

# Dielectric and molecular dynamic studies of sub-T<sub>g</sub> by thermally stimulated current (TSC) analysis for liquid crystalline epoxy thermosets

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## Abstract

Dielectric constant ( $\epsilon'$ ), loss factor ( $\tan \delta$ ) and molecular dynamic behavior of liquid crystalline epoxy cured with diamine were studied by thermally stimulated discharge current (TSC) technique and were compared with the conventional epoxy system. The relaxation time  $\tau$  and the activation energy of reorientation of the dipoles for each TSC characteristic band were expressed as Arrhenius relationship. Liquid crystalline epoxy (LCE) monomer was diglycidyl ether of biphenyl (DGEBP) and the conventional epoxy was diglycidyl ether of bisphenol A (DGEBA). The conventional epoxy had two sub-T<sub>g</sub> relaxations;  $\gamma$ -relaxation was related to the motion of glycidyl ether segment and  $\beta$ -relaxation was due to the crankshaft motion of the hydroxyether group. LCE thermoset exhibited another  $\gamma'$ -relaxation in addition to those two relaxations; the reorientation of mesogenic unit. The *para*-ether linkage of the biphenyl mesogenic unit allows it to rotate without disturbing neighborhood unit.

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**Keywords:** Liquid crystalline epoxy; TSC analysis; Dielectric characteristics; Sub-T<sub>g</sub> transition

## 1. Introduction

High performance polymers have been developed recently, such as high modulus fibers and self-reinforced molded articles, as a direct result of increased knowledge of structure–process–property relationships. Oriented materials have been produced as a result of two emerging technologies: modification of conventional polymers and the design of rod-like liquid crystalline polymers (LCPs), both of which result in extended chain structures in the solid state [1,2]. Liquid crystalline polyphenylene terephthalamide, commercialized by Du Pont under the trade name Kevlar (ultra high modulus fiber), is the first example of the practical application of LCPs. The liquid crystalline copolyesters produced by Dartco (Xydar) and by Celanese (Vectra) have very high tensile strength, stiffness and impact strength. Thermal expansion coefficient of these polymers is significantly lower than that of conventional polymers. Therefore, the shrinkage of molded parts after molding is negligible [3,4].

Recently, ordered networks have become the subject of intensive research in the field of liquid crystal polymer materials [5–8]. This can partly be attributed to the fact that, although main-chain LCPs have excellent properties such as mechanical, thermal and optical properties, dimensional stability, etc. these properties in the transverse direction are rather poor as compared with those in the orientational direction. These problems can be overcome by the introduction of crosslinks between the main chains, which improves the dimensional stability of these ordered systems. Also, from the scientific point of view, ordered networks provide many new challenges, such as the theoretical description of the mechanical deformation of such materials. Because of their high strength, dimensional stability and easy molding process, liquid crystalline thermosets (LCTs) will be used as replacements for complex shapes, metals and ceramic parts in electronic, aerospace and other industrial applications.

In this study, dielectric properties and molecular dynamic behavior of liquid crystalline epoxy (LCE) cured with diamine were studied by thermally stimulated discharge current (TSC) technique [9,10] and were compared with the conventional epoxy system. Knowledge of the molecular dynamic behavior of polymer materials at low tempera-

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ture is very important to understand mechanical, physical, electrical and thermal properties.

The principles of the TSC technique are as follows. When polymer is heated up to a temperature close to its glass transition temperature, the dipoles and the free charges present in the polymer are mobilized easily. Therefore, application of a static electric field to the polymer at the high temperature causes the dipoles orientation and a drift of the free charges. Then the sample is cooled to a lower temperature under the short-circuit condition to make the main chains of the polymer immobilized and the free charges frozen-in and the oriented dipoles return to the equilibrium state by the stimulation of a constant heating rate.

## 2. Experimental

### 2.1. Materials and curing condition

The LCE monomer, diglycidyl ether of 4,4'-biphenyl (DGEBP, smectic transition at 115 °C and isotropic transition at 153 °C) was synthesized as described in the literature by Kim and co-workers [11]. The conventional epoxy was diglycidyl ether of bisphenol A (DGEBA, Epon 828 grade) supplied by Shell Company. The curing agents were 4,4'-methylene dianiline (MDA) and sulphanilamide (SAA). The chemical structures are shown in Scheme 1.

The stoichiometric amount of DGEBP and MDA (or SAA) was dissolved in tetrahydrofuran until a clear solution was obtained and the solution was cooled to room temperature. Then the solvent was removed and dried in vacuum oven at room temperature. The mixtures were stored at -13 °C in a freezer. DGEBA/MDA or DGEBA/SAA system was also prepared by the same procedure except the

ethanol/acetone mixed solvent. The mixtures were cured at 120–180 °C for 2–5 h and the cured thermoset plaques were cut into the appropriate dimensions for the specimens of TSC analysis.

### 2.2. TSC analysis

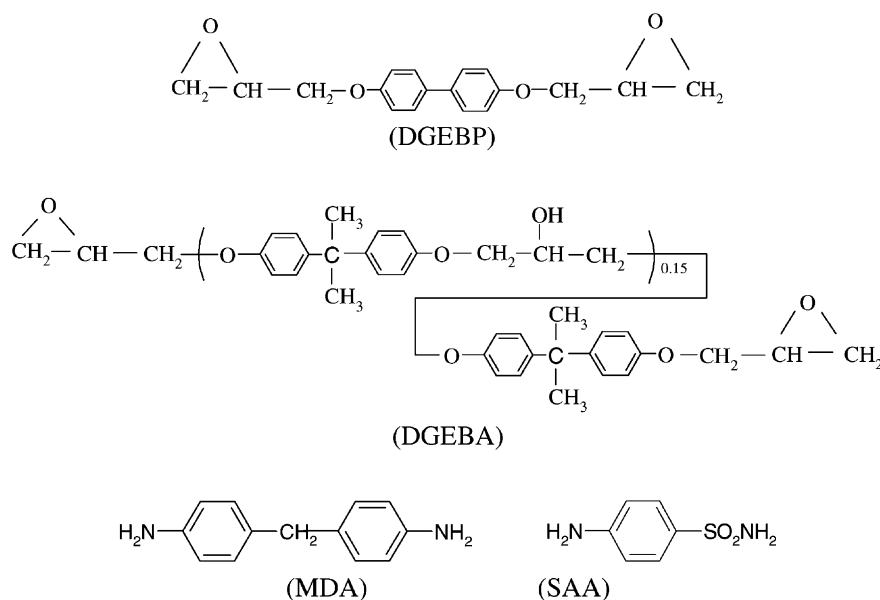
The TSC analysis was carried with a TSC/RMA spectrometer (Solomat 9100, USA) covering the temperature range from -180 to 400 °C. Both surfaces of the prepared epoxy with 50 μm thickness were covered in a diameter of 3 cm with evaporated gold films for electrodes. The specimen was polarized at a given temperature ( $T_p$ ) for the polarization time ( $t_p$ ) of 1 h under a polarization field ( $E_p$ ) of 2 kV/mm and the polarized specimen was frozen by cooling down to a lower temperature ( $T_0$ ). Then the depolarization current was measured at a constant heating rate of 4 °C/min from  $T_0$  to  $T_f$ , where  $T_f > T_p$ .

The relaxation time  $\tau$  of reorientation of the dipoles for each characteristic band is expressed as Arrhenius relationship as following equation [12]:

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) \quad (1)$$

where  $\tau_0$  is a pre-exponential factor,  $E_a$  the relaxation activation energy for the migration of the polarized molecule segments,  $k$  the Boltzmann's constant ( $1.38 \times 10^{-23}$  J/K) and  $T$  is the absolute temperature. To determine  $E_a$ , the relationship between  $-\ln I$  and  $1/T$  in Eq. (2), should be plotted by using only low-temperature part of the peaks in TSC curve.

$$I = \frac{P_0}{\tau_0} \exp\left(-\frac{E_a}{kT}\right) \Leftrightarrow -\ln I = \frac{E_a}{kT} - \ln\left(\frac{P_0}{\tau_0}\right) \quad (2)$$



Scheme 1. Chemical structures of epoxy and curing agents.

where  $I$  is the current density and  $P_0$  is the equilibrium polarization when the polarization time is far longer than  $\tau$ . Then  $\tau_0$  is calculated by substituting the following Eq. (3) [13] to Eq. (1) for  $T = T_m$ , which gives Eq. (4):

$$\tau(T_m) = \frac{kT_m^2}{qE_a} \quad (3)$$

where  $T_m$  is the peak temperature at which maximum  $I$  is appeared and  $q$  is heating rate.

$$\tau_0 = \frac{kT_m^2}{qE_a} \exp\left(-\frac{E_a}{kT_m}\right) \quad (4)$$

### 3. Results and discussion

Fig. 1 shows the TSC curve of DGEBP/MDA system cured at 150 °C for 3 h. It is polarized at  $T_p = 80$  °C and depolarized with a heating rate of 4 °C/min. The maxima of the weak characteristic peaks positioned at  $-112$  and  $-103$  °C are overlapped and the strong peak at  $-71$  °C and a weak shoulder at  $-57$  °C are shown in the same band. Those bands are related to the local molecular motions in glassy state of crosslinked epoxy networks. As the temperature increases with a constant heating rate, the charges trapped on the molecular chains and in the crystalline and amorphous regions or at the boundaries flow out by the relaxations of the polarized molecule segments.

To get relaxation time of the reorientation for the characteristic bands of Fig. 1, the straight relationships between  $-\ln I$  and  $1/T$  for the low temperature part of the first and third peaks are shown in Fig. 2. However, the second peak and the fourth shoulder are too small to use the Eq. (2). Therefore, these two peaks have not investigated in here. The

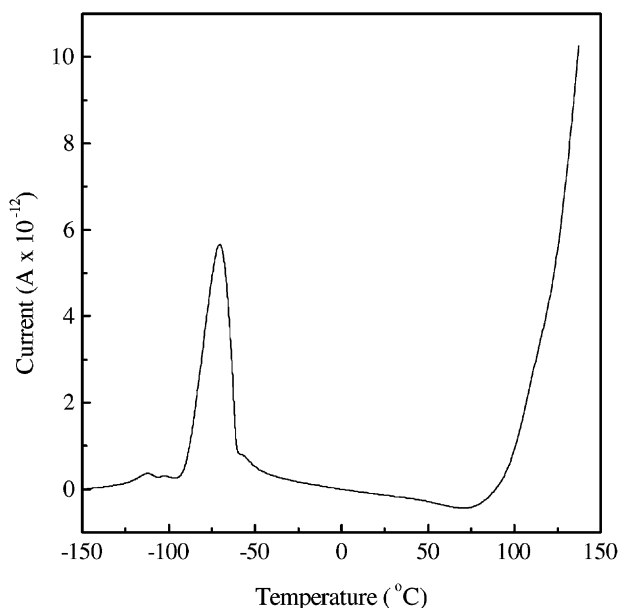


Fig. 1. TSC curve of DGEBP/MDA system cured at 150 °C for 3 h.

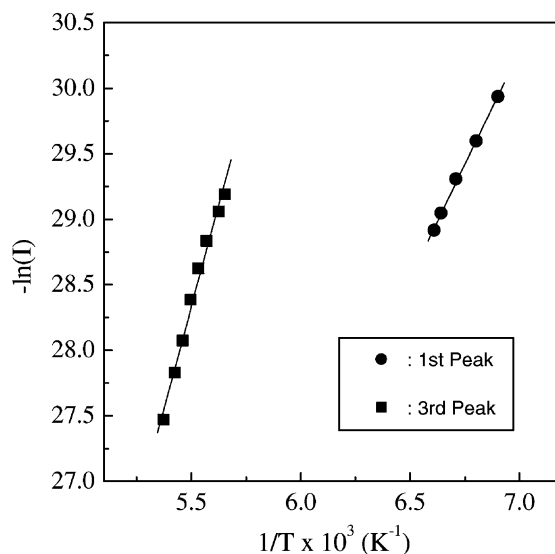


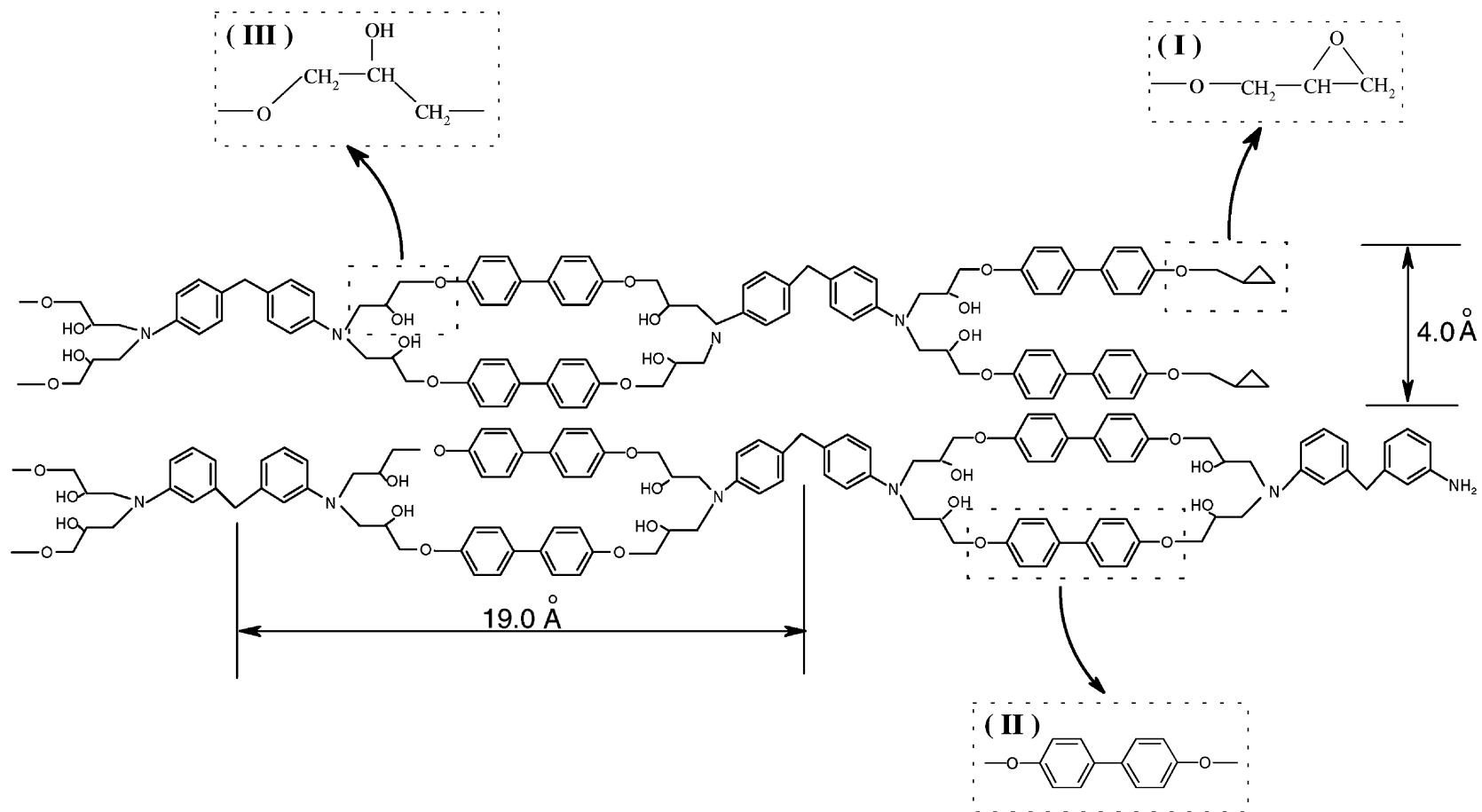
Fig. 2. Initial slope analysis for the peaks of Fig. 1 in the function  $-\ln I$  plotted against  $1/T$ .

activation energies indicating trap depth for the migration of the polarized molecule segments can be evaluated from the slopes. The value for the first peak is 0.30 eV and that for the third peak is 0.54 eV. It is a general result that the activation energy of a higher temperature peak is larger. Then Eq. (4) gives  $\tau_0$  for the characteristic peaks and that for the first peak is  $1.01 \times 10^{-7}$  s and that for the third is  $3.78 \times 10^{-12}$  s. Therefore, the relaxation time  $\tau$  for the reorientation of the dipoles for each characteristic band is expressed as follows:

$$\tau = 1.01 \times 10^{-7} \exp\left(3.48 \times 10^3 \frac{1}{T}\right), \quad -137^\circ\text{C} < T < -108^\circ\text{C} \quad (5)$$

$$\tau = 3.78 \times 10^{-12} \exp\left(6.26 \times 10^3 \frac{1}{T}\right), \quad -95^\circ\text{C} < T < -37^\circ\text{C} \quad (6)$$

The results of dielectric behavior of the quenched DGEBP/MDA network cured at 150 °C for 3 h are plotted with increasing temperature as shown in Fig. 3. Two weak peaks in dielectric constant  $\epsilon'$  are shown at ca.  $-112$  and  $-101$  °C, and a strong peak is observed at ca.  $-71$  °C. Rapid increase in  $\epsilon'$  characteristic of a dipolar relaxation is also shown starting at about 100 °C, which is related to  $\alpha$ -relaxation (glass transition). Loss factor ( $\tan \delta$ ) also shows the same results. The first weak peak,  $\gamma$ -relaxation corresponds to the onset of the motion of the unreacted glycidyl ether segment (I) [14] in Scheme 2 and the second weak peak  $\gamma'$ -relaxation is due to the reorientation of mesogenic unit (II) [15]. The *para*-ether linkage of the biphenyl mesogenic unit allows it to rotate without disturbing neighborhood unit. The strong  $\beta$ -peak is due to the crankshaft motion of the hydroxyether group (III) [16].



Scheme 2. Motion of the polarized molecule segments in the smectic phase of DGEBP/MDA network cured at  $150^\circ\text{C}$  for 3 h.

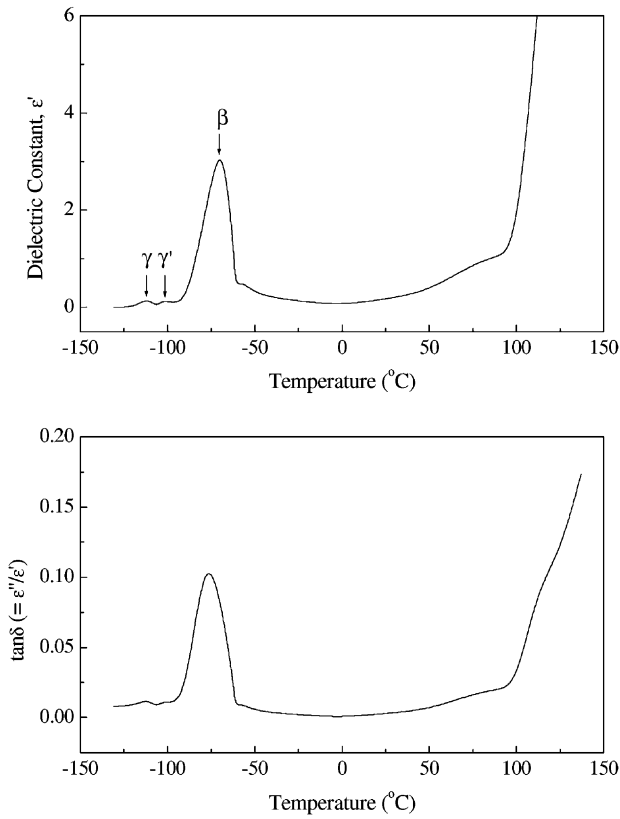


Fig. 3. Dielectric constant ( $\epsilon'$ ) and loss factor ( $\tan \delta$ ) vs. temperature for DGEBP/MDA system cured at 150 °C for 3 h.

Fig. 4 is the TSC curve of DGEBA/MDA system cured at 150 °C for 3 h. It is polarized at  $T_p = 150$  °C and depolarized with a heating rate of 4 °C/min. The maxima of two characteristic peaks are shown at  $-113$  and  $-12$  °C. To determine  $E_a$  for each relaxation, the relationship between

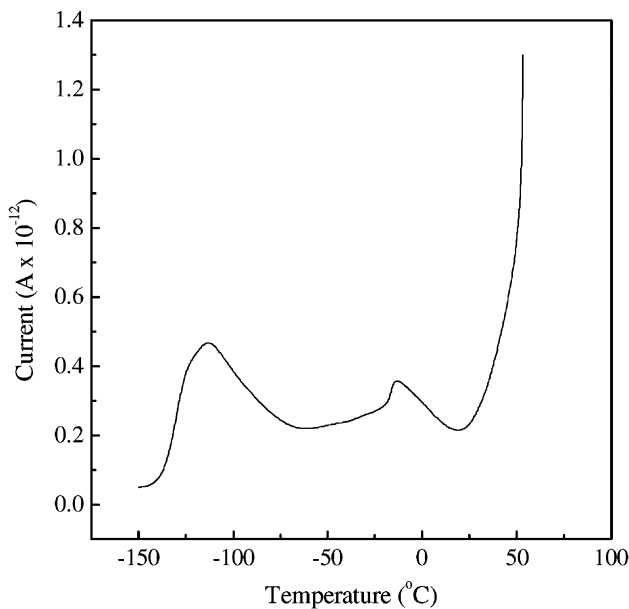


Fig. 4. TSC curve of DGEBA/MDA system cured at 150 °C for 3 h.

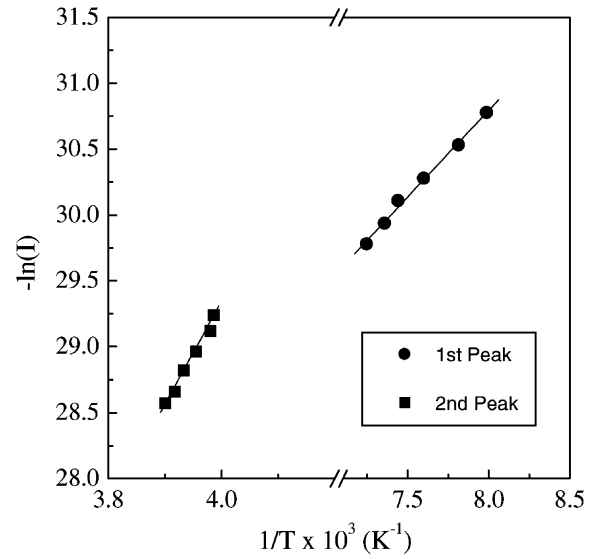


Fig. 5. Initial slope analysis for the peaks of Fig. 4 in the function  $-\ln I$  plotted against  $1/T$ .

$-\ln I$  and  $1/T$  in Eq. (2) is shown Fig. 5, which is plotted by using only low-temperature part of the peaks in Fig. 4. The activation energy for the first peak is 0.14 eV and that for the second peak is 0.64 eV. Then Eq. (4) gives  $\tau_0$  for the characteristic peaks and that for the first peak is  $3.18 \times$

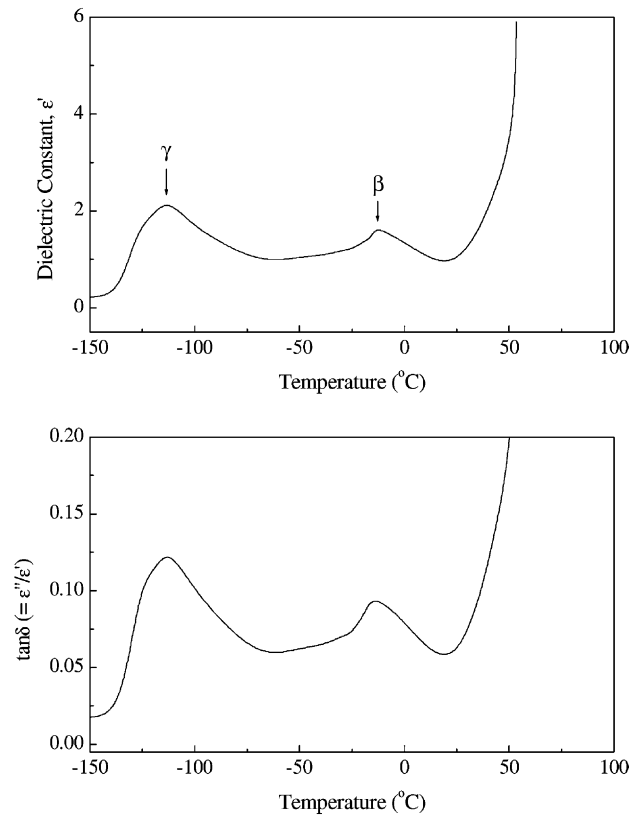


Fig. 6. Dielectric constant ( $\epsilon'$ ) and loss factor ( $\tan \delta$ ) vs. temperature for DGEBA/MDA system cured at 150 °C for 3 h.

$10^{-6}$  s and that for the third is  $9.22 \times 10^{-11}$  s. Therefore, the relaxation time  $\tau$  for the reorientation of the dipoles for each characteristic peak is expressed as follows:

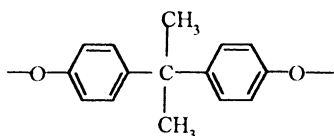
$$\tau = 3.18 \times 10^{-6} \exp\left(1.62 \times 10^3 \frac{1}{T}\right),$$

$$-142^\circ\text{C} < T < -64^\circ\text{C} \quad (7)$$

$$\tau = 9.22 \times 10^{-11} \exp\left(7.42 \times 10^4 \frac{1}{T}\right),$$

$$-40^\circ\text{C} < T < 19^\circ\text{C} \quad (8)$$

Fig. 6 shows dielectric constant ( $\epsilon'$ ) and loss factor ( $\tan \delta$ ) for the quenched DGEBA/MDA network cured at  $150^\circ\text{C}$  for 3 h with increasing temperature of  $4^\circ\text{C}/\text{min}$ . A medium peak in  $\epsilon'$  is shown at ca.  $-113^\circ\text{C}$  is  $\gamma$ -relaxation related to the motion of the glycidyl ether segment (I) in Scheme 2 and the following DGEBA [17];



$\beta$ -Peak is also appeared at ca.  $-12^\circ\text{C}$ , which is due to the crankshaft motion of the hydroxyether group (III) of Scheme 2 hindered by hydrogen bonding. It also contains rapid increase shown at about  $25^\circ\text{C}$ , which is related to  $\alpha$ -relaxation (glass transition). Loss factor ( $\tan \delta$ ) also shows the same results.

Fig. 7 shows the TSC curve of DGEBP/SAA system cured at  $180^\circ\text{C}$  for 2 h. It is polarized at  $T_p = 80^\circ\text{C}$  and depolarized with a heating rate of  $4^\circ\text{C}/\text{min}$ . It shows very similar results of DGEBP/MDA system.  $\gamma$ -,  $\gamma'$ -Relaxations

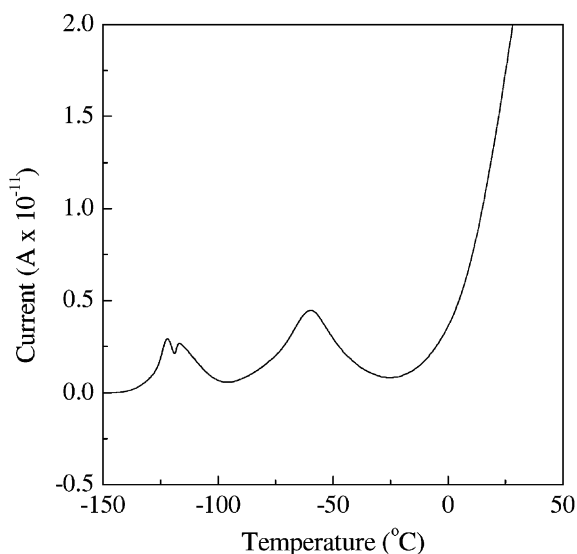


Fig. 7. TSC curve of DGEBP/SAA system cured at  $180^\circ\text{C}$  for 2 h.

are shown at ca.  $-122^\circ\text{C}$  and  $-116^\circ\text{C}$  and  $\beta$ -relaxation is appeared at ca.  $-59^\circ\text{C}$ .

#### 4. Conclusions

Dielectric characteristics and molecular dynamic behaviors of LCE cured with diamine were studied by thermally stimulated discharge current technique and were compared with the conventional epoxy system. TSC curve of DGEBP/MDA system had four characteristic peaks; weak peaks at  $-112$  and  $-103^\circ\text{C}$ , strong peak at  $-71^\circ\text{C}$  with a weak shoulder at  $-57^\circ\text{C}$ . The activation energies indicating trap depth for the migration of the polarized molecule segments for the first and the third peaks are 0.30 and 0.54 eV, respectively. TSC curve of DGEBA/MDA system had two characteristic peaks at  $-113$  and  $-12^\circ\text{C}$  and the activation energy for the first peak is 0.14 eV and that for the second peak is 0.64 eV. The conventional epoxy had two sub-Tg relaxations;  $\gamma$ -relaxation was related to the motion of glycidyl ether segment and  $\beta$ -relaxation was due to the crankshaft motion of the hydroxyether group. LCE thermoset contains another  $\gamma'$ -relaxation above two relaxations, the reorientation of mesogenic unit. The *para*-ether linkage of the biphenyl mesogenic unit allows it to rotate without disturbing neighborhood unit.

#### Acknowledgements

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