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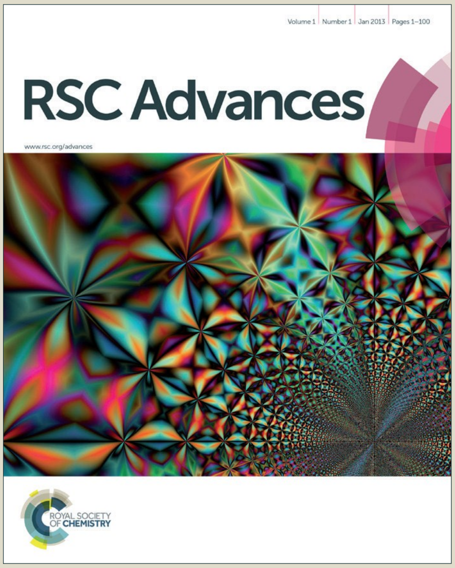

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Preparation and characterization of novel multi-branched polymers in situ cured from benzoxazine/epoxy resin/primary amines blends

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Abstract: High performance polymers with multi-branched structures were prepared in situ from ddm-based benzoxazine (M), cycloaliphatic epoxy resin (T) and diaminodiphenylmethane (ddm) or hexamethylenediamine (6a) *via* controlling the curing reaction sequence of the system. The curing behavior, cross-linked structures and properties of the system were investigated by Differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), Dynamic mechanical analysis (DMA) and mechanical properties test, respectively. The results suggest that the reaction between T and ddm or 6a easily processed than that of M and ddm or 6a, and the multi-branched polymers can be formed in situ in ternary system based on M, T and ddm or 6a. The heat resistance and mechanical properties of the cured resins with multi-branched structures were greatly improved compared with the polybenzoxazine or poly-benzoxazine/epoxy resin systems. The obtained results provide a new approach to control the chemical cross-linked structures and properties of polybenzoxazines.

Key words: benzoxazine, blends, multi-branched polymers, high performance

Introduction

Polybenzoxazines exhibit various attractive properties such as considerable molecular design flexibility[1-9], excellent heat resistance and mechanical properties[10-16], lower water absorption[17], no release of byproducts[10] and near zero volumetric shrinkage during the curing reaction[18,19]. However, the crosslink densities of the polybenzoxazine are relatively low due to the nature of benzoxazine chemistry. It has been reported that the copolymerization of benzoxazines and epoxy resins was an effective method to improve the properties of the polybenzoxazines[20-23]. This is because the phenolic hydroxyl group from the ring opening polymerization of benzoxazine (PHB) can react with the epoxy resin at elevated temperature to generate the additional crosslinking points. The increase of crosslink densities can enhance the

Tgs and flexural properties of the 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. Thus, in order to meet the requirement of the processing, it needs to add some suitable catalysts to lower the curing temperature and decrease the curing time of the resin. However, the catalytic effect of the catalysts on benzoxazine and epoxy resins is often different[24,25]. Consequently, the curing reaction sequence of the blend system could be changed by choosing different catalysts. The chemical cross-linked structures, aggregation structures and properties of resulted polymers may generate corresponding changes. Thus, the method of regulating the sequence of curing reactions is meaningful for controlling the polymer structures and properties. Our group[26,27] has prepared a novel benzoxazine/epoxy resin blend with multiphase structures by using imidazole as the catalyst to control the curing reaction sequence of the system. The result shown that the toughness and thermal properties of the novel blend were greatly improved compared with the polybenzoxazine or poly-benzoxazine/epoxy resin systems. However, the method of regulating curing reaction of benzoxazine/epoxy resin to control the chemical cross-linked structures and properties of the polymers has not been reported before.

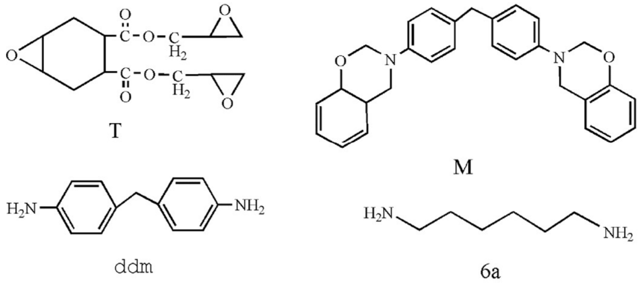
It is an effective method to introduce the branched polymers into the thermosetting resins to improve their properties. This method can enhance the impact toughness of the materials notably without sacrificing their heat resistance. Si et al.[28] have used the hyper-branched poly (resorcinol borate) to modify the benzoxazine resin and the impact strength was improved significantly. Boogh et al.[29] have used the hyper-branched polymers to improve the toughness of bisphenol F epoxy resin, where the critical strain energy release rate and the stress intensity factor were increased by a factor of 6 and 2.5, respectively. Thus, it is reasonable to suppose that the properties of poly-benzoxazine/epoxy resin blend system could be increased significantly by introducing the branched polymers into the cross-linked networks in situ through controlling the curing reaction sequence of the system.

In this paper, two multi-branched polymers were prepared in situ from the ternary system based on diamine-based benzoxazine (M), cycloaliphatic epoxy resin (T) with two different chemical reactivity epoxy groups (cycloaliphatic type epoxy group and diglycidyl ether type epoxy group) and diaminodiphenylmethane (ddm) or hexamethylenediamine (6a) through controlling the curing reaction sequence of the system. The curing behavior, cross-linked structures and properties of the systems were investigated by DSC, FTIR, DMA and mechanical properties test, respectively.

2. Experimental section

Materials

Cycloaliphatic epoxy resin (TDE-85, defined as T, the epoxy value of T is 0.85mol/100g) was purchased from Hubei Prosperity Galaxy Chemical Co., Ltd (China); diaminodiphenylmethane (ddm), hexamethylenediamine (6a) and Dimethyl formamide (DMF), with purities great than 99%, were purchased from Chengdu Kelong Chemical Regents (China). All regents and solutions were used as received. Phenol-diaminodiphenylmethane benzoxazine (M) was synthesized according to the procedures describe earlier[30]. The chemical structures of T, M, ddm and 6a are shown in scheme 1, respectively.



Scheme 1 The chemical structures of T, M, ddm and 6a

Preparation of the blends and their copolymers:

M was melted in a glass container at 110 °C, and then T was added and stirred for 15 min. The mole ratio of M to T is 1:1 (defined as MT). After that, ddm or 6a with 10% mol of the epoxy group was added and stirred for 1 min (defined as MT-ddm and MT-6a, respectively.). The blends were poured into a preheated metal mold and a cure profile (140°C/2h, 160°C/2h, 180°C/2h, 200°C/2h and 220°C/1h) was applied to get the PMT, PMT-ddm and PMT-6a.

The films of the mixtures were prepared through solution-casting and evaporation. The procedure was as follows. The resin was dissolved in DMF as a 20%wt solution, and then the solution was cast onto glass plates and dried at 110 °C for 20min to remove the solvent. Finally, the samples were put in an air circulating oven and a cure profile (140°C/2h, 160°C/2h, 180°C/2h, 200°C/2h and 220°C/1h) was applied to get the PMT, PMT-ddm and PMT-6a. The thickness of the membranes was about 100μm.

Characterization

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q20 using nitrogen purge and an empty aluminum pan as a reference. For the non-isothermal tests, the heating rate was 10 ^{o}C/min.

Fourier transform infrared (FTIR) spectroscopy was obtained on a Nicolet Magna 650 instrument. The range was 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were prepared by KBr pellets.

Heat resistant properties were measured with a dynamic mechanical thermal analyzer (DMA) (TA DMA Q800). Specimens with dimensions 30mm long, 10 mm wide and about 100μm thick were tested with stretching mode. The thermal transitions were studied from 35 to 250 °C at a heating rate of 5 °C/min and at a fixed frequency of 1 Hz.

Tensile properties of the cured resin were performed using a KQL KD-5 testing machine according to GB/T1040-2006. The dimension of sample was 30mm in long, 10mm in wide and around 100μm thick. Five specimens were tested to obtain an average.

Un-notched charpy impacted strength tests were carried out using a pendulum-type testing machine (XJJD-5, Jinjian, China) in accordance with GB/T2571-1995. The dimension of sample was 80mm in long, 10mm in wide and 4mm in thick. Five specimens were tested to obtain an average.

Results and discussion

Curing behavior

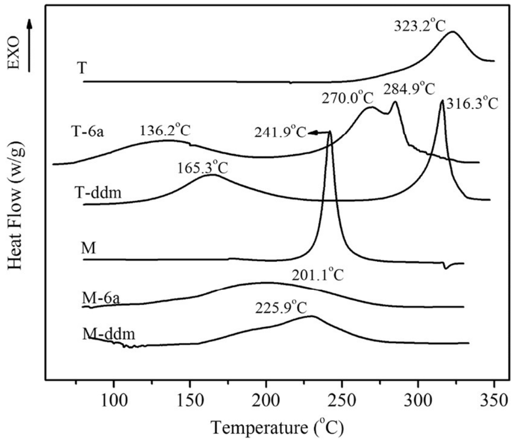


Figure 1 The DSC curves of M, M-ddm, M-6a, T, T-ddm and T-6a

Both benzoxazine and epoxy can react with ddm or 6a, but the catalytic effect of ddm or 6a on the reaction of M or T is different. In order to investigate the reaction reactivity of M or T with ddm or 6a, the curing behavior of M-ddm, T-ddm, M-6a and T-6a was studied by non-isothermal DSC and the results are shown in Figure 1. The DSC curves of M and T are also taken for comparison. M shows a typical polymerization exothermal peak centered at 241.9 °C and the exothermic peak is shift to 225.9 °C and 201.1 °C after the addition of ddm or 6a, respectively. It means that both ddm and 6a can promote the polymerization of benzoxazine and the results are consistence with the previous report[31]. The DSC curve of T shows an exothermal peak centered at 323.2 °C, however, two distinctively exothermal peaks (centered at 165.3 °C and 316.3°C, respectively) and three exothermic peaks (centered at 136.2 °C, 270.0 °C, and 284.9°C, respectively) were observed in T by adding ddm and 6a as curing agents, respectively. According to the previous studies, the exothermic peak of T-ddm or T-6a at lower temperature is the reaction between epoxy groups and ddm or 6a, respectively, and the peaks at higher temperature are attributed to the reaction between epoxy groups and alcohol hydroxyl groups[24,32]. Moreover, the difference between T-ddm and T-6a in the DSC curves at higher temperature may be attributed to the different catalytic effect of the hydroxyl group on cycloaliphatic epoxy groups and diglycidyl ether type epoxy groups. On the basis of the experimental facts above, we find that the curing reaction of T-ddm (or T-6a) can occur at a relatively lower temperature when compared with M-ddm (or M-6a). The result suggests that the catalyzing effect of ddm (or 6a) on T is more significant than that on M.

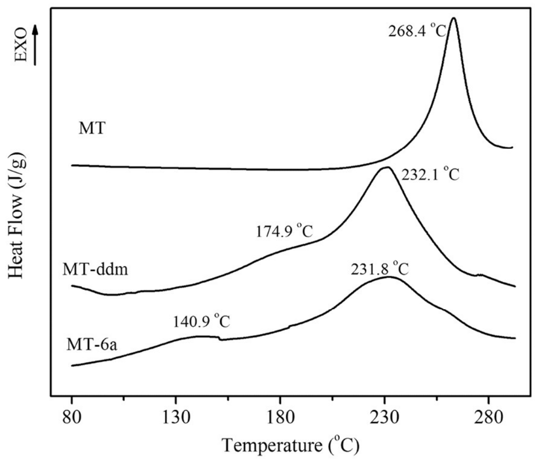


Figure 2 The DSC curves of MT, MT-ddm and MT-6a

To further study the curing reaction of the ternary system based on M, T and ddm or 6a, the curing behavior of MT-ddm and MT-6a were investigated by non-isothermal DSC, and the results are shown in Figure 2. Two exothermic peaks centered at 174.9 ^{o}C，232.1 ^{o}C and 140.9 ^{o}C，231.8 ^{o}C for MT-ddm and MT-6a can be observed, respectively. According to DSC results above, the exothermic peak at lower temperature is the curing reaction of T-ddm or T-6a, respectively, and the exothermic peak at higher temperature is mainly attributed to the polymerization of M and copolymerization between the phenolic hydroxyl group from ring opening polymerization of benzoxazine (PHB) and the remnant epoxy groups. To better understand the curing reaction of M, T and primary amines at each curing stage, the curing behavior of the blends after each curing stage is also investigated by non-isothermal DSC. MT-6a is taken as an example and the results are shown in Figure 3. As can be seen, the peak at lower temperature on the DSC curve disappeared completely and the peak at higher temperature almost no change can be observed after the sample cured at 140^{o}C/2h compared with that of uncured MT-6a. This illustrate that the copolymerization between epoxy group and 6a occur at the present condition, while the ring opening polymerization of benzoxazine and copolymerization between

PHB and epoxy groups can barely react at 140^{o}C. With increasing the curing temperature, the peak at higher temperature became smaller until totally disappeared after cured at 220^{o}C for 2h. It means that the polymerization of M and copolymerization between PHB and epoxy groups start and end at predetermined curing profile. These experiment facts suggest that the curing reactions between T and ddm or 6a occurred before the polymerization of M and copolymerization between PHB and epoxy groups in the MT-ddm or MT-6a, respectively. The results are consistent with the results in figure 1 and they will be further confirmed by the results of FTIR spectra in section 3.2.

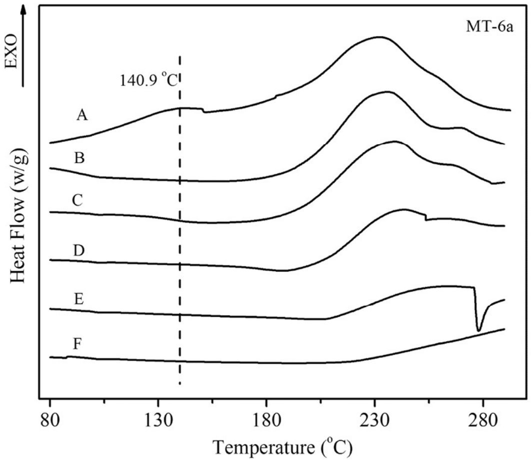


Figure 3 The DSC curves of MT-6a after each curing stage (A, uncured blend; B, 140℃/2h; C, 140℃/2h, 160℃/2h; D, 140℃/2h, 160℃/2h, 180℃/2h; E, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h; F, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h, 220℃/2h).

Cross-linked structures and curing mechanism

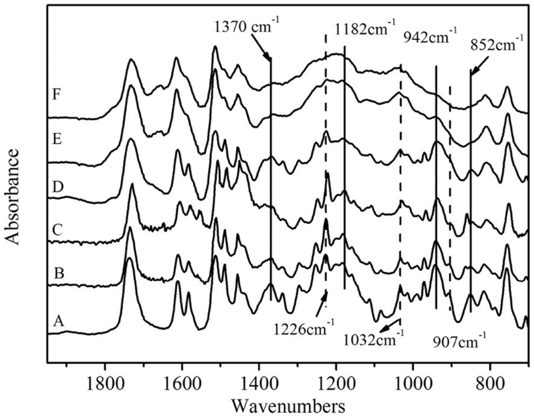


Figure 4 The FTIR spectra of MT cured at different stages (A, uncured blend; B, 140℃/2h; C, 140℃/2h, 160℃/2h; D, 140℃/2h, 160℃/2h, 180℃/2h; E, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h; F, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h, 220℃/2h).

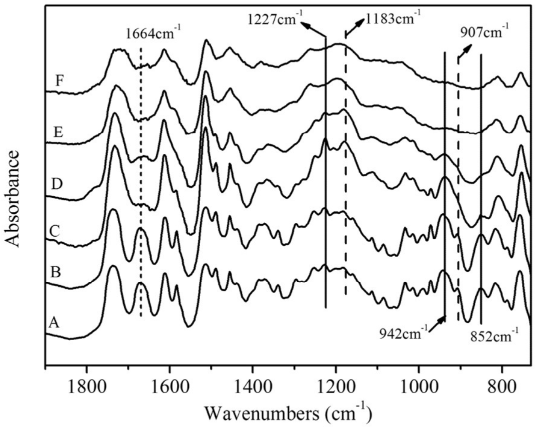


Figure 5 The FTIR spectra of MT-ddm cured at different stages (A, uncured blend; B, 140℃/2h; C, 140℃/2h, 160℃/2h; D, 140℃/2h, 160℃/2h, 180℃/2h; E, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h; F, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h, 220℃/2h).

To make clear the curing mechanism of MT, MT-ddm and MT-6a, the chemical structures of the blends cured at different stages were investigated by FTIR analysis. As seen in Figure 3, Figure 4 and Figure 5, the bands at 852 cm^{-1} for the cycloaliphatic type epoxy group of T, at 907 cm^{-1} for the diglycidyl ether type epoxy group of T, at 942 cm^{-1} for oxazine ring, at 1032 cm^{-1}and 1226 cm^{-1} for C-O-C stretching mode of oxazine ring and at 1182 cm^{-1} and 1370 cm^{-1} for C-N-C stretching mode of oxazine ring were observed clearly in these Figures.

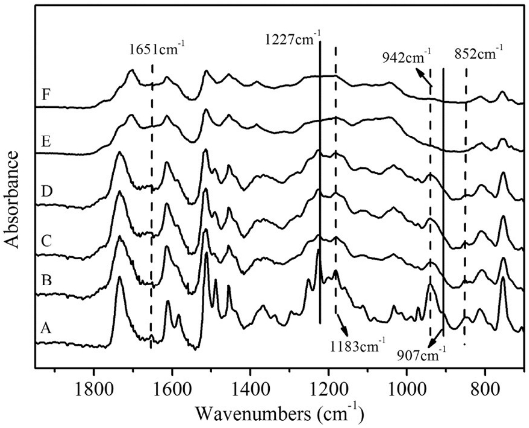
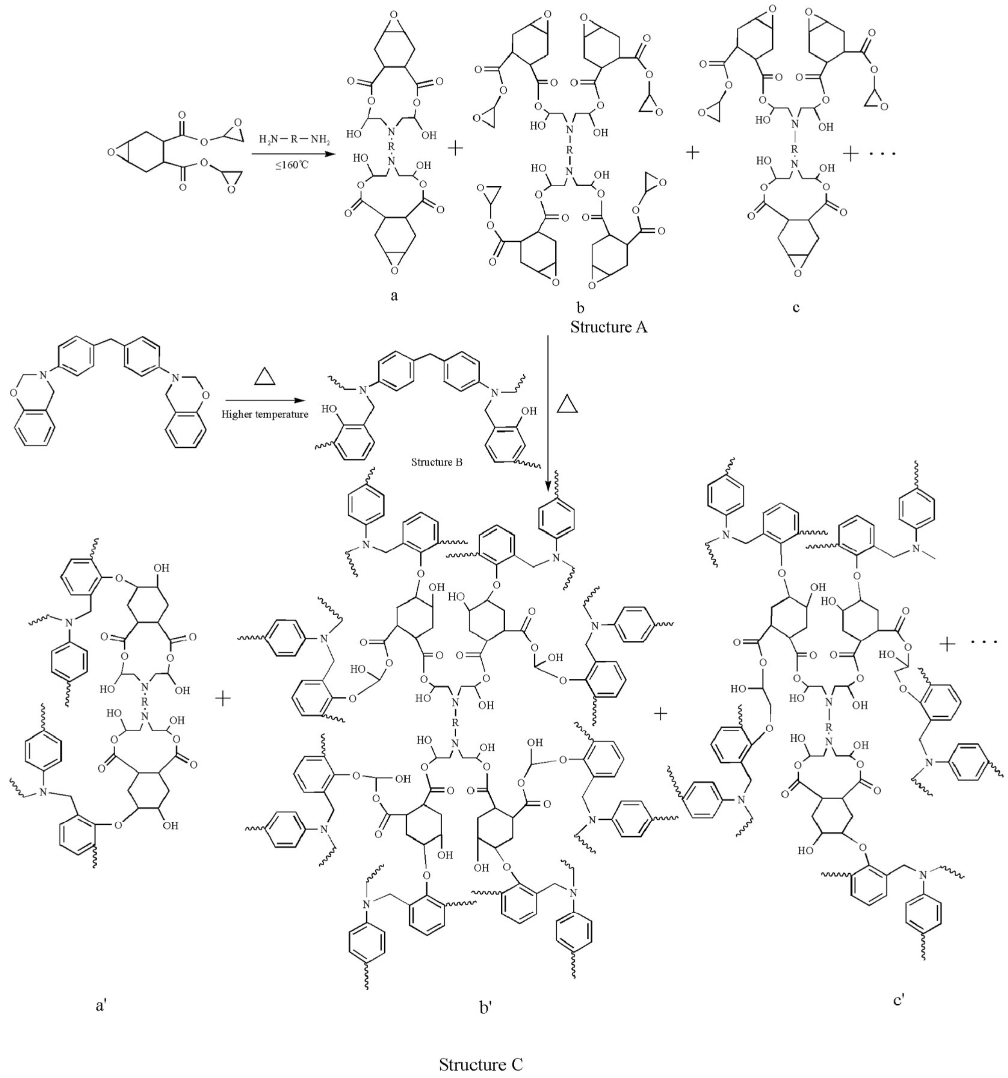


Figure 6 The FTIR spectra of MT-6a cured at different stages (A, uncured blend; B, 140℃/2h; C, 140℃/2h, 160℃/2h; D, 140℃/2h, 160℃/2h, 180℃/2h; E, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h; F, 140℃/2h, 160℃/2h, 180℃/2h, 200℃/2h, 220℃/2h).

For the MT, the intensity of bands at 852 cm^{-1}, 907 cm^{-1}, 942cm^{-1}, 1032 cm^{-1}, 1226 cm^{-1}, 1182 cm^{-1}and 1370 cm^{-1} had almost no variation after the sample cured at 140 ^{o}C for 2h, which means that M and T cannot react in this curing condition. With increasing the curing temperature, the intensity of above-mentioned bands decreases gradually until totally disappeared after cured at 220^{o}C for 2h. It means that M and T have reacted completely at the present curing profile.

Compare to the FTIR spectra of the MT, the band at 1664cm^{-1} for the N-H bending vibration of ddm can be observed clearly in uncured MT-ddm (Figure 5). With increasing the curing temperature, the intensity of band at 1664cm^{-1} gradually decreased and finally disappeared after curing at 160^{o}C for 2h. At this time, the band at 907 cm^{-1} for the diglycidyl ether type epoxy group of T decreased significantly, while the absorption of the cycloaliphatic type epoxy group of T at 852 cm^{-1} and oxazine ring at 942cm^{-1} had almost no change in this temperature. These results further support that the curing reaction between the diglycidyl ether type epoxy group of T and ddm occurred before polymerization of M and copolymerization between PHB and epoxy groups of T in the MT-ddm. With increasing the curing temperature, the bands at 852 cm^{-1}, 907cm^{-1}, 942cm^{-1}, 1032 cm^{-1} and 1182 cm^{-1} decreased generally. These results suggest that the polymerization of M and the copolymerization between PHB and the remnant epoxy groups occurred. After cured at 220^{o}C for 2h, all above-mentioned bands disappeared, which means the curing reactions in MT-ddm have finished. The curing reactions in the MT-6a are similar to that of MT-ddm, but the reaction between 6a and diglycidyl ether type epoxy group of T is more easily processed than that of ddm, because the band at 1652cm^{-1} for the N-H bending vibration of 6a disappeared completely after the sample cured at 140^{o}C for 2h (Figure 6). These experimental facts above illustrate that the curing reaction between the diglycidyl ether type epoxy group of T and primary amines (ddm or 6a) occurred before the polymerization of benzoxazine and the copolymerization between PHB and epoxy groups in the MT-ddm or MT-6a. And the results are consistent with the DSC analysis in section 3.1.

On the base of the DSC and FTIR results, the possible curing process and network structure is proposed and structural model as describe in scheme 2. First, the diglycidyl ether type epoxy groups of T reacted with ddm or 6a at relatively low curing temperature (160 ^{o}C or less) and primarily formed the corresponding multi-branched structures like structure A (a mixture of a, b and c et al. in scheme 2) according to the results of the DSC and FTIR analysis. With increasing the curing temperature, the ring opening polymerization of M occurred and gave the corresponding polymer having Mannich linkage structures (structure B in scheme 2). Finally, the copolymerization between the phenolic hydroxyl groups of structure B and the cycloaliphatic epoxy groups or remnant diglycidyl ether type epoxy groups of structure A occurred and in situ formed the multi-branched structures (structure C) in the cross-linked network of the PMT-ddm or PMT-6a, respectively.



Scheme 2 The cross-linked structures and curing mechanism of benzonxazine/epoxy/primary amine system

Thermal properties

There are a number of important material parameters can be derived from the dynamic thermal mechanical data. The storage modulus, E′, of a solid sample at room temperature provides a measure of material stiffness under tensile deformation, and the storage modulus of PM, PMT, PMT-ddm and PMT-6a as a function of temperature is shown in Figure 7 and the results are listed in Table 1. The initial storage modulus (at 50 ^{o}C) of PM and PMT are 3194 Mpa and 1878 MPa, respectively. It is evident that the addition of epoxy into benzoxazine has the effect of decreasing the initial storage modulus of the material over the pure polybenzoxazine. There are two main important factors that may be responsible for this phenomenon. First, a greater percentage of hydroxyl groups will have reacted with the epoxy and be unavailable for the intermolecular and intramolecular hydrogen bonding that was believed to increase stiffness in the glassy state. Additionally, the ether bonds in epoxy resin can also have effect of decreasing the materials stiffness in the glassy state. For the PMT-ddm and PMT-6a, the copolymerization of primary amines (ddm or 6a) and epoxy groups consumed the amount of epoxy groups of the system, and made the proportion of copolymerization between epoxy groups and PHB decrease. As a result, the amount of hydrogen bonding in PMT-ddm and PMT-6a increase, which led to their initial storage modulus higher than that of PMT and up to 2651 MPa and 2560 MPa, respectively.

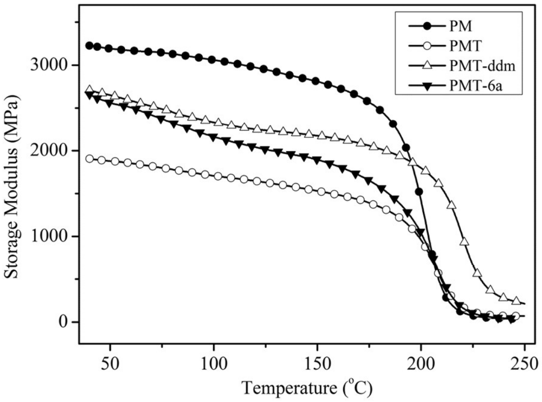


Figure 7 The Storage modulus-temperature curves of PM, PMT, PMT-ddm and PMT-6a

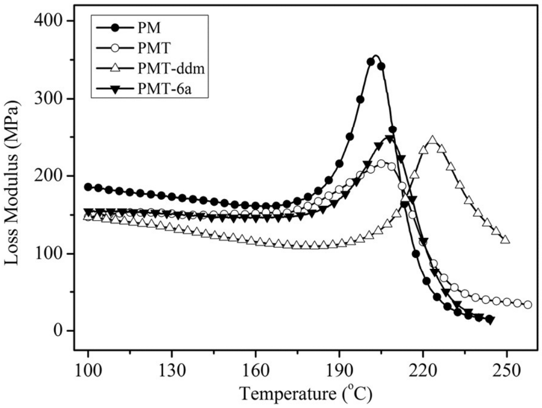


Figure 8 The Loss modulus-temperature curves of PM, PMT, PMT-ddm and PMT-6a

DMA also allows determination of Tg of each system and is detected in mechanical spectrum as the maximum of the loss modulus (E "). The plots of E " as a function of temperature for PM, PMT, PMT-ddm and PMT-6a are shown in Figure 8 and the results are listed in Table 1. The Tg determined from the peak of loss modulus is 202.8 ^{o}C and 206.2 ^{o}C for PM and PMT, respectively. The higher Tg of PMT than that of PM has been explained by the increasing of crosslink densities in the cured resins. The Tgs of PMT-ddm and PMT-6a are 223.4 ^{o}C and 207.4 ^{o}C, respectively, which are higher than that of PMT. The increase of Tg for PMT-ddm and PMT-6a also supported above conclusion that the amount of hydrogen bonds higher than that of PMT.

Mechanical properties

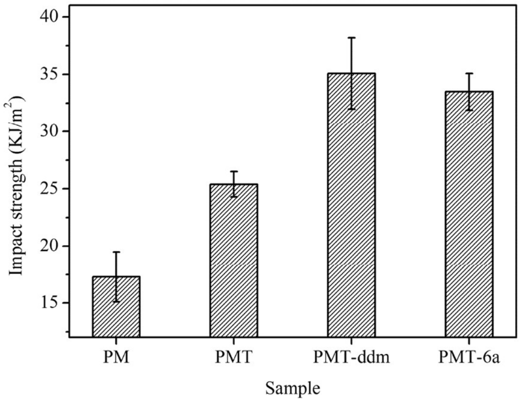


Figure 9 The impact strength properties of PM, PMT, PMT-ddm and PMT-6a

Table 1 The properties of cured resin

Sample	Tensile strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)	$E_{initial}$ at 50^{o}C (MPa)	Tg (E ") (^{o}C)	Tg (tanδ) (^{o}C)
PM	41.9±4.6	1.6	17.3±2.2	3193	202.8	215.6
PMT	55.4±7.1	4.3	25.4±1.1	1878	206.3	224.2
PMT-ddm	71.4±8.8	5.5	35.1±3.1	2651	223.4	242.9
PMT-6a	85.1±7.9	4.0	33.5±1.6	2560	207.4	220.4

The impact strengths of the PM, PMT, PMT-ddm and PMT-6a are shown in Figure 9 and the results are summarized in Table 1. The impact strength of PMT is 25.4 KJ/m^2, which is higher than that of PM (17.3 KJ/m^2). This means that the impact toughness of polybenzoxazines was improved by adding the epoxy resins into the benzoxazine. Surprisingly, the impact strength of the PMT-ddm and PMT-6a are 35.1 KJ/m^2 and 33.5KJ/m^2, respectively, which are far higher than that of PM and PMT. Their toughness properties were improved significantly without sacrificing its thermal resistance, which was probably caused by the formation of multi-branched structures in their polymers.

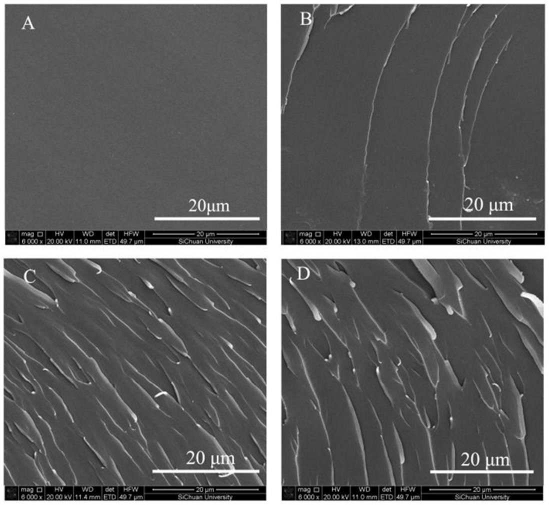


Figure 10 SEM micrographs of tensile fracture surfaces of PM (A), PMT (B), PMT-6a (C) and PMT-ddm (D)

The tensile properties of the cured films were also measured, and the values of tensile strength and elongation at break are summarized in Table 1. Typically, polybenzoxazines film (PM) shows a poor toughness which made the film easy to break at low elongation (1.6%). The tensile strength and elongation at break of PMT are 55.4 MPa and 4.3%, respectively, which are higher than that of PM. The increase in crosslink densities and the decrease in amount of hydrogen bonding by the addition of epoxy resin to benzoxazine would be expected to increase the tensile strength and elongation at break of the PMT. Unexpectedly, the tensile strength and elongation at break of the PMT-ddm and PMT-6a are 71.4 MPa, 5.5 mm and 85.1 MPa, 4.0mm, respectively. The high tensile properties of them are probably due to the formation of multi-branched structures in the cured resins. In order to explain the results mentioned above, SEM was used to detect the morphology of their tensile fracture. Figure 10 is the SEM of the fracture surface of PM, PMT, PMT-6a and PMT-ddm. The fracture surface of cured neat benzoxazine was clear and monotonous. It means that the crack propagation rate was very fast in PM. The wavy patterns surface was observed in PMT which indicates that the toughness of PM was improved by adding the epoxy resins into the system, In contrast, the rougher surfaces and more plastic deformation are observed in the fractographes of cured PMT-6a and PMT-ddm which can change the direction of crack propagation and absorb more energy during tensile failure. The results obtained indicate that the toughness of PM or PMT are improved significantly by the formation of multi-branched structures in their polymers. And these results are consistent with the results of mechanical properties tests.

Conclusion

The high performance polymer with multi-branched structures was prepared in situ from the ternary system based on diamine-based benzoxazine (M), cycloaliphatic epoxy resin (T) and diaminodiphenylmethane (ddm) or hexamethylenediamine (6a) through controlling the curing reaction sequence of the system. According to the results of DSC and FTIR, the reaction between epoxy resin and ddm or 6a easily processed than that of benzoxazine and ddm or 6a, and the PMT-ddm and PMT-6a is able to form the multi-branched polymers in situ during the curing process. Moreover, the heat resistance and mechanical properties of the cured resins with multi-branched structures were greatly improved compared with that of PM or PMT. The high properties of PMT-ddm and PMT-6a are attractive for further developments as a new class of thermosetting resin, and the obtained results provide new approaches to control the cross-linked structures and properties of polybenzoxazines, which has important theoretical significance and application value.

Acknowledgements

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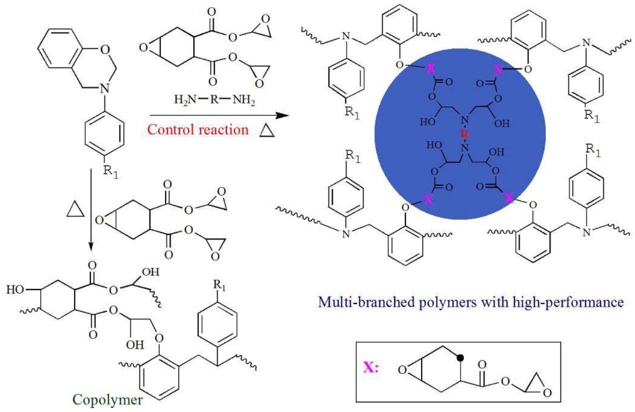

Graphical Abstract Text and Image: Novel high-performance multi-branched copolymers were prepared in *situ* from benzoxazine, epoxy resin and primary amines through controlling the curing reactions.