Dielectric Relaxation and Mechanical Properties of Liquid Crystalline Epoxy Thermosets

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ABSTRACT: This article describes the dielectric relaxation behavior and mechanical properties of novel liquid crystalline (LC) epoxy thermosets. Thermal simulated current experiments show that there is an additional relaxation caused by the local orientation of mesogens. From the mechanical test, it is found that the LC thermoset exhibits higher tensile strength and even little more deformation. It shows that the cured networks can be strengthened by LC domain orientation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1568–1573, 2000

Key words: liquid crystalline; epoxy network; dielectric relaxation; thermal simulated current; mechanical property

INTRODUCTION

Epoxides constitute a most important class of thermosetting polymers. The properties of epoxy resins—for example, excellent chemical resistance, very good mechanical and thermal properties, and good electrical insulation—have been utilized in many applications. The versatility of these crosslinked systems stems in large part from the fact that one can choose from a variety of resins, curing agents, and preparatory conditions, and often tailor resin to suit a particular need. Recently, it has been recognized that these properties could be greatly enhanced if liquid crystalline (LC) like structures are incorporated into the epoxy networks.[1,2]

It is common knowledge that LC main-chain polymers show a high modulus and a very low thermal expansion in the direction of the macroscopic orientation. In the direction transverse to the orientation of the chains, however, the properties are rather poor.[3] With mesogenic groups along the main chains of the polymer and crosslinking capability between chains, LC thermosetting polymers (LCTs) would exhibit desire properties in both the uniaxial and transverse directions, and should be candidates for self-reinforcing composites materials.

As the conventional isotropic thermosets, LCTs are infusible solids that have high glass transition temperature and high modulus at room temperature. In addition, the order of the liquid crystalline phase is frozen into the network—i.e., the materials no longer exhibit the liquid crystalline phase transition even over T_g. LCTs possess a unique microstructure in which in absence of external field, they tend to form a macroscopically disorder polydomain, where each domain is defined as a region of uniform orientation. Locally, the molecules are oriented along a reference direction.[4]

Although there have been relatively few reports on the mechanical properties of LCTs, they have shown potential for improved thermal stability, orientational stability, low shrinkage upon

cure, and improved impact resistance and fracture toughness. The classical rubber elasticity theory is also available to explain the deformation behavior of LC networks. A number of texts and reviews have been devoted to the theoretical and experimental treatment of the wide variety of LC textures and defects that have been observed.[5–7]
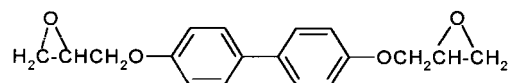
The molecular dynamic behavior of linear LC polymers have been extensively studied by dielectric relaxation spectroscopy.[8,9] Some researches on local motions in the networks also has been performed.[10] But little information was reported on the networks of LCTs. The thermal simulated discharge currents (TSC) technique is another very suitable tool for the study of the dielectric relaxation mechanisms in polymeric materials. A TSC experiment measures the thermally stimulated release of the polarization frozen in during a previous electric field poling. One advantage of the TSC method is its low equivalent frequency. In fact, it is possible to reach lower frequencies while working at lower temperatures, allowing a better resolution of the different relaxation mechanisms.

In the previous works,[11,12] we described the synthesis and the formation of LC phases on two types of epoxy monomers. In here, a biphenyl-based LC epoxide is chosen to dielectric relaxation and mechanical property measurement with different curing agents and curing temperatures. All of them were found to produce densely crosslinked polydomain LCTs with a smectic type of local order by polarized optical microscope and X-ray diffraction. The local molecular motions of LCTs in glassy state were analyzed by the TSC technique. The mechanical behavior was measured by tensile testing, and the resulting fracture surfaces were characterized by scanning electron microscopy (SEM).
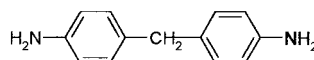
EXPERIMENTAL

Sample Preparation

To prepare samples for mechanical testing, stoichiometric amounts of LC epoxy (DGEBP) and amine methylene dianiline (MDA) are mixed as the procedures described previously. In general, the mixtures are first heated above their melting points. Second, they are quickly brought to the base curing temperature 140°C (approximately 1 min) where they are held for 3 h. Then the temperature is allowed to increase to 160°C for another 1 h, or the mixtures were placed directly
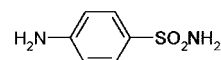
Scheme 1 Chemical structures of epoxy monomer and curing agents.

into the oven and cured at 180°C for 3 h. After curing, the thermoset plaques are cut to the appropriate dimensions with a water-cutting machine and polished. The sample dimensions for tension test are about $50 \times 12 \times 1$ mm. The thin films about 50 μm cured at 150°C for DGEBP/MDA and at 180°C for DGEBP-MDA and DGEBP-sulfanilamide (SAA) were used for TSC measurements. As comparison, the conventional isotropic epoxy polymer samples were also prepared with the same procedures described above.

The chemical structures of epoxy monomers and curing agents were illustrated in Scheme 1.

Instrument

The thermal simulated current experiments were conducted with a TSC/RMA spectrometer (Solomat 9100) covering the range $-180-400$°C. The samples were polarized at a given temperature (T_p), the polarization was frozen by cooling down to T_0, and the depolarization current was measured as the polarized sample was heated up to $T_f > T_p$ at a constant rate.

The uniaxial tensile test was carried out by an instron mechanical testing machine (SHIMADZU AGS 1000D) at a cross-head speed of 5 mm/min. The fracture morphology is characterized by SEM.

RESULTS AND DISCUSSION

Dielectric Relaxation

Local molecular motions are the only motions in glassy state and their importance is obvious in crosslinked materials. There is a number of literature data on the motions of γ and β types in

Figure 1 Thermally simulated discharge current spectrum of polymer DGEBA/MDA cured at 150°C.

glassy polymers. However, it is not clear that this picture is applicable to densely crosslinked LC networks.[13]

In Figures 1–3, TSC traces for LC and non-LC epoxy networks cured with MDA in the glassy state are shown. It is clearly seen that in the glassy state there exist several different types of TSC peaks. The maxima of these peaks for DGEBP/MDA are −116, −103, −72, and −59°C, respectively. However, the conventional epoxy polymers exhibit the broadened relaxation range in temperature from −150–10°C. Oleinik[14] et al. have pointed out that all those TSC peaks are a result of dipole relaxation but not of the migration
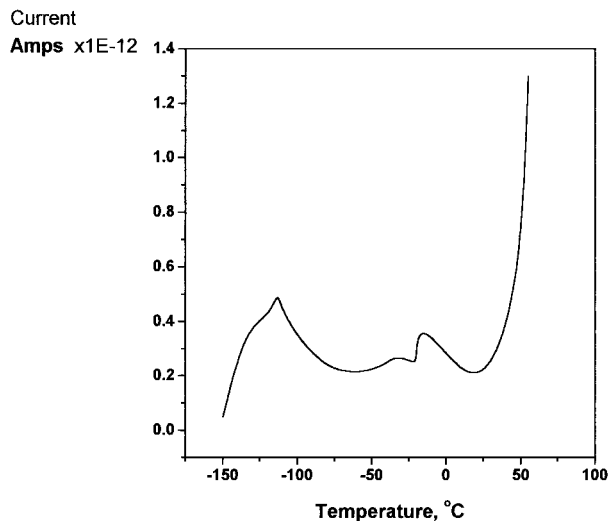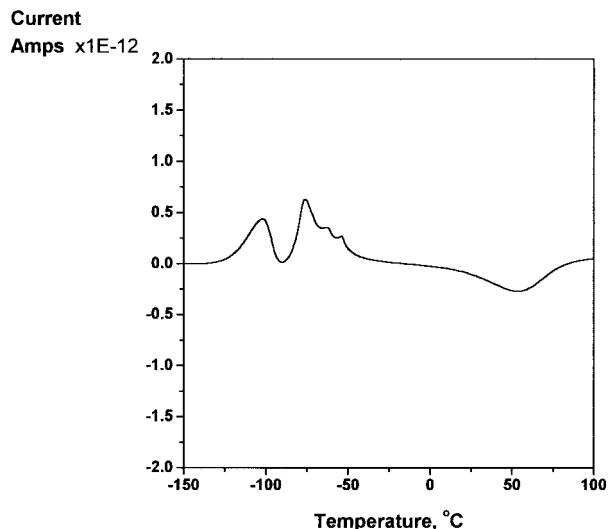

Figure 2 Thermally simulated discharge current spectrum of polymer DGEBP/MDA cured at 150°C.

Figure 3 Thermally simulated discharge current spectrum of polymer DGEBP/MDA cured at 180°C.

of ions or heterocurrents. For the conventional epoxy networks, it was reported that the γ peaks at −148°C belong to uncured epoxy groups; the β peaks near −90°C are related to some motions of aliphatic chains.[15] The γ peak corresponds to some rearrangements in the fragment

$$>NCH_2CH(OH)CH_2OR_2OCH_2CHCH_2$$
$$\diagdown\diagup$$
$$O$$

The β peak is referred to a crankshaft motion, which corresponds to fragment

$$CH_2\!\!-\!\!CH(OH)$$
$$\diagup \qquad\qquad \diagdown$$
$$-\!O \qquad\qquad\quad CH_2\!\!-\!\!$$
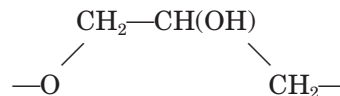
The DGEBP/MDA has the same flexible chain structure as the DGEBA/MDA. Therefore, it should have the same low temperature relaxation mechanism as in the DGEBA/MDA. Obviously, its shift of γ and β transitions to the higher temperatures is caused by the existence of rod-like mesogen groups. In other words, the local motions in LC epoxy networks are more constrained than in the conventional epoxy polymers. It is ascribed to the formation of LC phases where the mesogens are locally ordered.

Comparing the TSC traces in Figures 1–3 for different systems, it can be observed that the DGEBP/MDA cured at 180°C has the lowest and highest values of intensity for γ and β peaks,
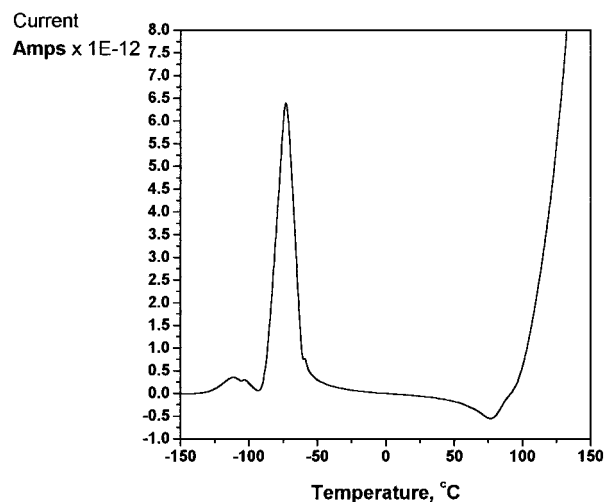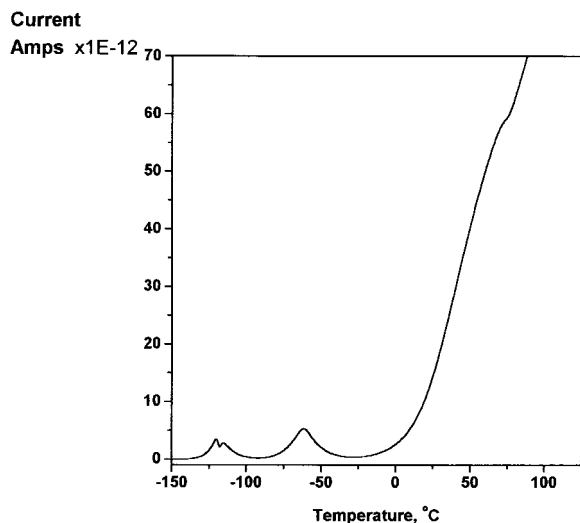
Current
Amps x1E-12

Figure 4 Thermally simulated discharge current spectrum of polymer DGEBP/SAA cured at 180°C.

respectively. As described in previous work, the formation of LC phase during curing facilitates the cure reaction and the resulting networks have a higher conversion. On the other hand, the LC epoxy system would show lower residual epoxy groups and higher concentration of ether groups. This result revealed here is in agreement with the observation in the literature where the intensity of TSC γ and β peaks was found to be proportional to the number of uncured epoxy groups and ether groups in polymers, respectively.[16]

Figure 4 shows the TSC trace of DGEBP/SAA network. As can be seen, the γ and β peaks are located in similar temperature range as DGEBP/MDA, but a higher intensity of both γ and β peaks is observed. In the previous work, we estimated that the reaction reactivity of SAA is lower than MDA. Therefore, the higher β peak intensity seems to deviate from the results mentioned above, where the intensity of γ and β peaks is proportional to the number of uncured epoxy groups and ether groups. The detailed mechanism is not clear now. However, it must be related to the mesophases because the SAA hardener with unequal reactivity hydrogens can result in different LC phases.[11] Of interest, the TSC curve of the DGEBP/SAA shows a additional peak that appears around 72°C. We have reported the glass transition temperature of DGEBP/SAA is 158°C by DSC after it was cured at 180°C for 3 h. Similar results can also be observed by TSC, as shown in Figure 5, where its T_g value is 163°C. So the relaxation occurred at 72°C must be assigned to the molecular motions of other fragment and has the different mechanism as discussed below.

Besides, although these data are accurate enough to discern the γ and β peak positions, the low temperature relaxations cannot be presumably a single transition where the double, shouldered, or wide peaks are observed. Therefore, the relaxation process is practically more complicated than that described above. Some local molecular motions caused by the small fragments such as the hydroxyl or sulfoamide group, even some coordinated torsion of mesogens, may be involved.

It has been reported that the content of different conformations in the aliphatic chains in network, linear polymer, and low molecular weight model compounds is practically the same in the glassy state for all systems.[17] Even the relative intensities of the conformational bands (in Fourier transform IR) remain unchanged during different thermal prehistories (quenching or annealing) of the samples. On the other hand, the situation in densely crosslinked conventional epoxy-aromatic amine glasses is similar to that in flexible polymers in the glassy state where the chains exist in the form of an unperturbed coil. Therefore, the transition at 72°C must be related to the existence of liquid crystalline phases. It may be ascribed to the aliphatic chain motions of ordered LC domain surfaces. It occurs at a higher temperature because those chains are highly restricted by the LC phase. A similar second transition has been observed in the crystallized polymers. As reported in literature, the SAA facilitates the formation of ordered smectic phase.[11] For DGEBP/MDA (Figs. 2 and 3), another kind transition is observed about 50–80°C. The origin
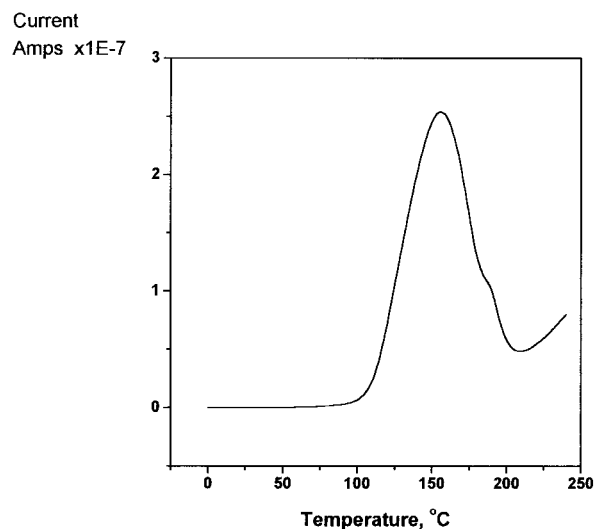
Current
Amps x1E-7

Figure 5 Thermally simulated discharge current spectrum of polymer DGEBA/SAA cured at 180°C.
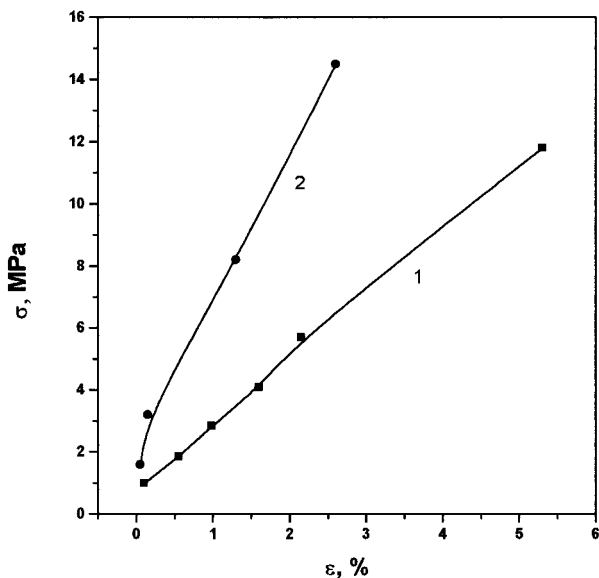
Figure 6 Stress-strain curves for cured DGEBP/MDA. (1) Normal tensile testing; (2) after keeping 1% of elongation for 30 s.

of this transition is still not clear now. The current value is negative, and may be related to the transformation of a three-dimensional crystalline phase into a mesophase accompanied by a further increase in the mobility of the mesogen.

From Figure 5, another small depolarization peak over the glass transition can be detected. It is frequently observed in TSC measurements and attributed to the compensation behavior of polymeric materials.[10] Similar results also can be found in other systems.

Mechanical Properties

A typical stress–strain curve for tensile test is shown in Figure 6. The obtained mechanical property data including tensile strength, Young's modulus and elongation at break are listed in Table I. Compared with the conventional epoxy resin, the LC thermosets exhibit the higher tensile strength and deformation, and similar Young's modulus. High tensile strength is attributed to the rigid structure and ordered LC polydomains.

Normally, in liquid crystalline polymers it is expected that the rigid molecules are highly extended. However, the molecular motion in the highly crosslinked networks will be very restrained, and only local ordered polydomain can be formed.[18] As a matter of fact, under uniaxial tensile conditions the orientation of LC domain and additional plastic deformation within LC do-

mains can occur, simultaneously, thus increasing the strength and elongation at break, as given in Table I. The partly orientation of molecular chains during tensile testing can be confirmed by keeping 1% of strain for 30 s, then continuing the tensile test to sample broken. The partly oriented materials show higher modulus value and less elongation at break. The result is also shown in Figure 6. As known, the conventional epoxy polymers are stiff and brittle, and generally not yieldable. Therefore, the orientation in LC epoxy is different from that occurred in the yielding deformation of thermoplastics and related to the alignment of LC polydomains.

It is not surprising that there may be a local orientation occurred in a crosslinked network. Recent experimental work on LC elastomers has revealed the existence of many remarkable phenomena,[2,19–21] e.g., spontaneous shape changes at LC phase transition, strain-induced orientational transitions leading to new LC morphologies. Warker et al.[22] have extended the theory of classical rubber elasticity to the case of LC networks and explained these effects as a result of the coupling between the entropy of the network, which tends to randomize its strands, and the enthalpies interaction between the rigid LC molecules, which tends to produce alignment along a preferred direction.

Figure 7 shows the fractural morphology of tensile testing samples. The SEM of fracture surfaces exhibits the elongated deformation makings and stable crack propagation for the duration of experiment, indicating a complex fracture. The SEM of the fracture surfaces also shows that the LC thermosets exhibit voiding and fibrillar fracture surface, suggesting that bulk plastic deformation occurred. It also can be considered as an evidence for the alignment of polydomains as shown in Figure 6.
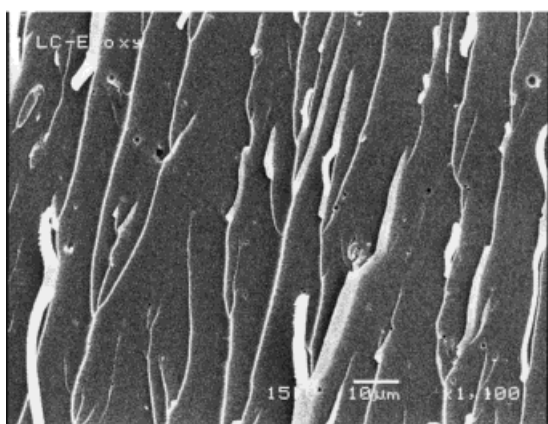
From the mechanical testing and SEM results, It is clear that, as the network is deformed, it is difficult to maintain the continuity of the polydomain microstructure, and instead, it is likely that

Table I   The Mechanical Properties of LC Thermosets

System	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
DGEBA/MDA	57.6	2.1	4.8
DGEBP/MDA	72.4	1.9	5.3
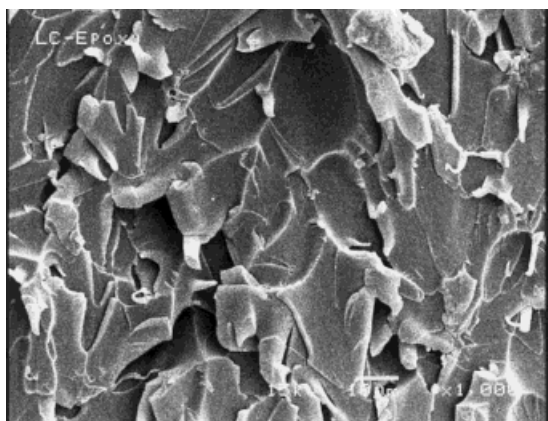
Figure 7 SEM of fracture surface for epoxy thermosets with biphenyl mesogen.

the LC domains prefer to fail in an individual and isolated manner. As reported by Ober et al.,[4] the network strands of unfavorably oriented domains should be softer and failed first, thus producing microscopic voids. Neighboring domains can then deform under uniaxial tensile and undergo significant deformation. The stable crack propagation observed most likely takes place through the slow growth and interconnecting of these voids.

CONCLUSIONS

The TSC experiments revealed that the local relaxation of crosslinked LC epoxy networks were caused by the motions of aliphatic fragments in a wide temperature range in the glassy state as the conventional epoxy polymers. However, the highly ordered LC phase results in the additional transition, which is related the local motion of LC polydomain surface molecules.

The mechanical properties of thermosets based on a liquid crystalline epoxy monomer have been studied and compared to an isotropic thermoset based on a non-LC monomer. The LC thermoset exhibits higher tensile strength and little more deformation. It shows that the cured networks can be strengthened by LC domain orientation. It has been interpreted by the SEM of fracture surfaces.

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