Curing behavior and kinetics of epoxy resins cured with liquid crystalline curing agent

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Abstract This article describes the synthesis of a liquid crystalline curing agent 4,4′-bis-(4-amine-butyloxy)-biphenyl (BABB), and its application as a curing agent for the epoxy resin (DGEBA) in comparison with normal curing agent, 4,4′-diaminobiphenyl (DABP). BABB was investigated with polarized optical microscopy, differential scanning calorimetry, and small-angle X-ray scatting, and the results showed that BABB displayed smectic liquid crystalline phase. The curing behaviors of DGEBA cured with BABB and DABP were studied by using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and dynamic mechanical analysis (DMA). The results indicated that BABB showed a higher chemical reactivity than DABP. The kinetics was studied under isothermal conditions using an isoconversional method, and the isothermal DSC data can be fitted reasonably by an autocatalytic curing model. The nematic droplet texture was observed for the resulting polymer network of DGEBA/BABB system, while the DGEBA/DABP system showed an isotropic state. The storage modulus of DGEBA/BABB system was enhanced in comparison with DGEBA/DABP system because of the formation of LC phase, whereas the glass transition temperatures decreased because of the introduction of flexible spacer group.

Keywords Epoxy resins · Liquid crystalline curing agent · Kinetics · Mechanical and thermal properties

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Introduction

Epoxy resins are one of the most important thermosetting engineering plastics and have been widely used as laminated circuit board, carbon fiber composites, electronic component encapsulations, and adhesives because of their characteristic properties, such as strong bonding strength, low shrinkage, high insulation resistance, and so forth [1–3]. In comparison with ordinary epoxies, liquid crystalline thermosets (LCTS) display a number of superior properties, such as greater thermal stability, toughness, and lower thermal-expansion coefficient because of the formation of many LC domains in the cured networks. Over the past few decades, various LCTS have been synthesized, and their curing behaviors, thermal properties, and phase behaviors have also been studied by many research groups [4–7]. Most of these reports focused on the preparation and characterization of liquid crystalline epoxy resins (LCERs) with different mesogenic groups [8–12]. As is known that curing agents can influence the structure of the networks, the formation of LC phase in the networks can also be affected (even be determined) by the structure of the curing agents to crosslink the epoxy monomers. However, there are only a few reports concerning the importance of the curing agent [13–16], and the reports studying LCTS based on liquid crystalline curing agents (LCCA) are still fewer [17].

In this study, the synthesis of a liquid crystalline curing agent 4,4′-bis-(4-amine-butyloxy)biphenyl (BABB) bearing a biphenyl-type mesogenic group and its influence on the LC phase in the cured system are described. The curing behaviors of epoxy resin DGEBA with BABB were investigated compared to commercial curing agent 4,4′-diaminobiphenyl (DABP) system. Thermal kinetics of the system was analyzed based on the isoconversional

method and Kamal model. The detailed dynamic mechanical properties and the liquid crystalline transition of DGEBA systems cured with BABB and DABP are further discussed.

Experimental part

Materials

4,4′-Dihydroxybiphenol was purified by recrystallization from ethanol. 1,4-Dibromo butane and N,N-dimethyl-formamide (DMF) were freshly distilled before use. Ethyliene dichloride, potassium hydroxide, phthalimide, and hydrazine hydrate were used as received. Epoxy resin was a liquid diglycidyl ether of bisphenol A (DGEBA), $W_{ep} = 196$, and the curing agent 4,4′-diaminobiphenyl (DABP) was of an analytic grade.

Synthesis

The liquid crystalline curing agent 4,4′-bis-(4-amine-butyloxy)-biphenyl (BABB) was synthesized according to the previous study [18]. Yield = 42%; mp: 146.8 °C; ^{1}H NMR (D-DMSO; δ, ppm): 1.48 (m, 4H, –CH$_2$–), 1.82 (m, 4H, –CH$_2$–), 3.66 (t, 4H, –CH$_2$–), 4.05 (t, 4H, –CH$_2$–), 6.98 (d, 4H, aromatic), 7.56 (d, 4H, aromatic). IR (KBr; v, cm^{-1}): 3317 (–NH$_2$), 2941, 2866 (–CH$_2$), 1604, 1520 (–Ar–), 1250 (Ar–O–C), 824 (C–H). ELEM. ANAL. Calcd. For $C_{20}H_{28}N_2O_2$ (328.45) C, 73.14%; H, 8.59%; N, 8.53%; Found: C, 73.20%; H, 9.41%; N, 8.07%.

Curing of epoxy resins

The respective stoichiometric amounts of curing agents DABP and BABB were added into epoxy resin DGEBA and dispersed by ultrasonic wave cleaner in some acetone for 4 h at 25 °C. The solvent in the mixture of DGEBA/DABP and DGEBA/BABB was allowed to evaporate at room temperature. The DGEBA/BABB system were first procured at 110 °C for 1 h and then further cured at 140 °C for 4 h. The DGEBA/DABP systems were procured at 110 °C for 1 h and then cured at 160 °C for 4 h. The networks cured with both curing agents containing the same mesogenic units (Fig. 1) were obtained.
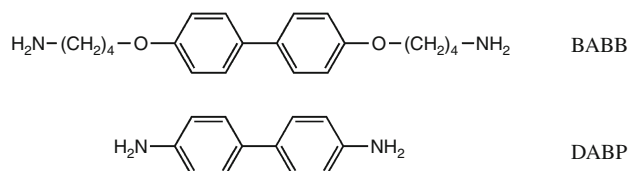

Fig. 1 Structures of curing agents BABB and DABP

Measurements

IR spectra were recorded on a Bio-Rad FTS-6000 Fourier transform infrared (FTIR) spectrometer. ^{1}H-NMR spectra were obtained with a UNITY Plus-400 (400 MHz) spectrometer with dimethyl sulfoxide-d$_6$ as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) were carried out on an Elementar Vario EL C, H, and N analyzer. Thermal kinetic studies were carried out on a NETZSCH DSC 200 F3 thermal analyzer with N$_2$ as a purge gas by isothermal and nonisothermal scanning. Small-angle X-ray scattering (SAXS) measurements were carried out on a Bruker Nanostar equipment with a 2D detector (Bruker Histar) and Cu K(radiation ($\lambda = 1.542$ Å) and were operated at 40 kV working voltage and 35 mA current. The textures of the LC phases were observed with an OLYMPUS BX51 polarized light microscope equipped with a Linkam THMSE600 hot stage. Dynamic mechanical analysis (DMA) of the cured system was performed with a dynamic mechanical thermal analyzer (NETZSCH DMA 200). The frequency and amplitude of the vibration were adjusted to 2.5 Hz and 7.5 μm, respectively. The heating rate was 3 °C min^{-1}, and the range of the measuring temperatures was −150 to 250 °C. The sample dimensions were approximately $4.0 \times 35 \times 0.5$ mm^3.

Results and discussion

Mesomorphic phase transition of BABB

To investigate the textures of BABB, DSC, and POM studies were carried out. Figure 2 shows the DSC curves of BABB with a scanning rate of 10 °C min^{-1}. It can be seen clearly that there are two phase transition peaks in both the heating and cooling curves. During the heating course, the first endothermic peak at 127.5 °C was associated with
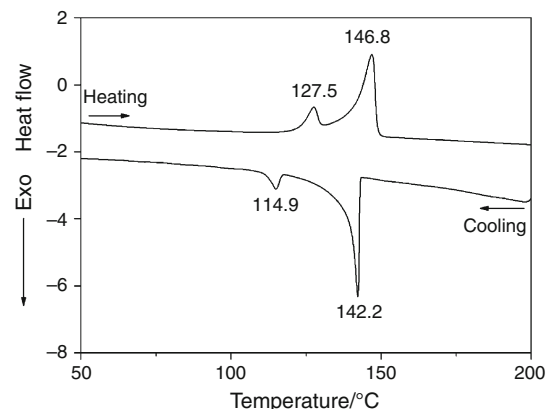

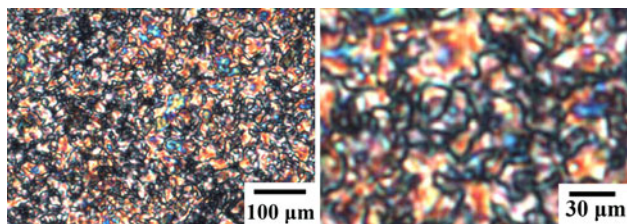**Fig. 2** DSC curves of BABB with a scanning rate of 10 °C min^{-1}

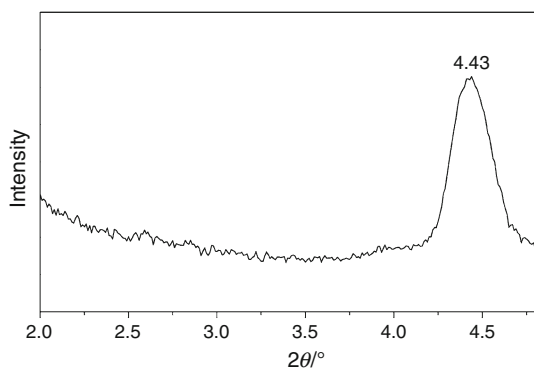Fig. 3 Polarized optical micrographs of BABB at 140 °C

Fig. 4 The SAXS pattern of BABB at 140 °C

the transition from crystallization to liquid crystalline phase which revealed schlieren textures of smectic phase (Fig. 3), when the temperature was heated above 146.8 °C, there was an isotropic transition for BABB from liquid crystalline phase. During the cooling course, when it was cooled below 140 °C from the anisotropic phase (about 142 °C), a clear smectic birefringent pattern of BABB can also be obtained. The SAXS pattern of BABB is shown in Fig. 4. The diffraction peak appearing at $2\theta = 4.43°$ at

140 °C corresponds to the layer spacing. The result reveals that BABB possesses a layered structure, which indicates the existence of a smectic structure.

Curing behaviors of DGEBA/BABB and DGEBA/DABP systems

The curing behaviors of DGEBA/BABB and DGEBA/DABP systems were investigated using dynamic DSC. The two systems were heated to 250 and 300 °C, respectively, with a series of scanning rates of 5, 10, 15, and 20 °C min⁻¹(Fig. 5). The data of curing reactions are listed in Table 1. It can be seen that the temperature of the peak position of the exotherm of DGEBA/BABB system was about 20 °C lower than DGEBA/DABP system, which indicated that BABB had a greater chemical reactivity. It is well known that the oxirane ring reacts with amine via the nucleophilic substitution reaction. Since the curing agent DABP is an aromatic amine, which can decrease the alkalinity of amine, DABP has a lower reactivity than the aliphatic amine BABB. Furthermore, the activation energy of the both curing system can be evaluated from the dynamic DSC data according to the Ozawa's study [19]. It can be seen (Table 1) that the LC system of BABB possesses a much higher E_a value than DABP system.

The glass transition of uncured DGEBA/BABB and DGEBA/DABP systems investigated by dynamic DSC heating with a rate of 10 °C min⁻¹ is shown in Fig. 6. It can be seen that the glass transition temperature of uncured DGEBA/BABB system is lower than DGEBA/DABP system. This is probably due to the incorporation of methylene unit for DGEBA/BABB system, which leads

Fig. 5 Dynamic DSC curves of DGEBA/BABB and DGEBA/DABP systems with different scanning rates of 5, 10, 15, and 20 °C min⁻¹
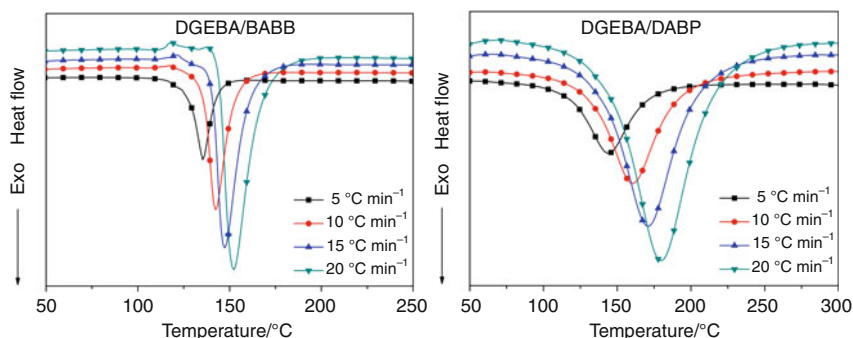
Table 1 Activation energy (E_a) and the temperature of the peak position of the exotherm (T_p) for curing systems of DGEBA with BABB and DABP

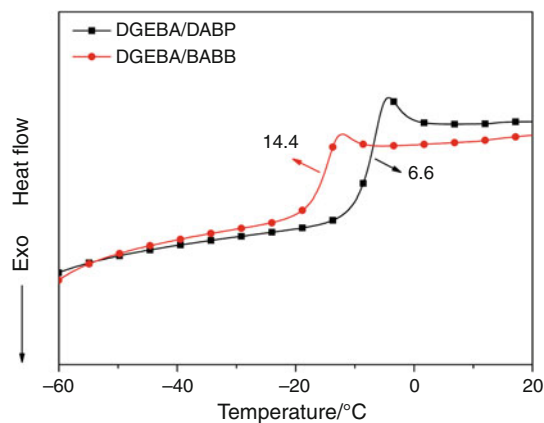| Sample	T_p/°C				E_a/kJ mol⁻¹
	20 °C min⁻¹	15 °C min⁻¹	10 °C min⁻¹	5 °C min⁻¹	
DGEBA/BABB	152.3	147.2	142.4	135.4	119.9
DGEBA/DABP	179.7	171.3	160.5	143.9	60.9

Fig. 6 The glass transition temperatures of uncured DGEBA/BABB and DGEBA/DABP systems

greater degree of freedom for the segmental motion in comparison with DABP system.

Curing kinetics analysis

Kinetic models developed from kinetic analysis of DSC data have been widely applied to the curing of epoxy resins [20, 21], and kinetics study is usually based on the equation as follows:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \tag{1}$$

where T is the temperature, α is the reaction conversion, A is the pre-exponential factor, R is the gas constant, and $f(\alpha)$ is a model function that depends on the reaction mechanism.

Assuming the heat flow is proportional to the change in the extent of curing reaction:

$$\frac{d\alpha}{dt} = \frac{1}{H_{tot}}\frac{dH}{dt} \tag{2}$$

where dH/dt represents the rate of heat generated during curing reaction. H_{tot} is the overall heat of reaction. The H_{tot} is calculated from the total area under the dynamic scan of curing curve at 10 K min^{-1}. The corresponding value

for the DGEBA/BABB system is 174.5 J g^{-1} and the DGEBA/DABP system is 403.7 J g^{-1}.

Under the isothermal condition, we can rearrange the Eq. 1 as follows using integral method [22]:

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_\alpha}{RT_i} \tag{3}$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1}d\alpha$ is the integral form of the reaction model; and $t_{\alpha,i}$ is the time required to reach a specified conversion α at temperature T_i. Therefore, from the Eq. 3, E_α can be evaluated from the slope of the plot—$\ln t_{\alpha,i}$ versus T_i^{-1}.

The rates of reaction as a function of time for curves for DGEBA/BABB and DGEBA/DABP systems at several isothermal temperatures are reported in Fig. 7. As we can see, the curing rate of the systems grows obviously with the increase of reaction temperatures, and the BABB system displays a narrower and slimmer cure exotherm profile than DABP system, which indicates that BABB is more reactive. It can also be learned that the autocatalytic kinetic behavior is shown from the non-zero initial reaction rate. To investigate the kinetics of curing reaction, the relationship between conversion α and the curing time under different curing temperatures can be obtained.

The values of the activation energies of DGEBA/BABB and DGEBA/DABP systems which were obtained from the plot—$\ln t_{\alpha,i}$ versus 1000/T varied with the conversion of the curing systems, and it is shown in Fig. 8. It can be seen that the values of activation energy are not a constant. The BABB system displays much higher E_α values than DABP system. The dependence of the activation energy on the conversion obviously displays the autocatalytic reaction character occurring in this system. At the initial curing stage, there was a high E value at low conversion (215.9 kJ mol^{-1} at $\alpha = 0.05$ for BABB and 78.5 kJ mol^{-1} at $\alpha = 0.05$ for DABP) because the hydroxyl groups generated during the curing reaction, and the hydroxyl groups formed facilitated ring opening, resulting in an auto-accelerating effect on the curing reaction and a decrease in E [21–23]. At the final curing stage, the activation energy possessed an obvious decrease, which indicated that the

Fig. 7 Conversion as a function of the reaction time at different reaction temperatures for DGEBA/BABB and DGEBA/DABP systems
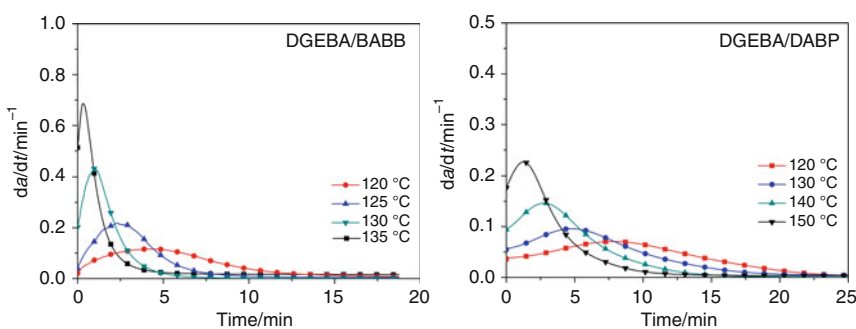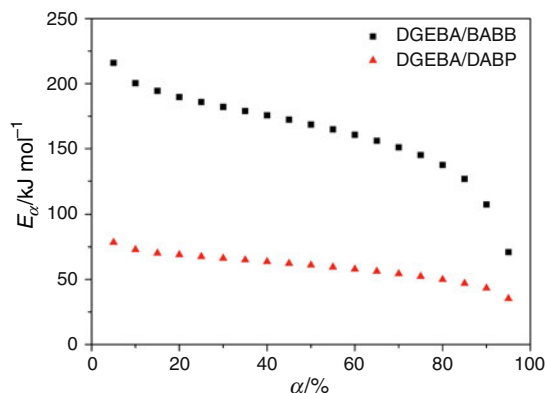
Fig. 8 The relationship between activation energy and the fractional conversion for DGEBA/BABB and DGEBA/DABP systems

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (4)$$

where k_1 is the externally catalyzed rate constant, and k_2 is the autocatalyzed rate constant with Arrhenius temperature dependency. The constant k_1 can be obtained using the initial reaction rate at $t = 0$ from the intercept of the isothermal curves.

The fitting curves from the experimental data to the autocatalytic kinetic model are studied for BABB and DABP systems, and the representative fitting curve of BABB system is shown in Fig. 9. As is shown, the maximum reaction rates under different temperatures were all found around 0.2–0.4 conversion, and there was a good fit with the chosen model for the experimental data from the start of reaction up to 90% conversion, and it is in accordance with the result of isoconversional method. The deviation in the last stage is because the diffusion effect dominates the reaction. The kinetic parameters confirmed are listed in Table 2. It can also be seen that the DGEBA/BABB system shows higher E_{a1} and E_{a2} values than DABP system. This result is consistent with the variety of the effective activation energy estimated from dynamic DSC study.

curing mechanism started to change from chemical kinetics control to control by diffusion because of the phenomena of gelification, vitrification, and high viscosity existed in the reaction medium [24].

In this study, we can also use an autocatalytic model proposed by Kamal [25], which gives a description of curing up to the vitrification point as follows:

Fig. 9 Comparison of experimental data with autocatalytic model for DGEBA/BABB system
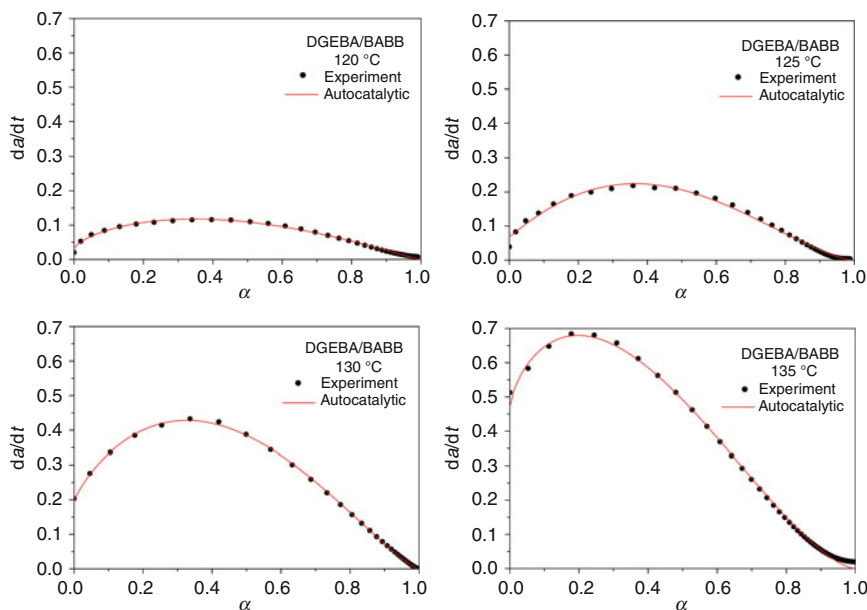
Table 2 Kinetics parameters for curing reactions of DGEBA with BABB and DABP

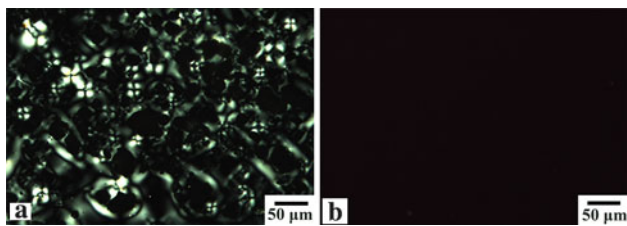| Sample	k_1/min^{-1}	k_2/min^{-1}	m_{avg}	n_{avg}	E_{a1}/kJ mol^{-1}	E_{a2}/kJ mol^{-1}
DGEBA/DABP	$8.52 \times 10^7 \exp(-8.57/RT)$ $r = 0.9697$	$3.93 \times 10^4 \exp(-4.77/RT)$ $r = 0.9871$	0.922	1.147	70.8	39.7
DGEBA/BABB	$3.86 \times 10^{15} \exp(-15.49/RT)$ $r = 0.9906$	$1.51 \times 10^{12} \exp(-11.38/RT)$ $r = 0.9058$	0.925	1.501	128.8	94.7

Fig. 10 Polarized optical micrographs of the DGEBA systems: **a** cured with liquid crystalline curing agent BABB; **b** cured with normal curing agent DABP

Phase structure of the DGEBA/BABB and DGEBA/DABP systems

The polarized optical micrographs of the DGEBA/BABB and DGEBA/DABP systems are shown in Fig. 10. The DGEBA/BABB system (Fig. 10a) was heated to 160 °C and cured at this temperature for 2 h. A birefringence pattern can be obtained during the process of curing, and the liquid crystalline phase belongs to nematic droplet texture [26]. This liquid crystalline texture can be kept to room temperature because the liquid crystalline molecules have a tendency of self-conglomeration, and the liquid crystalline phase had been fixed in the system at cure process. On the other hand, the DGEBA/DABP system (Fig. 10b) was cured at 180 °C for 2 h, but during the curing process, the system showed an isotropic state, while cooling to room temperature with a rate of 0.5 °C min^{-1}, there was no birefringence pattern observed. On the basis of these results, it indicates that the difference in the curing agents influence the formation of the LC phase. It can be predicted that the LC phase cannot certainly be formed even if there is an introduction of mesogenic groups into epoxy resin system, and it also becomes clear that the formation of LC phase of DGEBA systems can be decided by curing agents.

Mechanical properties of the DGEBA/BABB and DGEBA/DABP system

Dynamic mechanical properties and the evolution of transition temperature were investigated by dynamic mechanical analysis. The storage modulus of DGEBA cured with BABB and DABP are shown in Fig. 11. It shows that the storage modulus of DGEBA cured with liquid crystalline curing agent are higher than DGEBA/DABP system which can be attributed to the self-reinforcing effect of the LC phase, in other words, the LC phase and the anisotropic ordering can enhance the storage modulus of networks obviously. Commonly, the modulus of epoxy networks is mainly affected by the structure and the crosslinking density [27], while based on these results, it can be seen that the LC networks of BABB show higher modulus than
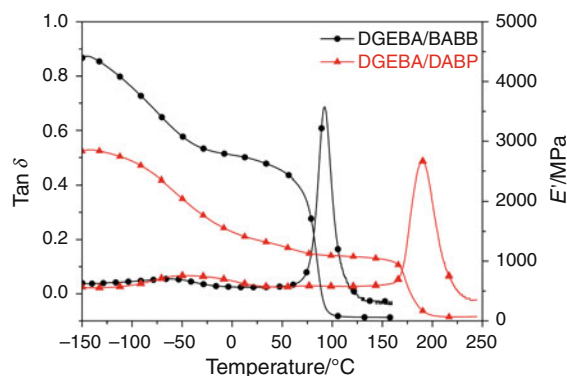

Fig. 11 Dynamic mechanical properties of DGEBA cured with BABB and DABP

DABP system which exhibited higher crosslink density with an isotropic state, even both the two systems have the same mesogenic groups. This result implies that liquid crystalline phase is more important than crosslinking density in determining the modulus of the epoxy thermosets. However, α relaxation (i.e., the glass transition) temperature of the networks cured with BABB decreases sharply in comparison with DGEBA/DABP system. As is known that α relaxation is generally ascribed to the segmental motion of the networks, and the glass transition temperature is determined by the degree of freedom for the segmental motion, crosslinking and entanglement constraints, and the packing density of the segments [28, 29]. In the networks cured with BABB, the incorporation of methylene units leads to the increase of the molecular weight between crosslinking points, which results in a lower packing density for the networks, and so the glass transition temperatures decrease. The result displays that the crosslink density plays a key role in determining the glass transition temperature in the cured networks.

Conclusions

The liquid crystalline curing agent BABB, synthesized, and characterized in this study, showed smectic liquid crystalline texture, and its influences on the LC phase in the cured system were described. Curing kinetics was studied using an isoconversional method under isothermal condition. The results revealed that the effective activation energy was dependent on the conversion, and the effect of diffusion on the curing reaction for BABB and DABP systems was found at about 90% conversion, and DGEBA/BABB system exhibited higher E_a value and chemical reactivity than DGEBA/DABP system, which is consistent with the study of dynamic DSC. The isothermal DSC data can be fitted well by Kamal model for the experimental data from the start of reaction up to 90% conversion. POM studies

indicated the presence of nematic phases for conventional epoxy resin DGEBA cured with BABB, while there was no birefringence pattern observed in DGEBA/DABP system. DGEBA/BABB system showed higher storage modulus than DGEBA/DABP system because of the self-reinforcing effect of the LC phase, whereas the glass transition temperatures decreased because of the introduction of flexible spacer group $(-(CH_2)_4-)$.

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