Study on an amine-containing benzoxazine: Homo- and copolymerization with epoxy resin

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Received 25 December 2015; accepted in revised form 23 February 2016

Abstract. An amine-containing benzoxazine (P-deta) based homopolymer and its epoxy (Ep) copolymers are investigated in this study. The structure of benzoxazine, prepared from phenol, diethylenetriamine and formalin, is confirmed by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR). The viscosity of P-deta is much lower than that of commercialized benzoxazine monomers. The curing profiles of P-deta with various Ep ratios are studied by deconvolution and the related mechanism is clarified. Epoxy will not increase the curing temperature of P-deta, instead, it helps P-deta overcome the conversion limitation and promotes the curing rate. The thermal and viscoelastic properties were determined and compared. The copolymer of P-deta/Ep = 50/50 (wt/wt) shows the highest glass transition temperature, higher than both individual homopolymers and other copolymers. Increasing benzoxazine fraction enhances modulus at room temperature but deteriorates the crosslink density. It can also enhance the char yield, but deteriorates the thermal stability of the copolymers.

Keywords: thermosetting resins, benzoxazine, epoxy resin, copolymerization

1. Introduction

Polybenzoxazines constitute a new generation of thermosets, which combine the thermal properties of phenolic resins with the mechanical properties and the molecular design flexibility of epoxy resin [1]. Moreover, they possess other features, such as low flammability, low water absorption, high chemical resistance and minimal shrinkage upon curing [2]. Therefore, they are considered as promising materials in IC packaging, aerospace engineering and HT-PCB industry and become one of the rare new polymers commercialized in the nearest 30 years [3].

However, several disadvantages appear in practical use. For instance, the solid phase of most benzoxazine (Bz) monomers and the high liquefying temperature hinder their handling [2, 4]. Adding reactive

diluents is one method to decrease the operation temperature, however, simultaneously sacrifice some properties, such as flexural strength and glass transition temperature (T_g) [5]. Another method is to develop more monomers with low liquefying temperature, but only very few related researches have been reported so far [4, 6].

Another drawback is the low crosslink density in consequence of hydrogen bonding constraint [7]. This can be addressed by copolymerization with epoxy resin (Ep), but will lead to higher curing temperature, known as Ep dilution effect [8]. Because epoxy group is inert to oxazine ring, introducing Ep dilutes the concentration of Bz, thus leads to higher Bz ring-opening temperature. Besides, copolymerization with Ep happens only when phenol generates after ring-

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opening of Bz. Similar phenomena were also found in a main-chain type Bz/Ep binary copolymer [9]. In addition, Bz fraction should be larger than 50 mol% in order to achieve copolymers with good quality. Generally, two methods can overcome the challenges. One is introducing a reactive promoter. Based on the cationic ring-opening mechanism [10], various promoters have been reported till now, among which, phenols, thiols, amines and imidazoles have attracted intensive attention since they are applied in epoxy curing as well. In 2000, phenolic resin was first selected due to its wide application in electronic packaging [11, 12]. The material properties were significantly enhanced although the dilution effect still can be observed. Besides, Chow *et al.* [13] had used a phenol monomer, 4,4'-thiodiphenol to study the curing behavior of a Bz/Ep/phenol ternary system. In 2005, Rao and Pathak [14] managed to use a phenalkamine to prevent the dilution effect through prior reaction between phenalkamine and Ep at room temperature before mixing with Bz. More recently, Grishchuk *et al.* [15] selected aliphatic, cycloaliphatic and aromatic amines to fabricate the Bz/Ep copolymers. They found that amines, which are both reactive to Bz and Ep, can efficiently promote the copolymerization. In addition, they also found that the promotion effect was influenced by both amine type and amount. The related mechanism was later clarified by Sun *et al.* [16], who purposed that the promotion effect is based on the basicity of amines. Moreover, Ambrožič *et al.* [17] used *o*-dianisidine to prepare novel Ep-Bz emulsions for water-based coatings to ensure a highly cross-linked structure. Meanwhile, Zhao *et al.* [18] and Wang *et al.* [19] studied a Bz/Ep/imidazole ternary system, through which the curing steps were optimized to motivate reaction-induced phase separation so that toughness can be enhanced. Ručigaj *et al.* [20] had implemented a comprehensive study on the curing Bz with many accelerators with different functional groups. Based on the conversion prediction, 4,4'-thiodiphenol is considered as the most effective accelerator among them. However, the solid forms of Bz and many additives generally require pretreatment before polymerization. Another method is to incorporate reactive groups, such as amine, onto the Bz structures. But, only few studies have been reported until now due to relatively tedious preparation procedure [21, 22].

In this research, we attempted to apply a low viscous amine-containing Bz to facilitate processing, promote polymerization as well as achieve homo- and copolymers with good performance. Meanwhile, we also tried to find its differences from a Bz/Ep/amine ternary system. The present study deals with the synthesis of the Bz, preparation of its homopolymer and copolymers, investigation of the curing behavior as well as evaluation of the thermal and mechanical properties.

2. Experimental

2.1. Materials

All reagents for synthesis are commercially available and used as received. Phenol (99%), bisphenol A (99%), aniline (99%) and deuterated chloroform (with 0.03 vol% of tetramethylsilane as reference) were purchased from Aladdin Reagent (Shanghai) Co. Ltd., Shanghai, China. Formaldehyde solution (40 wt%), paraformaldehyde (96%), sodium sulfate anhydrous (99%), diethylenetriamine (DETA) (99%) and potassium bromide (99.5%) were acquired from Sigma-Aldrich, St. Louis, U.S. Sodium carbonate anhydrous (99.9%) and dichloromethane (99.8%) were obtained from VWR, Radnor, U.S. A bifunctional diglycidyl ether bisphenol A (DGEBA) based epoxy resin (E51, epoxy equivalent weight: 185–208 g/ep.) was supported by Wuxi resin company, Wuxi, China.

2.2. Sample preparation methods

2.2.1. Synthesis of N,N-bis[2-(3,4-dihydro-2H-1,3-benzoxazin-3-yl)ethyl] amine (P-deta)

The synthesis method is a modification of preparing a main-chain type benzoxazine polymer reported elsewhere [23, 24]. Specifically, phenol (18.8 g, 0.2 mol) was dissolved in dichloromethane (50 mL) in a 250 mL flask before adding DETA (10.3 g, 0.1 mol). The mixture was then kept below 10 °C in an ice bath and stirred when formaldehyde solution was added dropwise. The molar ratio is maintained at phenol:DETA:formaldehyde = 2:1:4. The mixture reacted overnight and the solution gradually changed from colorless to yellow. Later on, the mixture was washed by 1 N sodium carbonate solution and deionized water, respectively. After being dried by sodium sulfate anhydrous, the obtained liquid was dried under vacuum at room temperature to evaporate solvent before obtaining a homogeneous yellow viscous liquid (Yield = 85%).

2.2.2. Synthesis of benzoxazine precursor (BA-a)

For comparison, N-phenyl bisphenol A based benzoxazine precursor (BA-a) was prepared according to the solventless method patented by Ishida [25]. (Yield > 90%)

2.2.3. Preparation of P-deta homopolymer and P-deta/Ep copolymers

P-deta was mixed with Ep under room temperature at ratios of P-deta:Ep = 100/0, 75/25, 50/50 and 25/75 (wt/wt) before intensively stirring for 5 min. After degassing at 50 °C for 10 min, all of them were stepwise cured at 125 °C/1 h, 150 °C/1 h and 180 °C/4 h.

2.3. Characterization methods

The Fourier transform infrared spectroscopy (FT-IR) spectra of P-deta were recorded by a Bruker TENSOR27 FT-IR spectrometer (Bruker Corporation, Karlsruhe, Germany) with 16 scans at a 4 cm⁻¹ resolution. It was also applied to monitor the curing process underwent isothermal treatment (100, 125, 150, 175, 200 °C). Potassium bromide (KBr) pellet technique was used.

The structures of the compounds were verified by nuclear magnetic resonance spectroscopy (NMR) using a Varian Mercury VX 300 NMR, Varian Inc., Palo Alto, U.S. The characterization was conducted at room temperature using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as internal standard.

The viscosity of the precursors was recorded by a rheometer, (AR2000ex, TA Instrument, New Castle, U.S.) under steady shear mode. The rotation frequency was set at 1 s⁻¹ with a temperature range from room temperature to above gel point and a heating rate of 2 °C/min. The polymerization processes of all samples were monitored by a differential scanning calorimeter (DSC), (Q200, TA Instrument, New Castle, U.S.). All samples with 3–5 mg were sealed in aluminum pans before measurement. The thermograms were obtained at a heating rate of 10 °C/min from room temperature to 300 °C under nitrogen atmosphere.

The viscoelastic properties of all samples were investigated by a dynamic mechanical analyzer (DMA), (Q800, TA Instrument, New Castle, U.S.). The specimen dimension was 10×70×2 mm. The measurement was performed in a three-point bending mode with 50 mm span length at a frequency of 1 Hz with

a strain value of 0.1% and a heating rate of 2 °C/min. The glass transition temperature (*T_g*) was determined by the peak temperature of loss factor (tan δ). The thermal stability and char yield are characterized through a thermogravimetric analyzer (TGA), (Q50, TA Instrument, New Castle, U.S.). The test was performed under nitrogen atmosphere at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterization of P-deta

The structure of P-deta was first studied by FT-IR, as shown in Figure 1. The reaction scheme is plotted in Figure 1 as well. The formation of oxazine ring was evidenced by the peak at 930 cm⁻¹ (1,2-substituted benzene with oxazine ring attaching), the sy4mmetric and asymmetric stretching of C–O–C at 1034 and 1226 cm⁻¹, and the peak at 1150 cm⁻¹ which indicates the formation of C–N–C bond. The peak at 1489 and 756 cm⁻¹ prove the presence of an ortho-substituted benzene ring. Since hydroxyl group is removed by base washing, the shoulder peak near 3300 cm⁻¹ is assigned to the heavily overlapped hydrogen bonded amino group. These results confirm the formation of the P-deta.

NMR was further applied to characterize the structures, the results of which are shown in Figure 2. Specifically, the characteristic proton resonances at 4.0 and 4.9 ppm are corresponding to the Ar–CH₂–N and N–CH₂–O structures of oxazine ring, respectively. The resonances at 6.8–7.2 ppm are assigned to the protons on aromatic rings. The peaks in the range of 3.7–3.9 ppm were assigned to Ar–CH₂–N and N–CH₂–N structures, which has been reported in other literatures as well [16, 23, 24]. A resonance chemical shift at 3.5 ppm confirms the formation of N–H. The aliphatic groups of amines are confirmed by the resonances at 2.7–2.9 ppm, respectively. The

Figure 1. FT-IR spectrum of P-deta

Figure 2. (a) ^1H -NMR and (b) ^{13}C -NMR results of P-deta

product was also characterized by ^{13}C -NMR (Figure 2b). The characteristic oxazine rings appear at 83 and 50 ppm. The peaks at 115–130 and 154 ppm indicate the phenyl carbons. The chemical shift at 158 ppm is assigned to the ring-opened Bz structures. The chemical shift at 76 ppm confirms the existence of triazine structure. The peaks between 50–60 ppm indicate various $\text{Ar}-\text{CH}_2-\text{N}$ and $\text{N}-\text{CH}_2-\text{N}$ structures, which is consistent with the ^1H -NMR results.

Before polymerization, the viscosity of P-deta and P-deta/Ep mixture was investigated (Figure 3). A typical benzoxazine monomer, BA-a, was used for reference. Comparing with BA-a, the viscosity of P-deta is very low ($<1\text{ Pa}\cdot\text{s}$) under room temperature. This makes it suitable for some specific processing methods, like resin transfer molding (RTM). The storage condition can significantly change the viscosity of P-deta. It can be seen that the viscosity of P-deta increased to above $2000\text{ Pa}\cdot\text{s}$ after being kept under room temperature for more than 1.5 month, which is due to the ring-opening of benzoxazine caused by amines. Therefore, low temperature storage is required for the resin. Here, the gel point is defined as the temperature when viscosity suddenly increases to above $100\text{ Pa}\cdot\text{s}$, and the processing window is de-

fined as the temperature range, within which the viscosity of the sample is lower than $100\text{ Pa}\cdot\text{s}$. The gel point of P-deta/Ep (50/50, wt/wt) mixture is at 150°C , while it is more than 200°C where BA-a reaches its gel point. The gel point of pure P-deta cannot be determined due to the extremely low viscosity when heated P-deta up to 100°C . The processing window of P-deta/Ep (50/50, wt/wt) mixture is larger than 125°C (R.T. to 150°C).

3.2. Polymerization of P-deta and P-deta/Ep mixtures

DSC and FT-IR were applied to investigate the polymerization of P-deta and P-deta/Ep mixtures of various ratios. Comparing with the reported mono-curing peak of BA-a [15], multi-curing peaks can be found in P-deta, which can be assigned to several different reactions. In fact, it becomes more complicated when Ep is introduced. In order to clarify the possible reaction of each peak, the curing profiles of P-deta and P-deta/Ep mixtures have been deconvoluted. The DSC profiles and peaks achieved by deconvolution are summarized in Figure 4. Specifically, three peaks appear during P-deta homopolymerization which, from low to high temperature, are related to amine catalyzed Bz ring-opening, Bz thermal-in-

Figure 3. (a) Processing window and (b) viscosity of P-deta, P-deta/Ep (50/50, wt/wt) and BA-a

Figure 4. DSC profiles (solid line) and deconvolution peaks (dash line) of P-deta with different amount of Ep. (P-deta/Ep = (a) 100/0, (b) 75/25, (c) 50/50 and (d) 25/75, wt/wt). Peak assignment: (□) amine-catalyzed Bz ring-opening; (■) amine-Ep ring-opening; (○) Bz ring-opening; (△) intermediate conversion; (▼) hydroxyl-Ep ring-opening.

duced polymerization and conversion of amine-Bz intermediate to final structure [16], respectively. It is worth to note that, intermediate conversion can happen at the temperature either higher [16] or lower [15] than the origin, it is higher than Bz polymerization in this case. When mixed with Ep at P-deta/Ep = 75/25 (wt/wt), one additional peak can be found at low temperature range. It can be assigned to the reaction between amine and Ep, which takes place at relatively low temperature. This reaction can also be proved by the shift of onset temperature from 90 °C to 60–70 °C as long as Ep was added. Further increasing Ep amount to 50 wt.% (Figure 4c) leads to an increase in intensity at 190 °C but a decrease around 240 °C. Although the peak at 190 °C is close to the second peak position in Figure 4b, it is impossible due to large consumption of amine during amine-Ep reaction. In fact, it is probably caused by Bz ring-opening, which is promoted by the hydroxyl group due to the same reaction [26]. The rest small amount of excess Ep can react with phenol (generated after Bz ring-opening) or hydroxyl group, which results in the third peak in Figure 4c. The intensity is obviously enhanced in Figure 4d due to the increase of Ep to 75 wt%. In addition, the last tiny peaks in both Figure 4c and Figure 4d may be as-

signed to the conversion of intermediate. Since the reactions between amine-Bz and amine-Ep are partially overlapped, it is possible that a small portion of amine reacts with Bz when simultaneously most of it reacts with Ep. It is worth to mention that, by prior reaction between Ep and amine (in Bz), the dilution effect caused by Ep can be eliminated, based on our study.

The possible reactions take place during the polymerization were further investigated through FT-IR, as shown in Figure 5. The samples are partially cured under different isothermal conditions. Concerning P-deta (Figure 5a and 5b), the peak at 930 cm^{-1} , which represents the out-of-plane bending of benzene ring with oxazine ring being attached, dramatically decreases after heating at 125 °C for 1 hour and almost disappeared after heating at 150 °C. The decrease of overlapped peaks near 3300 cm^{-1} proved the amine-promoted ring-opening process. The intensity increase around 3450 cm^{-1} is attributed to the hydroxyl group, which formed after Bz ring-opening. Moreover, the intensity decrease at 1489 cm^{-1} , which represents the consumption of Bz. However, no observable intensity change can be found in BA-a even heated at 175 °C for 1 hour (Figure 5c, 942 cm^{-1}). It is until 200 °C that most of the BA-a precursors un-

Figure 5. FT-IR spectra of (a) and (b) P-deta, (c) BA-a and (d) and (e) P-deta/Ep = 50/50 (wt/wt) after isothermally cured at 100, 125, 150, 175 and 200 °C for 1 hour, respectively

dergo ring-opening polymerization. The curing process changes when Ep was introduced. The FT-IR results of P-deta/Ep = 50/50 (wt/wt) are summarized in Figure 5d. Comparing with P-deta precursor, a conspicuous peak at 3450 cm^{-1} can be found even heated at 100 °C for 1 hour, which is attributed to the hydroxyl groups generated after the reaction between amine and Ep. This is also proved by the decrease at 920 cm^{-1} in Figure 5e, which represents the epoxy ring. Besides, the peaks at 1489 cm^{-1} (1,2-substituted benzene ring) and 930 cm^{-1} (out-of-plane benzene ring with oxazine attaching) disappear at 150 °C, which confirmed the ring-opening of oxazine as well. These results are consistent with the DSC peaks observed in Figure 4.

The partially cured polymers under isothermal conditions are examined by DSC as well (Figure 6). The degree of conversion (α) in Figure 6d is calculated through Equation (1), based on the DSC thermograms:

$$\alpha [\%] = \left(1 - \frac{\Delta H_p}{\Delta H_0} \right) \cdot 100 \quad (1)$$

where ΔH_p is the curing enthalpy change of the partially cured samples and ΔH_0 is the curing enthalpy change of the original samples. Initially, the conversion rate of P-deta is much faster than BA-a, due to the amine-promoted ring-opening reaction. However, the degree of conversion reached a limit and no further progress was observed. Comparing with Fig-

Figure 6. DSC thermograms of (a) P-deta, (b) BA-a, (c) P-deta/Ep = 50/50 (wt/wt) and (d) conversion based on enthalpy change after isothermal curing at 100, 125, 150, 175 and 200 °C for 1 hour, respectively

ure 4, the residue peak in Figure 6a at above 150 °C is assigned to intermediate conversion. It cannot be the Bz ring-opening, otherwise, the conversion (Figure 6d) will be more like an autocatalytic process, similar to BA-a, rather than reaching a limit. Copolymerization of Ep and P-deta changes the reactions, thus conversion will not be confined by the equilibrium, as shown in Figure 6c and 6d. A mixture of P-deta/Ep = 50/50 (wt/wt) can almost be thoroughly cured after heating at 200 °C for 1 hour. Besides, the conversion rate of P-deta/Ep mixture is higher than P-deta and BA-a. This is attributed to the hydroxyl group generated from the reaction between epoxide and amine, which can promote the ring-opening polymerization of Bz [26].

3.3. Thermal and viscoelastic properties of P-deta and its epoxy alloy

The storage moduli and loss factors of all samples are measured through DMA, and the results are shown in Figure 7. The important data is summarized in Table 1. It is worth noting that, a P-deta/Ep = 25/75 (wt/wt) copolymer, beyond the mixing limit (Bz > 50%) of general Bz/Ep binary system [8], had been successfully prepared with good mechanical properties. This is due to the reaction between amine in P-deta and Ep. Besides, amine can increase the

Figure 7. Storage moduli (E') and mechanical loss factors ($\tan \delta$) as a function of temperature for P-deta/Ep mixtures at various ratios

hydrogen bond density, thus enhancing the storage modulus at room temperature of P-deta homopolymer (4.8 GPa). The modulus of copolymers decreases with the increase of Ep fraction. This is due to the concentration of hydrogen bond density of Bz decreasing when Ep is incorporated. Moreover, since glass state stiffness is related to the resistance of molecular segments motion, the DGEBA structure appears less able to store elastic energy, which leads to a lower modulus than Bz [9]. The peak temperature of loss factor is applied to determine the T_g of the samples. Unlike modulus, the T_g of P-deta homopolymer is relatively low (100 °C). The highest T_g at 147 °C

is obtained in a P-deta/Ep (50/50, wt/wt) copolymer, which is 47 °C higher than P-deta homopolymer and 17 °C higher than the reported Ep (cured by DETA) [15]. It is interesting to find that the result is quite different from the Bz/Ep/amine ternary copolymers, the T_g of which is between the Bz and Ep homopolymers or worse [15, 27]. In fact, it is more close to Bz/Ep binary copolymers, which has a T_g higher than both homopolymers at certain mixing ratios [10]. Specifically, at low Ep fraction, the polymer network is enhanced by Ep-amine and Ep-hydroxyl reactions. When Ep amount is in excess, it acts as a plasticizer to deteriorate the mechanical properties. The mono-peak of $\tan\delta$ showed that no apparent phase separation can be found, which is consistent with other Bz/Ep binary systems [8]. The height and width of $\tan\delta$ are summarized in Table 1. The 50/50 copolymer shows the lowest $\tan\delta$ height, which indicates strongest segmental restriction. The FWHM (full width at half mount) of $\tan\delta$ implies the variety of structure species. Although no certain trend of FWHM can be observed among all samples, the FWHM of 50/50 sample shows the largest FWHM value (43 °C), which indicates the most various structures in the polymer. Based on the statistical theory on rubbery elasticity [28], the crosslink density can be estimated through Equation (2) by obtaining the elastic modulus in rubbery state:

$$\nu = \frac{E'_R}{3\phi RT} \quad (2)$$

where ν is the crosslink density, R is the gas constant and ϕ equals to 1 for ideal rubber. In this experiment, the elastic modulus E'_R is selected at the absolute temperature T equals to $T_g + 30$ °C. It is worth to note that, this equation is only valid in light crosslink polymers since high crosslink density results in a failure of Gaussian chain assumption [29, 30]. Therefore, an empirical Nielsen equation (Equation (3)),

Figure 8. TGA thermograms of P-deta and P-deta/Ep polymers

which shows better results among high crosslink structures, is also selected here [31]:

$$\lg\left(\frac{E'_R}{3}\right) = 7 + 293\nu \quad (3)$$

The calculated results based on both methods are concluded in Table 1. Specifically, the crosslink density of P-deta is very low, which is 1790 and 2660 mol/m³ based on different calculation methods. Increasing Ep fraction was found to enhance the crosslink density of the copolymers, which is consistent with the trend of Bz/Ep binary copolymers [8] but different from some Bz/Ep/amine ternary copolymers [14, 27]. The thermal stability of all samples was studied by TGA (Figure 8) and the results have been summarized in Table 1. The decomposition temperature of P-deta homopolymer is similar to MCBP BA-tepa [24] and P-ad6 [32]. The similar aliphatic diamine structure is probably the dominant cause of the initial decomposition. Incorporation of Ep enhances the thermal stability of the copolymers. This can be explained by the increase in crosslink density when increasing the Ep fraction. Meanwhile, the residual weight after heating at 800 °C becomes lower when less Bz is introduced into the copolymers. The decrease in char yield percentage is quite consistent

Table 1. Viscoelastic and thermal properties of P-deta and P-deta/Ep polymers

Sample (P-deta/Ep, wt/wt)	T_g [°C] ^a	E' [MPa]		Crosslink density [·10 ³ mol/m ³]		Loss factor		$T_{5\%}$ [°C] ^b	Char yield [%] ^c
		RT	$T_g + 30$ °C	Rubber elasticity	Nielsen's equation	FWHM [°C]	Height		
100/0	100	4785	18	1.79	2.66	37	0.93	251	33
75/25	128	3876	16	1.49	2.48	30	0.82	263	27
50/50	147	3928	26	2.32	3.20	43	0.43	299	20
25/75	137	3220	29	2.64	3.36	26	0.55	339	12
0/100 ^d	130 ^e	2690 ^e	33 ^e	3.06 ^e	3.55	–	–	350	9

^apeak temperature of $\tan\delta$; ^btemperature at which 5% weight loss is monitored; ^cweight residue at 800 °C; ^dEp was cured by DETA; ^edata obtained from reference [15].

with the decrease in benzoxazine fraction. Apparently, rather than crosslink density, Bz fraction is more dominant to determine the char yield of the copolymers.

In summary, comparing with a Bz monomer (P-ad6 in [32]) and a main-chain type Bz polymer (BA-tepa in [24]) of similar molecular structures, P-deta homopolymer exhibits higher modulus under room temperature than both while thermal stability and char yield in-between. P-deta/Ep copolymers inherits the high modulus from P-deta homopolymer. Meanwhile, they also show comparable properties with other Bz/Ep binary copolymers [8] and Bz/Ep/amine tertiary copolymers [14, 15] in T_g , crosslink density and char yield. The thermal stability is worse when P-deta fraction in the copolymers is high.

4. Conclusions

This study focuses on an amine-containing Bz prepared from phenol, diethylenetriamine and formaldehyde, its homopolymerization and copolymerization with Ep. The viscosity of P-deta is lower than 1 Pa·s, which is much lower than BA-a and suitable for low temperature RTM. Polymerization of P-deta undergoes amine-promoted ring-opening, Bz ring-opening and intermediate conversion. However, the conversion is confined to lower than 40%, based on enthalpy calculation. Mixing Ep-with P-deta changes reaction pathways. The copolymerization can be sufficiently proceeded with a faster conversion than P-deta and BA-a. The limit of Bz fraction (>50%) and the dilution effect of EP in general Bz/Ep binary system are eliminated in this study. The viscoelastic properties of the homo- and copolymers are also studied. At a 50/50 (wt/wt) ratio, the copolymer exhibits higher T_g than both P-deta homopolymer and Ep cured by DETA. This is quite different from those ternary systems, in which amines were introduced as additives. Accompanied with increasing Ep fraction, the crosslink density is enhanced, while the moduli at room temperature is decreased. Concerning the thermal properties, incorporating more Ep improves the thermal stability of the copolymer, although the char yield becomes less. In conclusion, P-deta homopolymer and P-deta/Ep copolymers show comparable properties with many other reported Bz polymer and copolymer systems, while the liquid phase and low viscosity make it more attractive than those solid Bz in application.

Acknowledgements

This research has been supported by the Nansha Innovation Project (2013Z01 3) and Nansha International Cooperation Project (2014GJ01) of Nansha District, Guangzhou, China.

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