted against c for the calculation of the intercept point when $c \to 0$, as illustrated in Figure 4. The intercept value is (-5.3754).

Table 1: Oligomer solution information.

sample	freezing point (^{o}C)	ΔT (K)	c (g/cm^3)	ΔT/C
Solvent T	11.686			
S1	11.585	-0.101	0.0137	-7.367
S2	11.517	-0.169	0.0183	-9.239
S3	11.465	-0.221	0.0231	-9.548
S4	11.371	-0.315	0.0300	-10.517

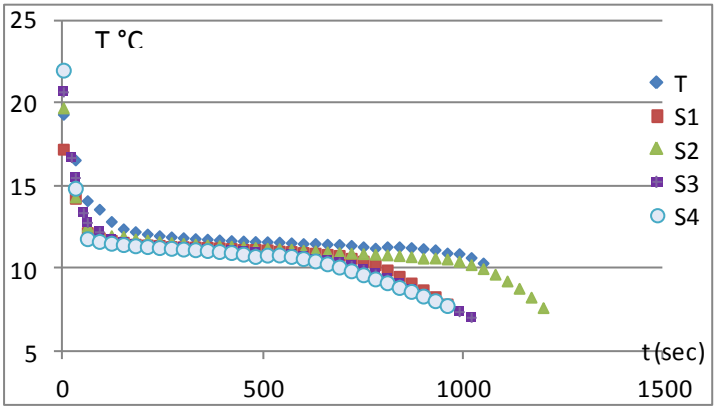


Figure 3. Cooling temperature of solvent and oligomer solutions against time in seconds.

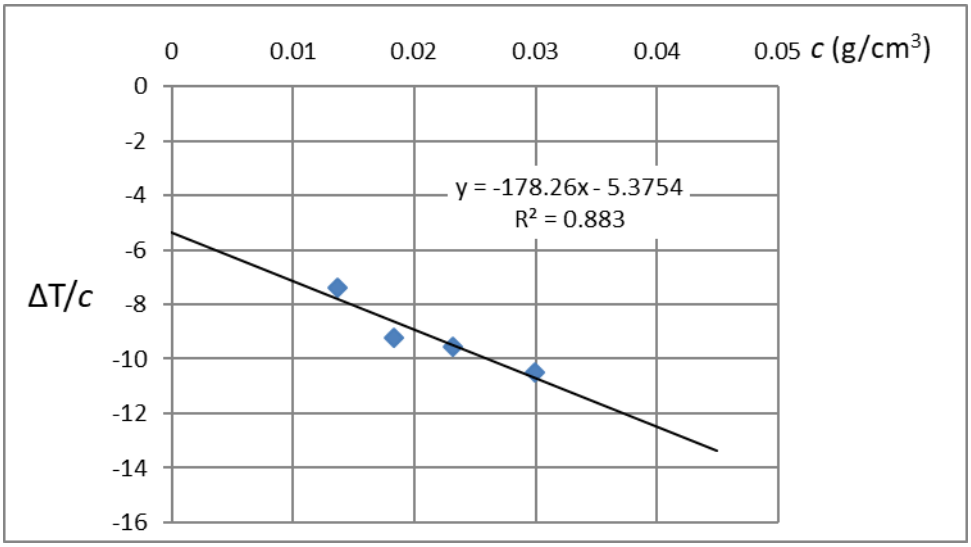


Figure 4. $\frac{\Delta T}{c}$ plotted against oligomer concentration.

The number average molecular weight can be calculated according to

$$\frac{M_5 \times R \times T_5^2}{\rho \times \Delta H_f \times \overline{M}_n} = 5.3754 \xrightarrow{yields} \overline{M}_n = 833.583\ g/mol$$

We can estimate the number of repeating units by subtracting the weight of end group (phenol) from $\overline{M}_n$, then dividing the result by the weight of repeating unit:

(833.583-93.11)/133.16=5.56

The structure of MCBOs(PH-p.APH) was further confirmed by ^{13}C-NMR analysis which clarified that there is more than one benzoxazine unit in the structure, as can be observed in Fig. 5. Three characteristic (C-O) peaks for the carbon atoms 12,18 and 8 at 148.48, 153.40 and 154. 37 ppm, respectively, are observed and more than one type of (C-N) peak are also visible. The peaks around 50 and 80 ppm are due to the Ph-CH_2-N and O-CH_2-N of oxazine ring, respectively, thus verifying the formation of benzoxazine oligomers. Epoxy MCBOs(PH-p.APH) was successfully prepared by a nucleophilic substitution of MCBOs(PH-p.APH) and epichlorohydrine, as depicted in Scheme 2.

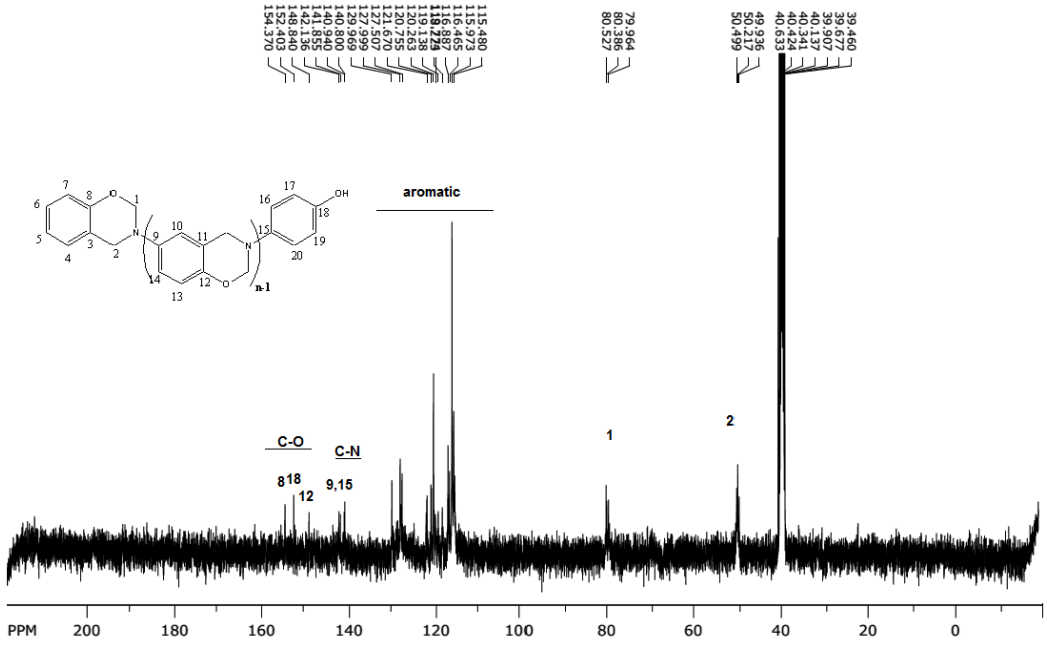
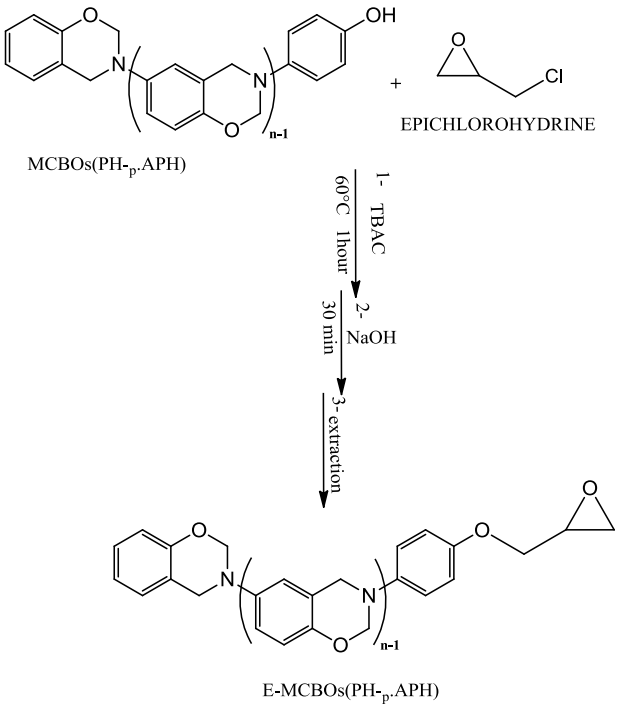


Figure 5. ^{13}C-NMR of MCBOs(PH-p.APH).

Scheme 2. **Synthesis of E-MCBOs(PH-p.APH).**



Concerning the epoxy MCBOs(PH-p.APH), as can be observed in the ^{1}H NMR spectrum depicted in Fig. 6, the resonance peaks are overlapped, but still allow a clear distinction of the epoxy species. Nevertheless, the characteristic peaks of the epoxy moiety c, d and e are observed at 4.02, 3.26 and 2.73 ppm, respectively and two characteristic peaks of benzoxazine ring (a) and (b) are shifted to 5.16 and 4.43 ppm, which attests for the formation of the desired precursors. Additional information supporting the complete epoxidation reaction is provided by the absence of resonance signal assigned to phenolic hydroxyl proton, as well as the integral values of methylene protons a, b, c and e and the integral value of methyne proton d.

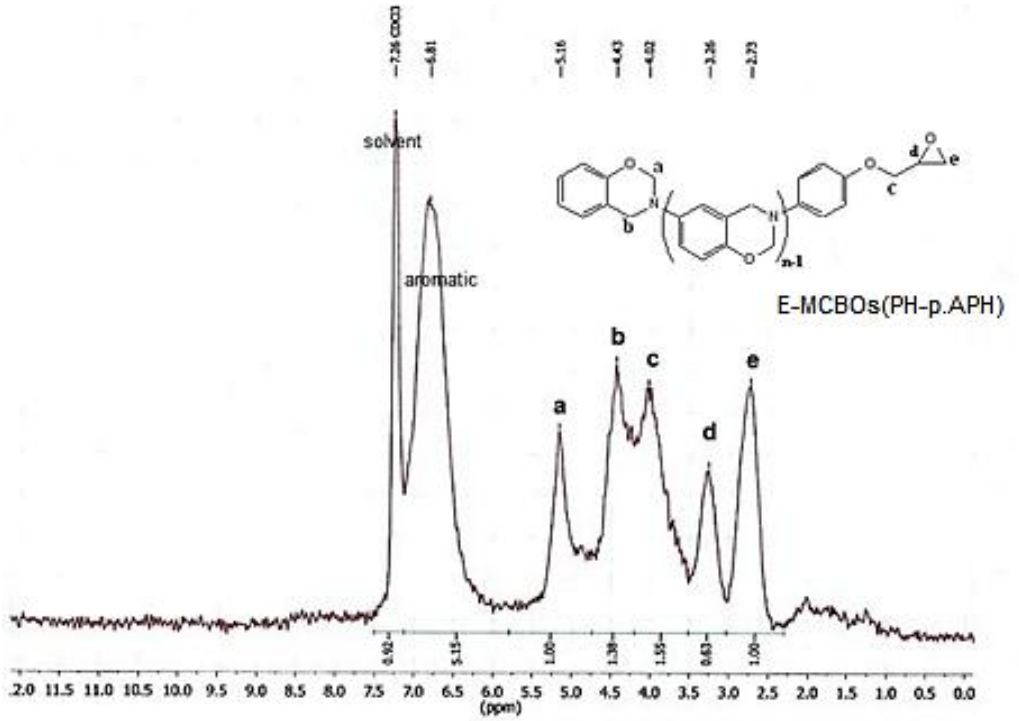


Figure 6. ^{1}H NMR spectrum of E-MCBOs(PH-p.APH).

Figure 7 shows the IR spectra of the novel precursors. The IR spectra of the benzoxazine oligomers and epoxy benzoxazine precursors showed that the characteristic absorption of the benzoxazine structure appeared at 1236 cm^{-1} (asymmetric stretching of C-O-C), at 1036 cm^{-1} (symmetric stretching of C-O-C), at 953 cm^{-1} (trisubstituted benzene ring) and at 1363 cm^{-1} (CH_2 wagging into the closed benzoxazine ring) and a characteristic absorption for the phenolic hydroxyl was observed at 3400 cm^{-1}. Characteristic absorption bands for epoxy structure at 916 cm^{-1} were not clearly identified because of the weakness of absorption, but the absorption band CH_2-Epoxy was clearly observed at 3005 cm^{-1}.

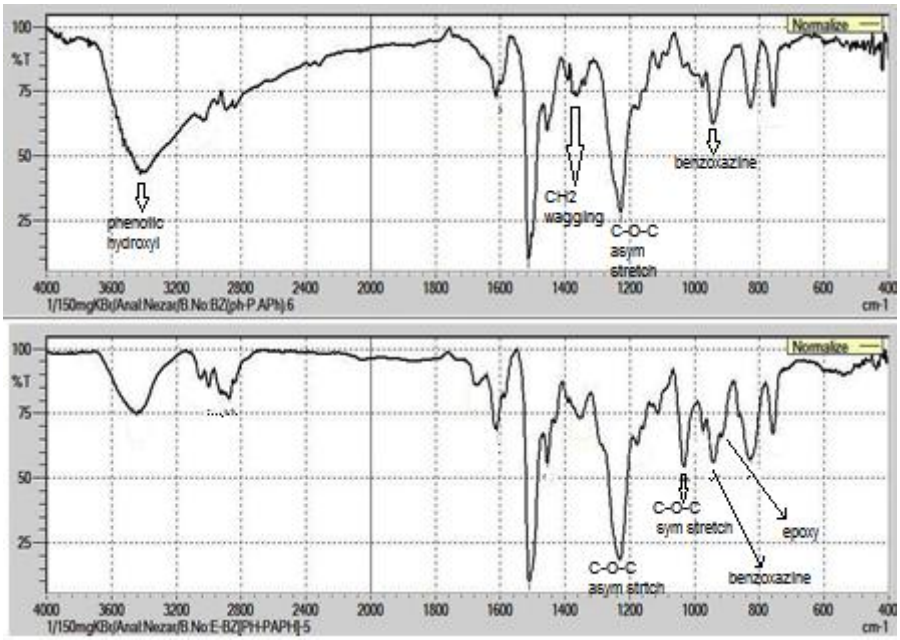


Figure 7. FTIR spectra of MCBOs(PH-p.APH) (part) and E-MCBOs(PH-p.APH) (part).

Curing Behavior of Precursors

The polymerization process of MCBOs(PH-p.APH) was verified using DSC. The thermogram in Figure 8 indicates that the endothermic peak observed at 70°C is due to melting process and a wide exothermic peak starting at 134ºC (T_i) and ending at 225 ºC (T_e), with a top peak at 196ºC (T_p). This is due to ring opening reaction of benzoxazine. The wide curing window due to the difference between the temperature of onset polymerization and that of the peak of polymerization (T_p) enables polymerization to be controlled. The larger the gap between the beginning and the peak of polymerization, the easier to maintain the polymerization at low temperature. Thermoset polymerization is usually performed at or near the T_p temperature, but it is preferable to conduct the process at a slightly lower temperature to avoid the formation of voids formed by sudden heating.

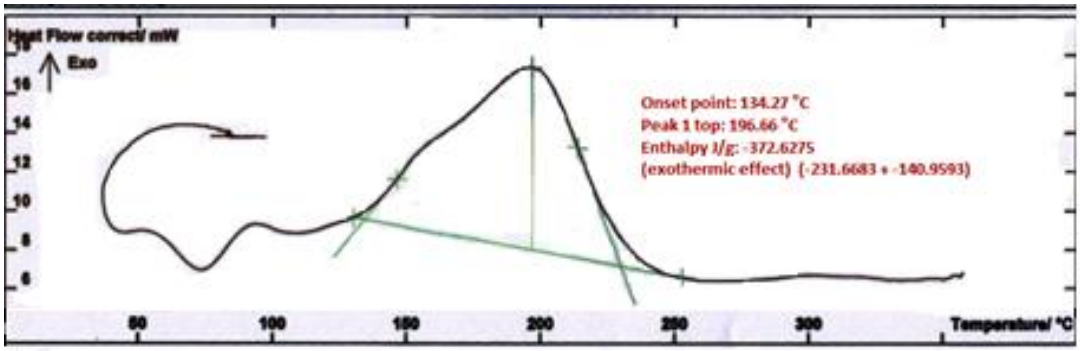


Figure 8. DSC thermogram of curing behavior of MCBOs(PH-p.APH) at a heating rate of 10 °C/min under argon atmosphere.

Concerning E-MCBOs(PH-p.APH), the crosslinking exotherm is observed at about 80°C higher than that of MCBOs(PH-p.APH) and the T_p temperature is shifted from 196 to 238°C. This shift clarifies the catalytic effect of phenolic hydroxyl in lowering the curing temperature of benzoxazine and the retardation effect of epoxy group. The DSC of epoxy and benzoxazine blends shows two exothermic peaks. The first peak is located in the range of the benzoxazine curing [190-240°C], while the second smaller peak compared to the first is located at higher temperatures [280-335ºC] and is due to epoxy curing.[12,28] Hence, we find from Figure 9 that the first exotherm in the field [215-270°C] is due to the benzoxazine ring opening polymerization and partial polymerization of the epoxy group, while the second exotherm in the field [270-340ºC] is due to the completion of epoxy polymerization. The raise in the baseline which occurs after the temperature 350ºC is due to the beginning of degradation of the formed polymer as will be illustrated by TGA.

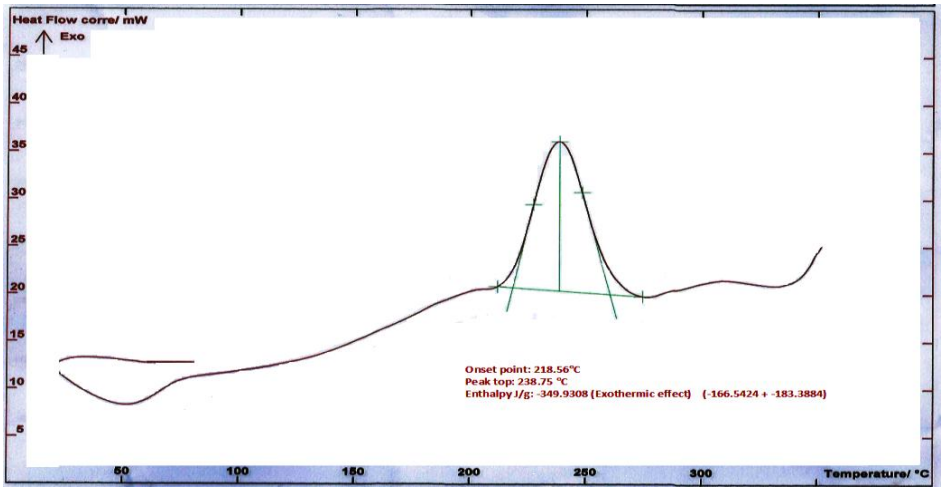


Figure 9. DSC thermogram of curing behavior of E-MCBOs(PH-p.APH) with a heating rate of 10 °C/min under argon atmosphere.

The structural changes of precursors that occur before and after curing were monitored by FTIR. The spectra are presented in Figs. 10 and 11 and reveal that typical characteristic peaks due to the benzoxazine structure at 943, 1032, 1236 and 1363 cm^{-1} disappeared by the cure cycle, confirming the ring-opening reaction of benzoxazine and the forming of Mannich-type

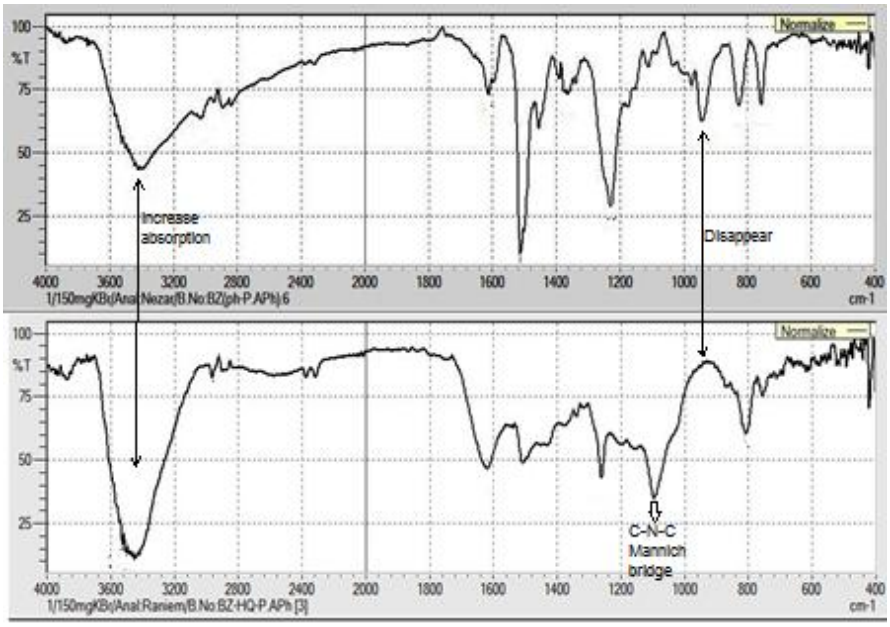


Figure 10. FTIR spectra of MCBOs(PH-p.APH) (upper part) and cured polybenzoxazine (PH-p.APH) (lower part).

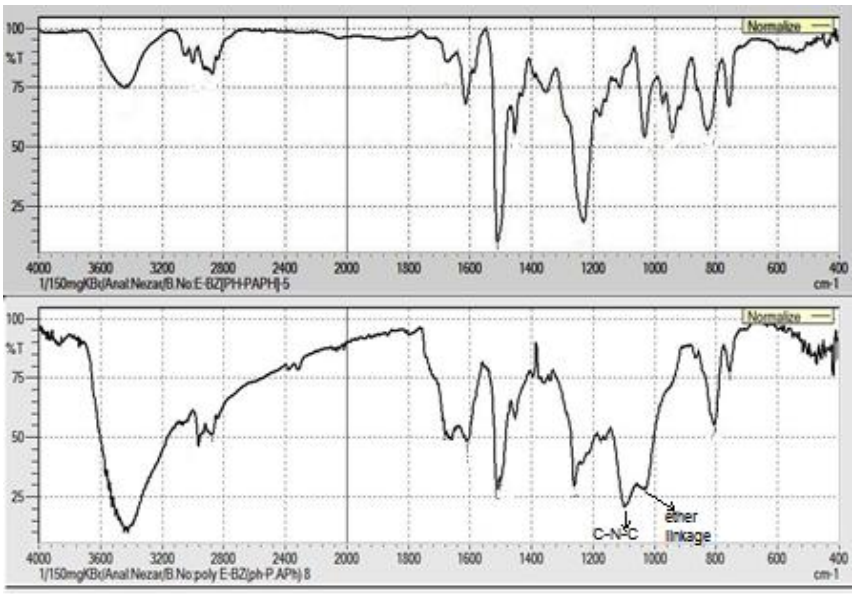
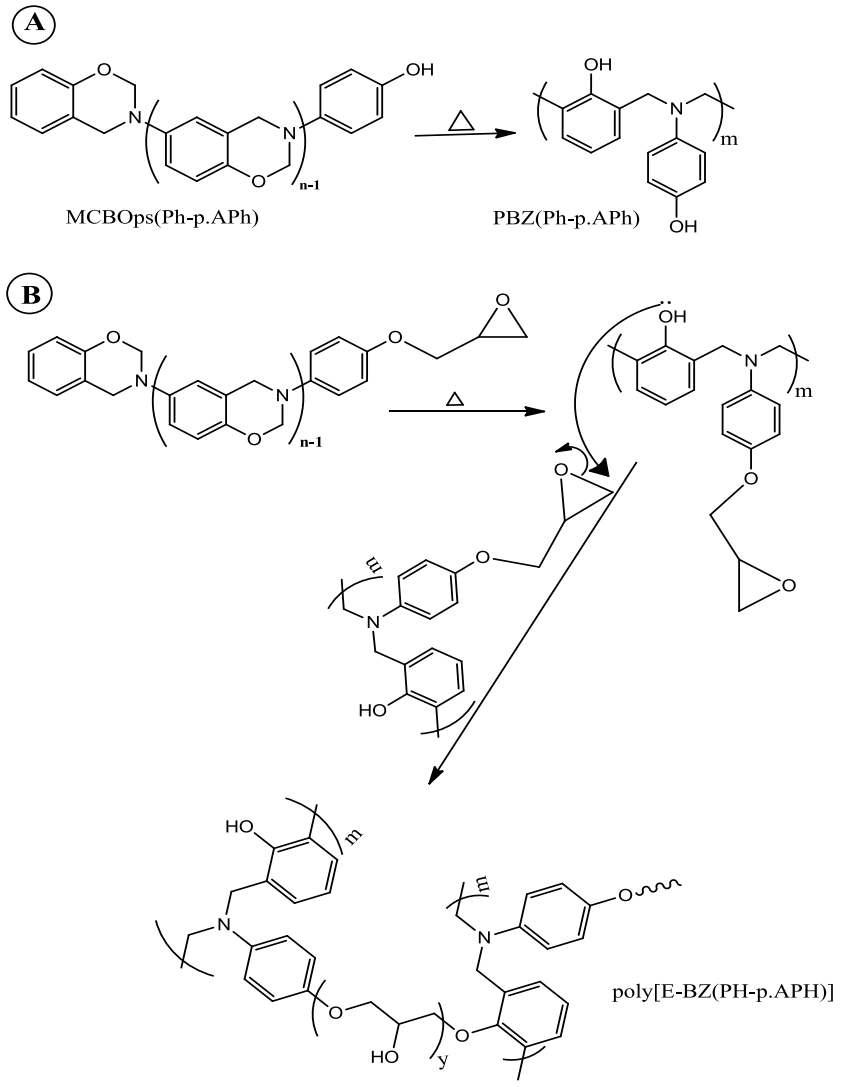


Figure 11. FTIR spectra of E-MCBOs(PH-p.APH) (upper part) and cured poly[E-BZ (PH-p.APH)] (lower part).

Scheme 3. Schematic illustration of thermally curing process of: A. MCBOs(PH-p.APH) and B. E-MCBOs(PH-p.APH).



bridge structures at 1085 cm^{-1}. By the way, as can be seen in Fig. 10 (lower part), a new absorption band at 1618 cm^{-1} appears, which may be attributed to aromatic C=C stretching vibrations of benzene ring with a higher degree of substitution and intermolecular hydrogen bonding. The bands around 1500 cm^{-1}, characteristic of the substituted benzene ring, have shifted to lower wave numbers, witnessing a variation of the degree of substitution of the benzene ring. The absorption band located around 3400 cm^{-1} has severely increased. This can be considered an additional evidence on the benzoxazine polymerization as it produces phenol entities, as illustrated by Scheme 3[29]. After the curing step, characteristic absorption bands due to epoxy structure at 916 cm^{-1} and at 3005 cm^{-1} disappeared by the cure cycle, confirming the ring-opening reaction of epoxy and the formation of ether-type linkage structures.

Thermal Stability of Polybenzoxazine(PH-p.APH) and Poly[E-BZ(PH-p.APH)]

The thermal stability of the polybenzoxazines was investigated by thermo-gravimetric analysis under argon flow. The TGA curves are illustrated in Figures 12 and 13 and the results are summarized in Table 2. Both TGA thermograms show high charring ability. Indeed, at 800ºC, the char yield of the polybenzoxazine (PH-p.APH) is high (69 wt%) compared to that of P[E-BZ(PH-p.APH)] (53 wt%). This high charring ability is due to the intrinsic phenolic structure of the cross-linked polybenzoxazine with high degree of aromaticity. LOI values indicate high flame resistance polymers. The limited oxygen indexes were calculated according to van Krevelen and Hofwitzer[30]:

$$LOI = 17.5 + 0.4\,CY, CY: Char\ yield$$

Table 2: Thermo-gravimetric data of cured polybenzoxazine (PH-p.APH) and P[E-BZ(PH-p.APH)].

polymer	5%	10%	Char yield% at 800ºC	LOI
polybenzoxazine(PH-p.APH)	358	435	69	45.1
poly[E-BZ(PH-p.APH)]	337	372	53	38.7

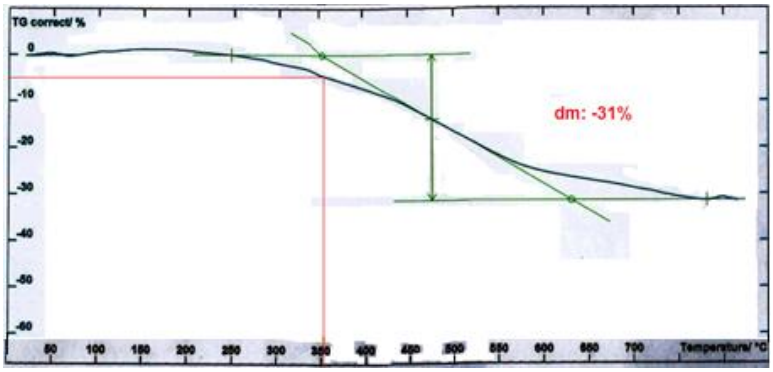


Figure 12. TGA thermogram of cured polybenzoxazine (PH-p.APH) with a heating rate of 10°C/min from room temperature to 800°C under argon atmosphere.

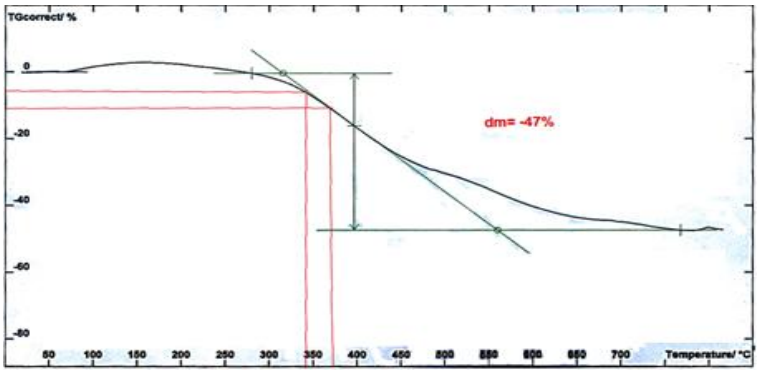


Figure 13. TGA thermogram of the cured poly[E-BZ(PH-p.APH)] with a heating rate of 10°C/min from room temperature to 800°C under argon atmosphere.

Conclusions

Main chain benzoxazine oligomers have been synthesized by a solvent-free and scalable method and epoxy benzoxazine precursor has been synthesized successfully by nucleophilic substitution of MCBOs(PH-p.APH) with ECH. The novel precursors were cross-linked through ring-opening polymerization of benzoxazine and of epoxy group. The ring-opening polymerization of benzoxazine occurred at a lower temperature due to catalytic effect of phenolic hydroxyl, whereas when the phenolic hydroxyl end was capped by epoxy group, the onset of polymerization temperature raised 80ºC higher than that of polymerization of benzoxazine. The two cured thermoset systems exhibit excellent thermal stability and present remarkable inherent charring ability upon pyrolysis. Better thermal properties were observed for the polybenzoxazine (PH-p.APH), which were correlated to a higher aromatic content of the resulting network. These excellent thermal properties make these resins promising candidates for inherent flame resistance applications.

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