Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding

Lei Zhang[a,b,*], Yong Yang[a], Yingxin Chen[a], Hongwei Lu[a,*]

[a] *College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, PR China*
[b] *Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

ARTICLE INFO

Keywords:
Main-chain benzoxazine oligomer
Cardanol
Resin transfer molding
Viscosity
Thermal properties

ABSTRACT

Main-chain benzoxazine oligomers can be phenol-capped now. In this article, cardanol, a renewable phenol extracted from agricultural byproduct, is designed as the capping agent for the oligomers. Benefiting from the long alkyl chain of cardanol, the oligomers possess good processability to satisfy resin transfer molding without adding any diluents. The structures of the oligomers are verified by Fourier transform infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy. The molecular weight and distribution have been measured by size exclusion chromatography. The thermal properties, including glass transition temperature, coefficient of thermal expansion, thermal stability and char yield, are characterized and discussed in this study.

1. Introduction

Cashew nut shell liquid (CNSL) is an abundant byproduct (450 kiloton/year) of cashew nut agriculture [1]. It is a non-edible oil, thus will not suffer food supply when used as a raw chemical. Cardanol is the main component of the technical CNSL [2] which has already been used to produce epoxy curing agents [3], frictional materials [4], and rigid polyurethane [5]. With its long alkyl chain, cardanol can efficiently enhance the processability of the resin during molding.

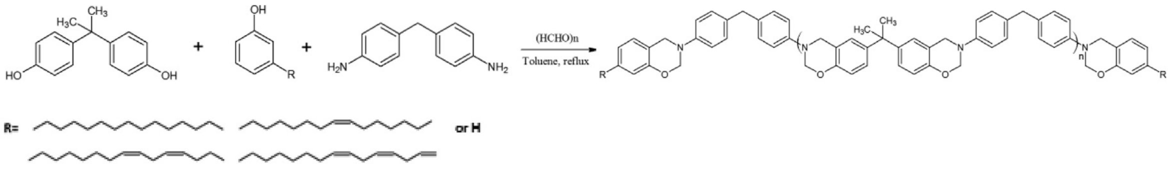
Resin transfer molding (RTM) is capable to make large complex 3D structures with good dimensional tolerance, fine surface finish and confined void fraction with low facility investment [6]. Thus, it has been widely applied in industry nowadays. Typically, the resin used for RTM should have a low viscosity (< 1 Pa s), low curing shrinkage and not release small molecules during polymerization [6,7]. Epoxy and phenolic resin are the conventional resins for RTM [6,8]. However, epoxy resin shows poor reliability under hot-humid condition, while phenolic resin would release small volatile molecules during condensation reaction. Thus, developing new resin for RTM is carrying out continuously [9].

Polybenzoxazine constitutes a new generation of thermosets, which combines the advantages of both phenolic and epoxy resins [10–12]. Since its unique properties fit to various applications, such as aviation composites and electronic packaging, it becomes one of the rare new polymers which has been industrialized during the last 30 years [10,13,14]. However, cured benzoxazine monomers are usually brittle, which is similar to many other thermosets [12,15]. Besides, the intramolecular hydrogen bonding leads to many branched structures and end groups, thus decreases the thermal stability [16]. Preparation of benzoxazine monomers with the constituents of CNSL (cardanol, cardol and methylcardol) is a way to enhance ductility and processability [17], but still requires further improvement on the thermal properties [7,18,19]. Thermosets prepared by main-chain benzoxazine polymers (MCBP) can address the brittleness, but their high viscosity and reactivity are drawbacks to preparation [15,20,21]. Main-chain benzoxazine

---

[*] Corresponding authors at: College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, PR China (L. Zhang and H. Lu).
E-mail addresses: lzhang@hdu.edu.cn (L. Zhang), luhongwei@hdu.edu.cn (H. Lu).

http://dx.doi.org/10.1016/j.eurpolymj.2017.06.006
Received 12 March 2017; Received in revised form 31 May 2017; Accepted 2 June 2017



Scheme 1. Synthesis of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P based on BPA, DDM, phenol and cardanol.

oligomer (MCBO) has been purposed to overcome the challenges [8]. However, without using diluents, the viscosity of the resin remains large. Till now, there is only very few works on this topic [8,22] and these works mainly focus on amine-capped MCBO. Phenol-capped MCBO has long been ignored.

To address the difficulties mentioned above and study phenol-capped MCBO, this manuscript reports the synthesis of new MCBO materials with phenol and cardanol as capping reagents. Herein, the function of the bio-based cardanol is to enhance the processability of the petroleum-based main-chain. On the other hand, although preparation of cardanol-containing benzoxazine monomers [7,23,24] and asymmetric benzoxazine monomers have been reported before [25,26], research on asymmetric MCBO structure has not been conducted yet. In this study, three MCBOs with different capping agents are synthesized. Their chemical structures are characterized by FT-IR and NMR. Their processability and curing profiles are evaluated through rheometer and DSC. The material properties, especially the thermal performances after curing are investigated as well.

2. Experimental

2.1. Materials

Cardanol is purchased from Jinin Baiyi Chemical Co., Ltd., Jinan, China. Phenol (99%), 4,4′-dihydroxyldiphenyl isopropane (BPA, 99%) and paraformaldehyde (96%) are obtained from Aladdin Reagent Co., Ltd., Shanghai, China. 4,4′-diaminodiphenyl methane (DDM, 97%), sodium carbonate anhydrous (Na_2CO_3), sodium sulfate anhydrous (Na_2SO_4) and deuterated chloroform ($CHCl_3$-d) are achieved from Sigma-Aldrich, St. Louis, US with tetramethylsilane (TMS) as standard. Toluene is acquired from VWR, Radnor, US. All chemicals are directly used without further purification.

2.2. Synthesis of cardanol-capped main-chain benzoxazine oligomer MCBO(BPA-ddm)C

Based on the nomenclature rule of benzoxazine [10], the MCBO with BPA and DDM in the main-chain and cardanol-capping is named as MCBO(BPA-ddm)C. Specifically, BPA (0.025 mol, 5.7 g), DDM (0.05 mol, 9.9 g) and cardanol (0.05 mol, 15.2 g) are dissolved in 100 mL toluene in a 250 mL round-bottom flask before adding paraformaldehyde (0.22 mol, 6.6 g). The mixture is then heated up. An insoluble triazine gel forms after 10 min's refluxing and disappears after 4 h's reaction, results in a transparent maroon solution. After refluxing for 24 h, the solution is cooled down, washed by 1 N Na_2CO_3 solution and DI water until the solution becomes neutral. It is then dried by Na_2SO_4 and put into vacuum to remove the solvent at 80 °C. A brown solid is obtained after sufficient drying (Yield = 65%).

FT-IR (KBr, cm^{-1}): 3009 (Ar—H), 2962 (—CH_3), 2924, 2851 (—CH_2—), 1510 (Ar), 1232, 1036 (C—O—C), 1192 (C—N—C), 945 (Ox).

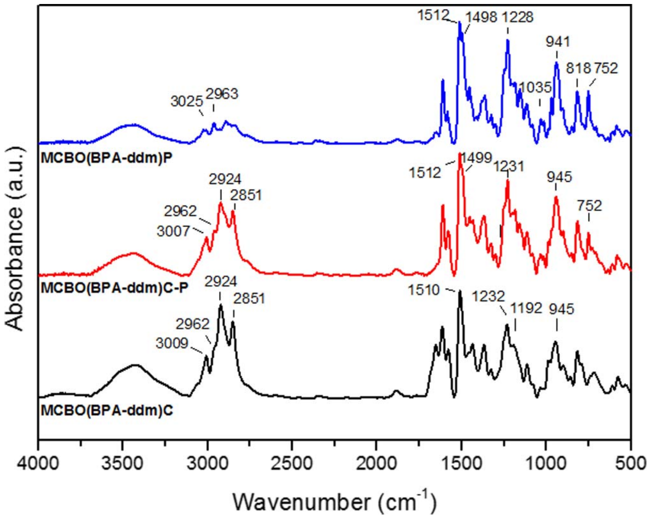


Fig. 1. FT-IR spectra of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

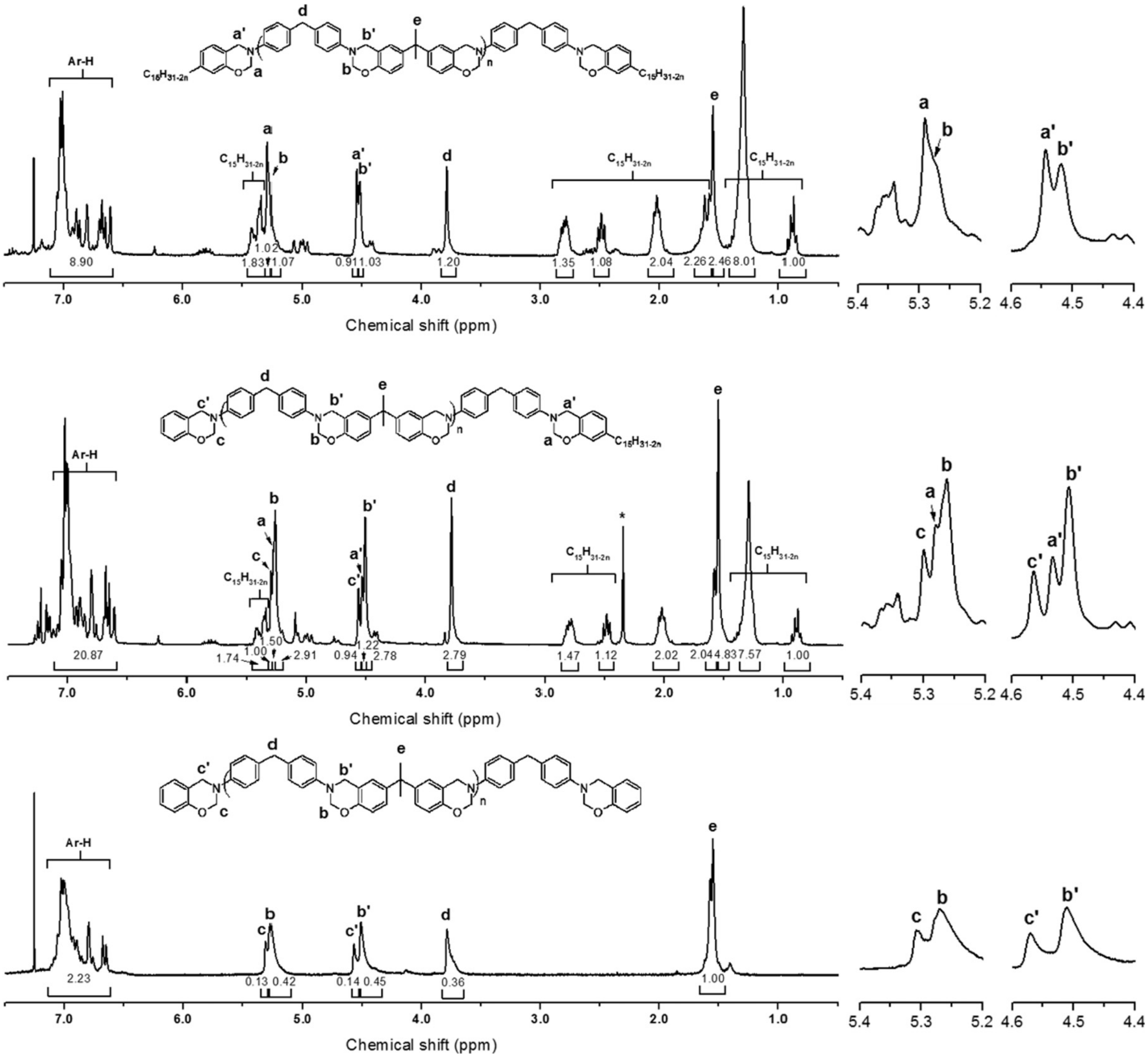


Fig. 2. ^{1}H NMR spectra of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

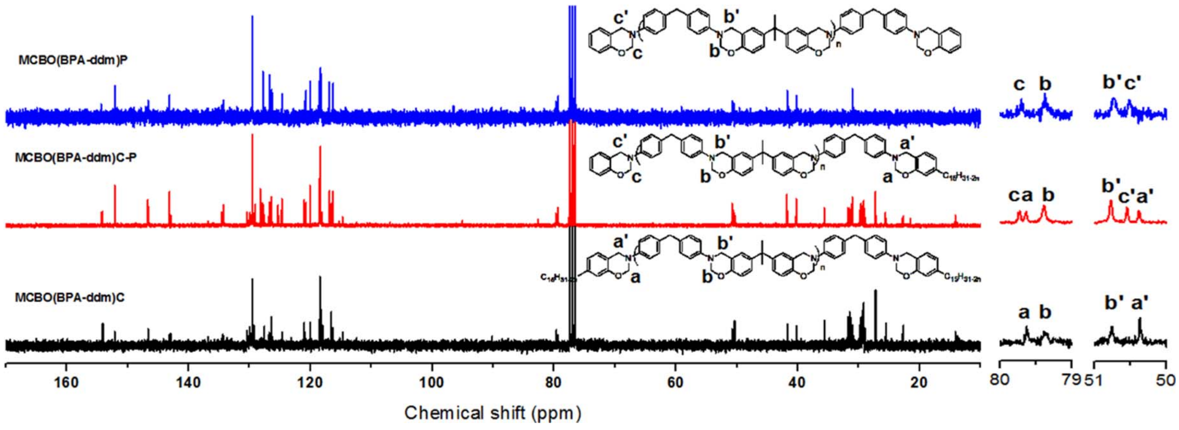


Fig. 3. ^{13}C NMR spectra of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

Table 1
Molecular weight and polydispersity index of the oligomers.

Oligomer	M_n (Daltons)	M_w (Daltons)	PDI
MCBO(BPA-ddm)C	11370	21050	1.85
MCBO(BPA-ddm)C-P	4396	6536	1.49
MCBO(BPA-ddm)P	7732	23570	3.05

^{1}H NMR ($CHCl_3$-d, ppm): 6.60–7.05 (Ar—H), 5.42, 5.34 (—CH═C—), 5.29, 5.27 (N—CH_2—O), 4.54, 4.52 (N—CH_2—Ar), 3.79 (Ar—CH_2—Ar), 2.78, 2.49, 2.02, 1.58 (—CH_2—), 1.55 (Ar—C—CH_3), 1.29 (—CH_2—), 0.88 (—CH_3).

^{13}C NMR ($CHCl_3$-d, ppm): 79.63, 79.39 (N—CH_2—O), 50.77, 50.37 (N—CH_2—Ar).

2.3. Synthesis of cardanol and phenol-capped main-chain benzoxazine oligomer MCBO(BPA-ddm)C-P

The preparation method of MCBO(BPA-ddm)C-P is similar to MCBO(BPA-ddm)C instead of using phenol (0.025 mol, 2.35 g) to replace the same molar amount of cardanol. A dark-orange solid is obtained after sufficient drying. (Yield = 73%).

FT-IR (KBr, cm^{-1}): 3007 (Ar—H), 2962 (—CH_3), 2924, 2851 (—CH_2—), 1512, 1499 (Ar), 1231, 1034, 1016 (C—O—C), 1186 (C—N—C), 945 (Ox), 752 (Ar).

^{1}H NMR ($CHCl_3$-d, ppm): 6.60–7.25 (Ar—H), 5.42, 5.34 (—CH═C—), 5.30, 5.28, 5.26 (N—CH_2—O), 4.56, 4.53, 4.51 (N—CH_2—Ar), 3.78 (Ar—CH_2—Ar), 2.78, 2.49, 2.02, 1.58 (—CH_2—), 1.55 (Ar—C—CH_3), 1.29 (—CH_2—), 0.88 (—CH_3).

^{13}C NMR ($CHCl_3$-d, ppm): 79.75, 79.64, 79.39 (N—CH_2—O), 50.77, 50.55, 50.38 (N—CH_2—Ar).

2.4. Synthesis of phenol-capped main-chain benzoxazine oligomer MCBO(BPA-ddm)P

The preparation method of MCBO(BPA-ddm)P is similar to MCBO(BPA-ddm)C instead of using phenol to completely replace cardanol. An orange powder is obtained after sufficient drying. (Yield = 33%).

FT-IR (KBr, cm^{-1}): 3025 (Ar—H), 2963 (—CH_3), 1512, 1498 (Ar), 1228, 1035 (C—O—C), 941 (Ox), 818, 752 (Ar).

^{1}H NMR ($CHCl_3$-d, ppm): 6.60–7.10 (Ar—H), 5.31, 5.27 (N—CH_2—O), 4.57, 4.52 (N—CH_2—Ar), 3.79 (Ar—CH_2—Ar), 1.57, 1.55 (Ar—C—CH_3).

^{13}C NMR ($CHCl_3$-d, ppm): 79.71, 79.38 (N—CH_2—O), 50.74 50.52 (N—CH_2—Ar).

2.5. Polymerization of the MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P

Curing carries out by placing the MCBO in a mold and stepwise heating at 125 °C/1 h, 140 °C/1 h, 160 °C/1 h, 180 °C/2 h and 200 °C/2 h, successively.

2.6. Characterization methods

A Fourier transform infrared spectrometer (FT-IR) Bruker Tensor 27 is used to record the FT-IR spectra with 16 scans at a 4 cm^{-1} resolution in 500–4000 cm^{-1} range. The molecular structure is verified by a Varian Mercury VX300 nuclear magnetic resonance spectroscopy (NMR). The molecular weight of the oligomers is determined by size exclusion chromatography (SEC) using a Waters 1515 gel permeation chromatography (GPC) system. The samples are dissolved in N,N-dimethylformamide and measured under room temperature. The polymerization behavior and the glass transition temperature (T_g) is examined using differential scanning calorimetry (DSC) by a Q200 TA Instrument. The heating and cooling rates are maintained at 10 °C/min. The thermal stability and char yield are evaluated through a thermogravimetric analyzer (TGA), TA Instrument Q5000. The tests are carried out under nitrogen atmosphere at a heating rate of 10 °C/min. The T_g and coefficient of thermal expansion (CTE) are characterized on a thermal mechanical analyzer (TMA), Mettler SDTA840 with a heating rate of 10 °C/min. The viscosity of the MCBO is recorded by a TA Instrument, AR2000ex rheometer. The test is conducted under steady shear mode with a shear rate of 1 s^{-1} and a heating rate of 2 °C/min.

3. Results and discussion

3.1. Preparation of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P

Cardanol-capped MCBO(BPA-ddm)C is synthesized from BPA, DDM, cardanol and paraformaldehyde (Scheme 1). To evaluate the contribution of cardanol on the processability and thermal properties, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P are prepared in a similar way, except using phenol as a co-capping agent. The chemical structures of the obtained oligomers are verified by FT-IR, ^{1}H NMR and ^{13}C NMR. Fig. 1 shows the FT-IR spectra of the oligomers. The peak at 2962 cm^{-1} is assigned to the methyl group in BPA and cardanol. The high absorbance peaks at 2924 and 2851 cm^{-1} imply the long alkyl chain of cardanol in the oligomer. These peaks are smaller in MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P due to less cardanol amount. The oxazine ring is supported by the

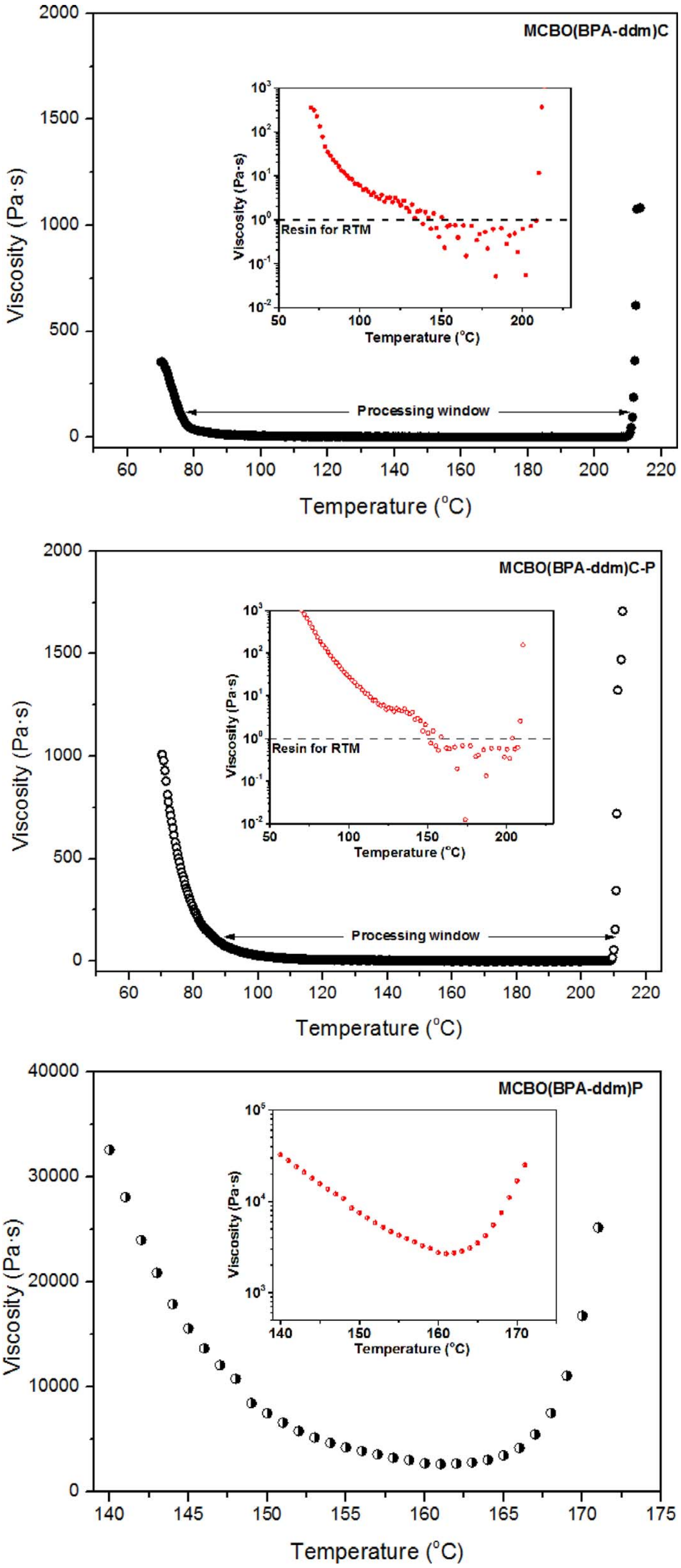


Fig. 4. Viscosity of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

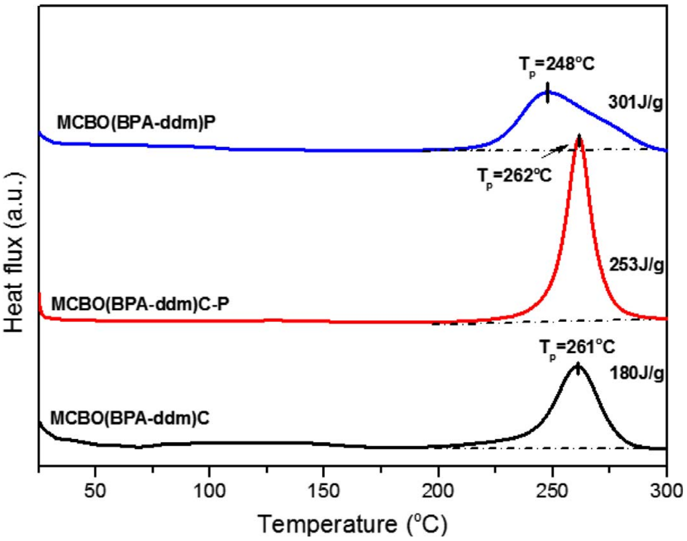


Fig. 5. DSC curves of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

absorbance peaks around 1230 cm^{-1}, which indicates the asymmetric stretching mode of C—O—C bond. The characteristic peak of oxazine ring attached benzene appears near 945 cm^{-1}. The absorbance peak at 1510 cm^{-1} represents the tri-substituted benzene ring due to the attached oxazine ring on the benzene of BPA and cardanol. The incorporation of the phenol is proved by the shoulder peak at 1499 cm^{-1} and the peak at 752 cm^{-1}, which indicates the 1,2-bi-substituted benzene ring of the phenol attached by oxazine ring.

The structures of the three oligomers are further verified by ^{1}H NMR (Fig. 2). The multiplets in 6.60–7.10 ppm are assigned to the protons of the aromatic ring. The peaks at 5.34–6.00 ppm are assigned to the protons of vinyl group, which are consistent with the results of pristine cardanol [7,19]. The resonance peak at 3.79 ppm is attributed to the $-CH_2-$ structure in DDM. The peaks within the range of 1.00–3.00 ppm are assigned to the protons of $-CH_2-$ in the alkyl chain. The high peak at 1.55 ppm is corresponding to the proton of $-CH_3$ in BPA. The main differences between the three oligomers are the peaks imply the characteristic oxazine rings. As shown in the enlarged spectra in Fig. 2, the resonance peaks at 5.29 ppm (**a**), 5.27 ppm (**b**) and 4.54 ppm (**a′**), 4.52 ppm (**b′**) are assigned to the $O-CH_2-N$ and $Ar-CH_2-N$ of the oxazine rings in MCBO(BPA-ddm)C. Among them, the peaks at 5.29 ppm (**a**) and 4.54 ppm (**a′**) signify the oxazine ring formed by cardanol and DDM while the other two peaks belong to the oxazine ring generated by BPA and DDM. Other than the four peaks mentioned above, additional two peaks appear at 5.30 ppm (**c**) and 4.56 ppm (**c′**) in the spectrum of MCBO(BPA-ddm)C-P are corresponding to the oxazine ring generated by phenol and DDM. These two peaks appear in the spectrum of MCBO(BPA-ddm)P as well. Furthermore, ^{13}C NMR is applied to characterize the oligomers, which is especially useful to distinguish the oxazine rings (Fig. 3). The oxazine rings of MCBO(BPA-ddm)C formed by cardanol and DDM are evidenced by the

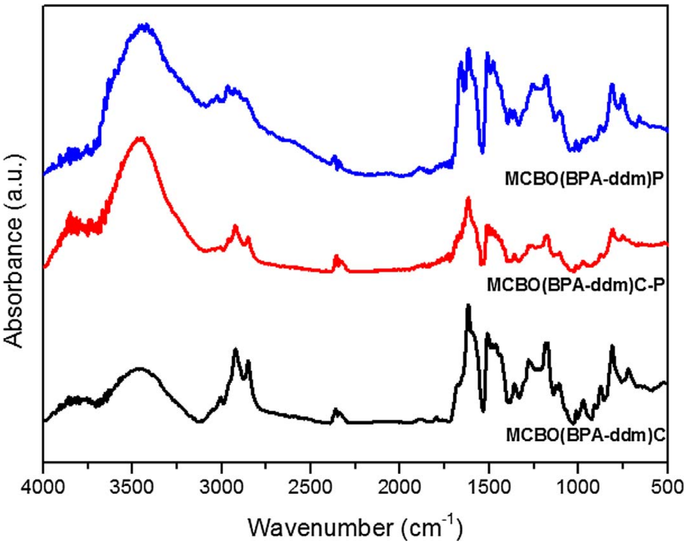


Fig. 6. FT-IR spectra of the polymers prepared by MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

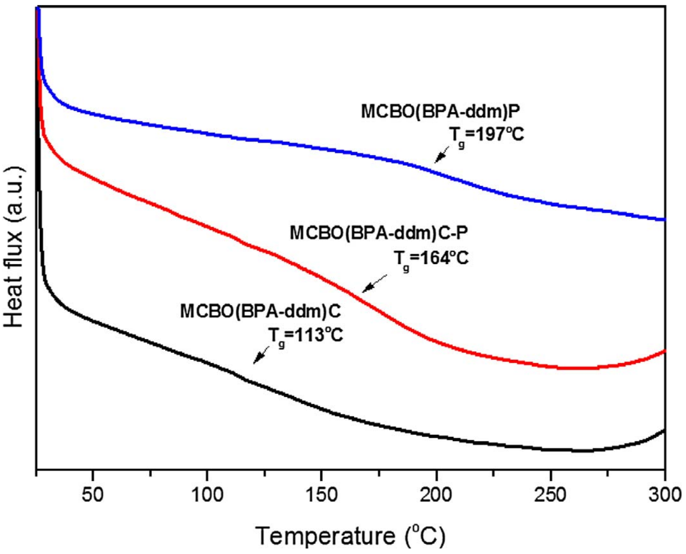


Fig. 7. T_g of the polymers prepared by MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P.

resonances at 79.63 ppm (**a**) and 50.37 ppm (**a′**). The resonances at 79.39 ppm (**b**) and 50.77 ppm (**b′**) prove the reaction between BPA and DDM. In the spectrum of MCBO(BPA-ddm)C-P, the reaction between phenol and DDM results in the appearance of two additional resonances at 79.75 ppm (**c**) and 50.55 ppm (**c′**). These two peaks are also found in the spectrum of MCBO(BPA-ddm)P. Meanwhile, the peaks of oxazine ring generated by cardanol (**a** and **a′**) is not found since cardanol is not applied in this oligomer.

The molecular weights of the oligomers are measured through SEC and the results are presented in Table 1. The number average molecular weights (M_n) of MCBO(BPA-ddm)C,MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P are 11,370 Da, 4396 Da and 7732 Da, respectively. The corresponding polydispersity indexes (PDI) are 1.85, 1.49 and 3.05. These results imply that the prepared oligomers are a groups of chain mixtures with long repeating units.

3.2. Properties of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P

The viscosity of the oligomers is critical for RTM technology. Generally, the processing window refers to the temperature range between the liquefying temperature and gel temperature [27]. Herein, the liquefying and gel temperatures define the temperature at a viscosity right below and above 100 Pa s. As shown in Fig. 4, the liquefying temperature of MCBO(BPA-ddm)C is 76 °C while the gel temperature is 211 °C. Thus, the corresponding processing window is 135 °C. For MCBO(BPA-ddm)C-P, due to less cardanol content, the liquefying temperature becomes higher (87 °C). The corresponding processing window is 123 °C. Importantly, for both of them, the liquefying temperature are much lower than conventional MCBP [28] and MCBO [8]. Meanwhile, to clarify the contribution of cardanol to the processability, the viscosity of MCBO(BPA-ddm)P is measured as well. The MCBO starts to melt at a temperature around 140 °C and the detected minimum viscosity is above 1000 Pa s. Therefore, cardanol-capping is proved to facilitate processing at a lower temperature. Besides the processing window, RTM also prefers the resin to have a viscosity below 1 Pa s during soaking [8]. By plotting the viscosity in a logarithmic axis (small figures in Fig. 4), it is clear that both MCBO(BPA-ddm)C and MCBO(BPA-ddm)C-P satisfy the requirement at a temperature higher than 135 °C and 150 °C, respectively, without blending with diluents.

The curing profiles of the benzoxazine oligomers are plotted in Fig. 5. Regarding MCBO(BPA-ddm)C, the curing peak appears at 261 °C, together with an exothermic curing enthalpy change of 180 J/g. The peak temperature is similar to conventional cardanol based benzoxazine monomer, while the exothermic curing enthalpy is much larger [7,14,19]. This can be explained by the less diluent effect caused by less cardanol amount and enhancement in oxazine ring concentration generated by the main-chain structure. Meanwhile, by replacing cardanol with phenol, higher curing enthalpy change can be achieved in MCBO(BPA-ddm)C-P (253 J/g) and MCBO(BPA-ddm)P (301 J/g). The peak curing temperature of MCBO(BPA-ddm)P is lower than the others, which is corresponding to the lower ring-opening temperature of phenol-ended benzoxazine [29].

3.3. Properties of polymers cured from the oligomers

The prepared oligomers are thermally cured through the curing steps mentioned in the experimental section. The obtained polymers are characterized by FT-IR (Fig. 6). In the spectra of all polymers, the disappearance of the peaks at around 945 cm^{-1} signify the complete consumption of oxazine ring. The elimination of absorbance at 1231 cm^{-1}, corresponding to the cleavage of C—O—C bond, also verifies the ring-opening process. On the other hand, tetra-substituted benzene ring generated after polymerization results in a new peak at 1484 cm^{-1}. The intensive broad absorbance peak at 3450 cm^{-1} indicates the generation of phenol structure after benzoxazine ring-opening.

The glass transition temperature (T_g) of the thermosets prepared from the oligomers is first determined by DSC through a second

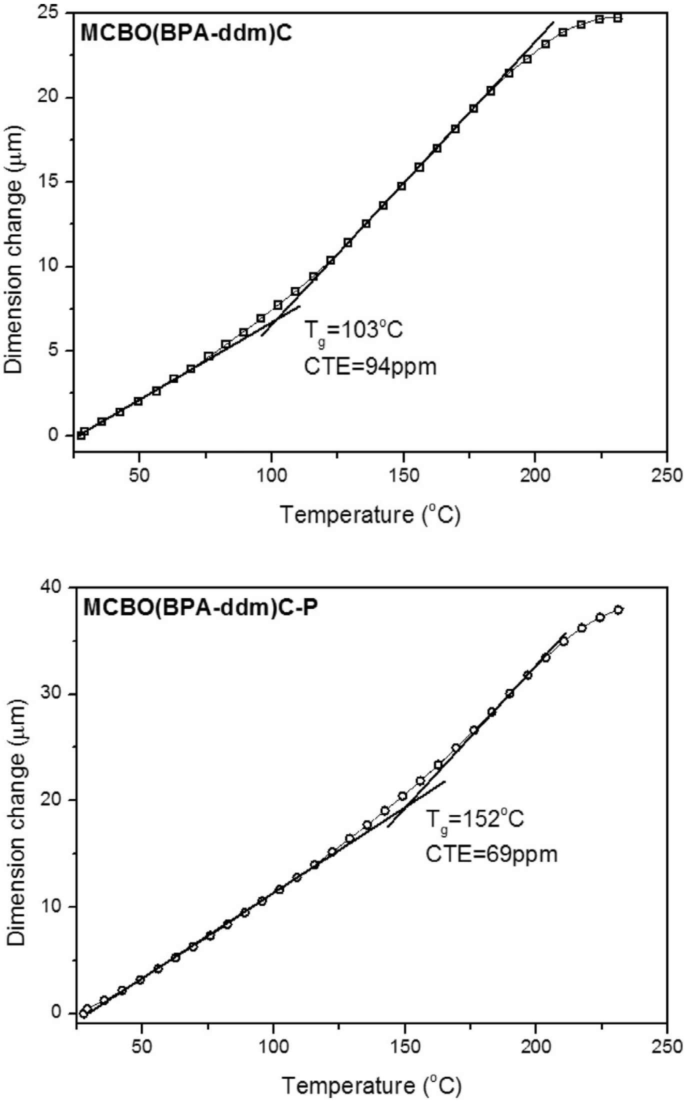


Fig. 8. Thermal mechanical analysis of MCBO(BPA-ddm)C and MCBO(BPA-ddm)C-P.

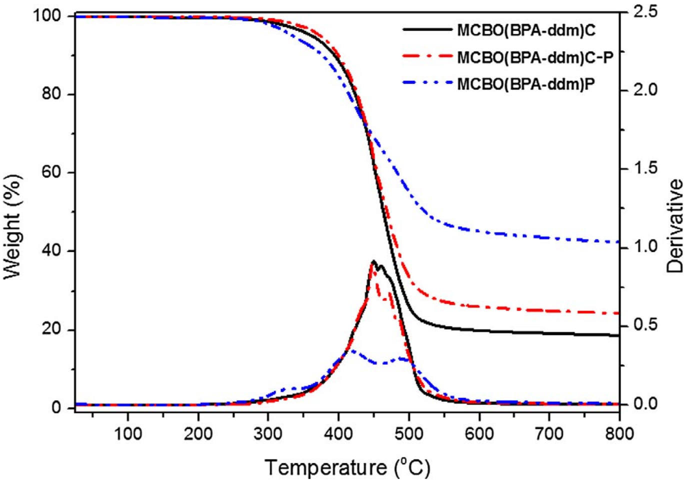


Fig. 9. TG and DTG results of the polymers obtained from MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P after thermal polymerization.

heating (Fig. 7). It is identified by the change in thermal capacity, performs as a stage on the curve. The obtained T_g of cured materials are 113 °C (MCBO(BPA-ddm)C) and 164 °C (MCBO(BPA-ddm)C-P), respectively. The achieved T_g of the material prepared by MCBO(BPA-ddm)C is at least 25 °C higher than the cured cardanol-based monomers and precursors. Moreover, with a little sacrifice in processability, a further enhancement of more than 50 °C in T_g can be achieved by partially replacing cardanol with phenol. In both cases, the enhancement in T_g can be explained based on the viewpoint of chain rigidity. Other than DSC, the T_g of the materials is also characterized based on thermal mechanical analysis (Fig. 8). The cured MCBO(BPA-ddm)C and MCBO(BPA-ddm)C-P have a T_g at 103 °C and 152 °C, which are similar to the DSC results. The CTE below T_g are measured as well. Specifically, MCBO (BPA-ddm)C-P exhibits a CTE of 69 ppm, which is comparable to conventional polybenzoxazines. Meanwhile, MCBO(BPA-ddm)C has a CTE at 94 ppm. The high CTE value is probably due to the larger alkyl chain amount. Unfortunately, due to the poor processability of MCBO(BPA-ddm)P (Fig. 4), preparation of cured shaped sample fails.

The thermal stability and char yield of the cured polymers are evaluated by TGA, which are presented in Fig. 9. In general, thermal degradation of polybenzoxazines includes chain-end degradation, Mannich bridge cleavage and char formation, successively [30]. For cured amine-ended benzoxazines, the related DTG peaks appears at 300 °C, 410 °C and 520 °C. Regarding the thermal stability, the cured MCBO oligomers show the 5% weight loss at 362 °C and 375 °C and 335 °C, which are better than traditional polybenzoxazines obtained from amine-ended benzoxazines. This is because the two oligomers are capped by phenols, the capping phenol can participate the reaction and incorporate in the chain structure, rather than exists as a dangling group. Besides, there is less chain-end in the MCBO than monomers. As expected, the first degradation peak (near 300 °C) is almost ignorable in the DTG curves. The maximum DTG peaks of the three cured oligomers appear at 449 °C (MCBO(BPA-ddm)C), 447 °C (MCBO(BPA-ddm)C-P) and 418 °C (MCBO(BPA-ddm)P), respectively. The char yield is obtained by heating the cured materials to 800 °C under nitrogen atmosphere. The char yield of cured MCBO(BPA-ddm)C at 800 °C is 19%. When phenol is applied to replace cardanol partially, the obtained polymer shows a 5% enhancement in char yield. Meanwhile, complete replacing cardanol with phenol results in significant improvement in char yield (43%). Apparently, decrease in alkyl chain amount facilitates the formation of compact char structure, which enhances char generation.

4. Conclusion

This manuscript reports the synthesis of three phenol-capped MCBO. Among them, two oligomers which are completely or partially capped by cardanol show very large processing window as well as low viscosity. Attractively, without adding diluents, they can satisfy the viscosity requirement of RTM. The main-chain type structure enhances the T_g of the cardanol-based polybenzoxazines while the phenol-capping structure benefits their thermal properties and processability. In sum, this study proposes a new idea to fabricate MCBO materials with good processability and material performance by introducing cardanol as capping agent.

Acknowledgements

The authors appreciate Mr. Jiale Mao from School of Electrical Engineering, Xi'an Jiaotong University, for helping on testing the molecular weight of the oligomers.

References

[1] A. Velmurugan, M. Loganathan, World Acad. Sci. Eng. Technol. 58 (2011) 889–894.
[2] C. Voirin, S. Caillol, N.V. Sadavarte, B.V. Tawade, B. Boutevin, P.P. Wadgaonkar, Polym. Chem. 5 (2014) 3142–3162.
[3] B.S. Rao, S.K. Pathak, J. Appl. Polym. Sci. 100 (2006) 3956–3965.
[4] P.H. Gedam, P.S. Sampathkumaran, Prog. Org. Coat. 14 (1986) 115–157.
[5] K.I. Suresh, V.S. Kishan Prasad, US 20060004115 A1, 2006.
[6] S. Laurenzi, M. Marchetti, in Composites and Their Properties, N. Hu (Ed.), INTECH, Rijeka, pp. 197–226.
[7] B.S. Rao, A. Palanisamy, Prog. Org. Coat. 74 (2012) 427–434.
[8] J. Liu, T. Agag, H. Ishida, Polymer 51 (2010) 5688–5694.
[9] H. Xiang, H. Ling, J. Wang, L. Song, Y. Gu, Polym. Compos. 26 (2005) 563–571.
[10] H. Ishida, in: H. Ishida, T. Agag (Ed.), Handbook of Benzoxazine Resins, Elsevier, Amsterdam, 2011, pp. 3–81.
[11] S.B. Shen, H. Ishida, Polym. Compos. 17 (1996) 710–719.
[12] T. Agag, T.J. Takeichi, J. Polym. Sci. Part A Polym. Chem. 45 (2007) 1878–1888.
[13] N. Dansiri, N. Yanumet, J.W. Ellis, H. Ishida, Polym. Compos. 23 (2002) 352–360.
[14] B.S. Rao, A. Palanisamy, Euro. Polym. J. 49 (2013) 2365–2376.
[15] T. Takeichi, T. Kano, T. Agag, Polymer 46 (2005) 12172–12180.
[16] Y. Bai, P. Yang, Y. Song, R. Zhu, Y. Gu, RSC Adv. 6 (2016) 45630–45635.
[17] O.A. Attanasi, M.S. Behalo, G. Favi, D. Lomonaco, S.E. Mazzetto, G. Mele, I. Pio, G. Vasapollo, Curr. Organ. Chem. 16 (2012) 2613–2621.
[18] E. Calo, A. Maffezzoli, G. Mele, F. Martina, S.F. Mazzetto, A. Tarzia, C. Stifani, Green Chem. 9 (2007) 754–759.
[19] T. Agag, S.Y. An, H. Ishida, J. Appl. Polym. Sci. 127 (2013) 2710–2714.
[20] C.H. Lin, S.L. Chang, C.W. Hsieh, H.H. Lee, Polymer 49 (2008) 1220–1229.
[21] C.H. Lin, S.L. Chang, T.Y. Shen, Y.S. Shih, H.T. Lin, C.F. Wang, Polym. Chem. 3 (2012) 935–945.
[22] Z.W. Tan, X. Wu, M. Zhang, J.J. Qiu, C.M. Liu, High Perform. Polym. 26 (2014) 906–913.
[23] L.R.V. Kotzebue, F.W.M. Ribeiro, V.G. Sombra, J.P.A. Feitosa, G. Mele, S.E. Mazzetto, D. Lomonaco, Polymer 92 (2016) 189–200.
[24] G. Mele, D. Lomonaco, S.E. Mazzetto, Cardanol-Based Heterocycles: Synthesis and Applications, in: Cashew Nut Shell Liquid, Springer International Publishing, 2017, pp. 39–56.
[25] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman, P. Dubois, J. Mater. Chem. A 11 (2015) 6012–6018.
[26] L. Puchot, P. Verge, T. Fouquet, C. Vancaeyzeele, F. Vidal, Y. Habibi, Green Chem. 11 (2016) 3346–3353.
[27] S. Rimdusit, P. Kunopast, I. Dueramae, Polym. Eng. Sci. 51 (2011) 1797–1807.

[28] Alhassan S, Schiraldi D, Qutubuddin S, Agag T, Ishida H. in Handbook of Benzoxazine Resins, ed. Ishida H, Agag T. Elsevier, Amsterdam, 2011, 309–318.
[29] C. Jubsilp, T. Takeichi, S. Rimdusit, J. Appl. Polym. Sci. 104 (2007) 2928–2938.
[30] K. Hemvichian, H. Ishida, Polymer 43 (2002) 4391–4402.