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Properties of Liquid Crystal Epoxy Thermosets Cured in a Magnetic Field

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ABSTRACT: Two liquid crystal diepoxides [1,4-phenylene bis(4-(2,3-epoxypropoxy)benzoate) (**A**) and 4,4′-diglycidyloxydiphenyl (**B**)] were cured with a diamine [4,4′-diaminobiphenyl (**C**)] in the nematic phase to obtain liquid crystalline thermoset (LCT) materials. The systems were studied using different curing conditions and different ratios of the compounds. The mechanical properties were investigated by stress/strain experiments to determine ultimate properties (break strength and elongation at break) and dynamic mechanical thermal analysis (DMTA) to determine small strain properties as a function of temperature. An **A**/**C** mole ratio of 4/1 gave materials with the best combination of high strength and percent elongation. The addition of a small amount of diepoxide **B** to the system (with a mole ratio of **A**/**B** = 4/1) improves the mechanical properties. Dynamic mechanical thermal analysis shows that increasing diamine content or curing time increases the cross-linking density. Macroscopic orientation of the LCTs was achieved by curing the mixtures in the presence of a magnetic field. The samples show that the tensile modulus, break strength, elongation at break, and the storage modulus below the glass transition all increase by a factor of about 2.

Introduction

Oriented polymers possess anisotropic optical and mechanical properties and are very useful in the development of new materials.[1,2] Various methods can be utilized to achieve macroscopic orientation. Some common approaches are to apply external shear to common polymer melts or electric or magnetic fields to liquid crystalline polymers.[3−7] The polymer materials are then cooled to freeze macroscopic ordering. However, polymer molecules can relax with time and eventually lose their macroscopic ordering.[8−11] Cross-linking can reduce or, in some cases, eliminate this relaxation.

A different approach to making highly ordered polymer materials is in situ polymerization of oriented liquid crystal monomers.[2,12−35] The idea is to orient low-molecular-weight liquid crystalline monomers in an external field and subsequently freeze the orientation by polymerization, either thermally, chemically, or photochemically. Obviously, it is much easier to orient low-molecular-weight liquid crystals than polymeric liquid crystals. More importantly, the macroscopic ordering might be irreversibly fixed by the chemical reaction, resulting in optical anisotropy and additional mechanical strength. The use of a magnetic field to prepare macroscopically oriented polymers[2,12,15,23−35] has an important advantage over mechanical stretching or electrical alignment since samples with different geometries (rods, sheets, and blocks) can be readily prepared. For example, we have shown that oriented polymer rods prepared from polymerizing liquid crystalline diacrylate monomers in a magnetic field possess microwave (MW) birefringence[30] and have potential applications in microwave (MW) and millimeter wave (MMW) modulation devices such as phase shifters and scanning antennas.

Epoxy polymers are widely used as engineering materials due to their excellent mechanical and thermal properties. These properties can be enhanced if liquid-crystal-like structures are incorporated into the epoxy networks.[36] The mesogenic diepoxide monomers have been extensively studied by Mormann et al.[37−43] and found suitable for in situ polymerization by curing with a diamine. The final materials are usually called liquid crystalline epoxy thermosets, which differ from liquid crystal polymers in that the mesophases are no longer present. Other investigators have also reported similar work in this area.[44−51] A major effort has been to synthesize different kinds of diepoxides, which are cured by diamines to form highly cross-linking thermosets. The kinetics of the curing process and the liquid crystalline properties have also been investigated. Several groups have prepared oriented epoxy thermosets by polymerizing liquid crystalline monomers in a magnetic fields,[2,24,25,28,29,31,33−35] and high-modulus materials were achieved. For instance, Benicewicz et al.[33] reported that at a very high magnetic field (12.0 T) the oriented materials had a tensile modulus of about 8.1 GPa. However, only one of these publications reported other properties such as break strength and elongation at break,[28] and one other reported results of dynamic mechanical thermal analysis.[2]

We have prepared a series of liquid crystalline epoxy thermosets from two diepoxides and a diamine. An aromatic diamine is chosen as the cross-linker, since it is of lower reactivity than aliphatic amines, which allows the diepoxide to form the nematic mesophase before a substantial degree of cross-linking has occurred.[44] The mechanical properties of the LCTs with different mole ratios of diepoxide/diamine (E/D) and curing time were studied. The relationship between mechanical properties and degree of cross-linking was analyzed to find the best E/D ratio. The best systems

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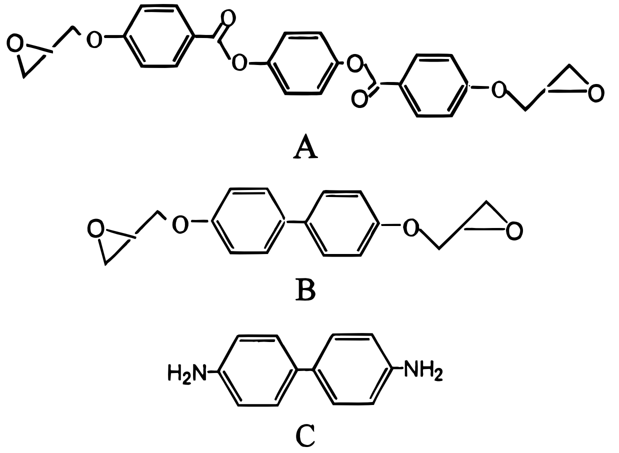

Figure 1. Chemical structures of diepoxide monomers and cross-linking agent.

Table 1. Samples Prepared, Their Composition (Mole Ratio), and Curing Time

no.	diepoxide **A**	diepoxide **B**	diamine **C**	curing time (h)
1	1	0	1	6
2	2	0	1	6
3	3	0	1	6
4	4	0	1	6
5	6	0	1	6
6	10	0	1	6
7	4	0	1	1
8	4	0	1	3
9	4	0	1	12
10	3.2	0.8	1	6
11	2.67	1.33	1	6
12	4	0	1	6[a]
13	3.2	0.8	1	6[a]

[a] Cured in magnetic field.

were chosen to prepare oriented LCTs by curing the liquid crystalline monomers in a magnetic field. Dynamic mechanical thermal analysis experiments were also carried out for these LCTs.

Experimental Section

Two diepoxides, 1,4-phenylene bis(4-(2,3-epoxypropoxy)-benzoate) (**A**) and 4,4′-diglycidyloxydiphenyl (**B**), were synthesized according to published procedures.[38,42,47,50] Their structures are shown in Figure 1. The main reason for choosing these compounds in our study is the simplicity in their syntheses, which would be an important factor if they are to be used in large-scale applications. Furthermore, compound **A** has a large nematic range, which is very advantageous for maintaining the mesomorphic behavior during polymerization. They were recrystallized from methylene chloride/hexane (1:3). The EEW (epoxide equivalent weight determined by HBr titration) of diepoxide **A** is 247 (theoretical 231). ^{1}H NMR (400 MHz) gave the following data (ppm): $CDCl_3$: 2.8, 2.9, 3.4 (ABM, 6H); 4.0, 4.3 (dd, 4H); 7.0, 8.1 (m, 8H); 7.2 (s, 4H). The EEW value of diepoxide **B** is 163 (theoretical 149). ^{1}H NMR (400 MHz) data (ppm): $CDCl_3$: 2.8, 2.9, 3.4 (ABM, 6H); 4.0, 4.2 (dd, 4H); 7.0 (d, 4H); 7.5 (s, 4H). A diamine curing agent, 4,4′-diaminobiphenyl (**C**), was synthesized from 1,2-diphenylhydrazine[42,52] and purified by column chromatography using ethyl acetate/hexane (1:1) as an eluent.

Each of these compounds was ground up to fine powders (~10 μm) and mixed together thoroughly in different mole ratios of diepoxide monomers to diamine cross-linker. The mixture was then put into a home-built mold (75 mm × 15 mm × 1 mm) with an electrical heater and a thermocouple for temperature control. To prepare LCTs from the monomers in their nematic phase, the mixture was heated to 180 °C for 1 h and then cooled to 150 °C to anneal for a fixed period. The total time is referred to as the curing time. The same procedure was applied to several samples cured in the presence of a 7.0 T magnetic field, with the long edge of the mold parallel to the field. The conditions for preparing the samples are shown in Table 1.

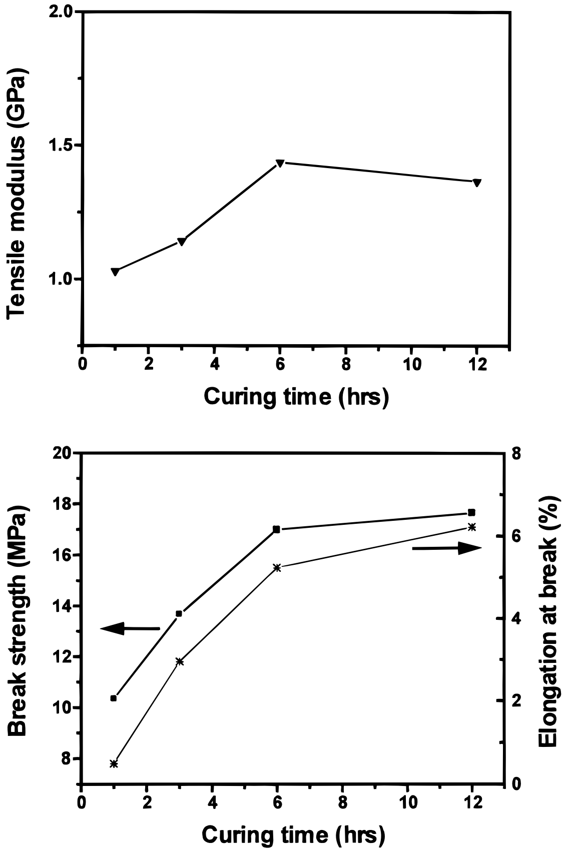

Figure 2. Young's modulus, tensile strength and elongation at break for LCTs formed from diepoxide **A**/diamine **C** (4:1) as a function of curing time.

Tensile properties for both the oriented and unoriented samples were tested using an Instron type TT-C-L tensile tester with a home-built computerized data acquisition system. Samples were cut using a D-1708 die. The Young's modulus, break strength, and elongation at break were obtained from the stress−strain curves.

A Rheometrics RSA II dynamic mechanical thermal analyzer was used to measure the storage modulus (E'), loss modulus (E''), and dampening factor (tan δ). Specimens (50 mm × 12.7 mm × 1 mm) were deformed under flexure using a three-point bend tool and measured at a frequency of 1 Hz. Samples were heated from −150 to 250 °C using 2 °C temperature steps.

The transition temperatures of the monomers were determined, and the curing experiments were studied using an Olympus BH-2 polarized optical microscope (POM) equipped with a Linkam PR 600 hot stage, as well as using a Perkin-Elmer DSC-7 differential scanning calorimeter with a scanning rate of 10 °C/min under a nitrogen atmosphere.

Results and Discussion

POM and DSC studies show that diepoxide **A** exhibits a nematic phase from 175 to 250 °C. Diepoxide **B** melts directly to form a liquid at 155 °C, but a monotropic smectic phase was observed upon cooling of the isotropic phase to 147 °C. Mixtures of **A** and **B** exhibit an enantiomeric nematic phase when the weight percentage of **B** ranges from 0 to 50%. The diamine **C** melts at 124 °C and does not exhibit any mesomorphism but can form nematic mixtures with compound **A** or **B**.[38,42]

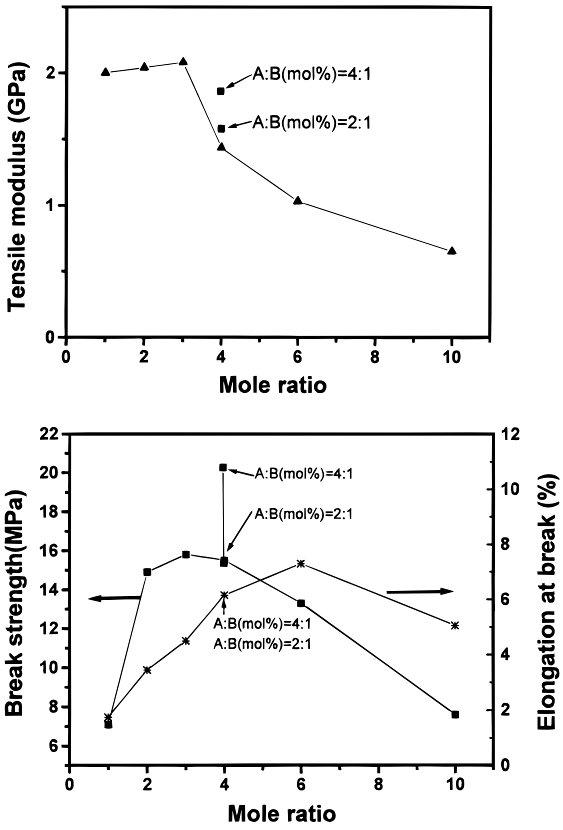

Figure 3. Young's modulus, tensile strength, and elongation at break for LCTs formed from diepoxide **A** (and **B**)/diamine **C** with different mole ratios.

A study of the mesogenic behavior of the diepoxide/diamine mixtures was performed at different curing temperatures. It was found that the mixtures exhibited a nematic phase when cured between 160 and 265 °C. The best curing condition was 160−180 °C, and the nematic texture of mixtures remained after curing. At higher temperaure, the reation proceeded more rapidly, and the nematic texture was less well preserved after curing.

The tensile properties were studied, and they are dependent on the curing time (Figure 2). Since the mechanical properties reach a plateau at about 6 h of curing, all other samples were cured for 6 h.

Figure 3 shows that tensile properties are very dependent on the diepoxide/diamine ratio. The tensile modulus increases slightly with the increase of the ratio up to about 3:1 and then decreases rapidly. This behavior is related to the decrease in the cross-linking density, which will be discussed in more detail later. The break strength reaches a maximum for the ratio between 2:1 and 4:1, and the elongation is the largest for a ratio of 6:1. The reason for the observed trends is probably the following. As the ratio of diepoxide/diamine increases, the extent of cross-linking in the polymer decreases, making it less brittle. Therefore, the break strength and elongation at break first increase with this ratio. However, when the extent of cross-linking becomes too small with insufficient amount of diamine, the mechanical properties of the polymer deteriorate, and the break strength and elongation decrease correspondingly. This explanation is also supported by the data presented in Figure 4, which will be discussed later. Polymers with a 4:1 diepoxide/diamine ratio seem to have the best overall tensile properties, possibly due to a suitable degree of cross-linking.

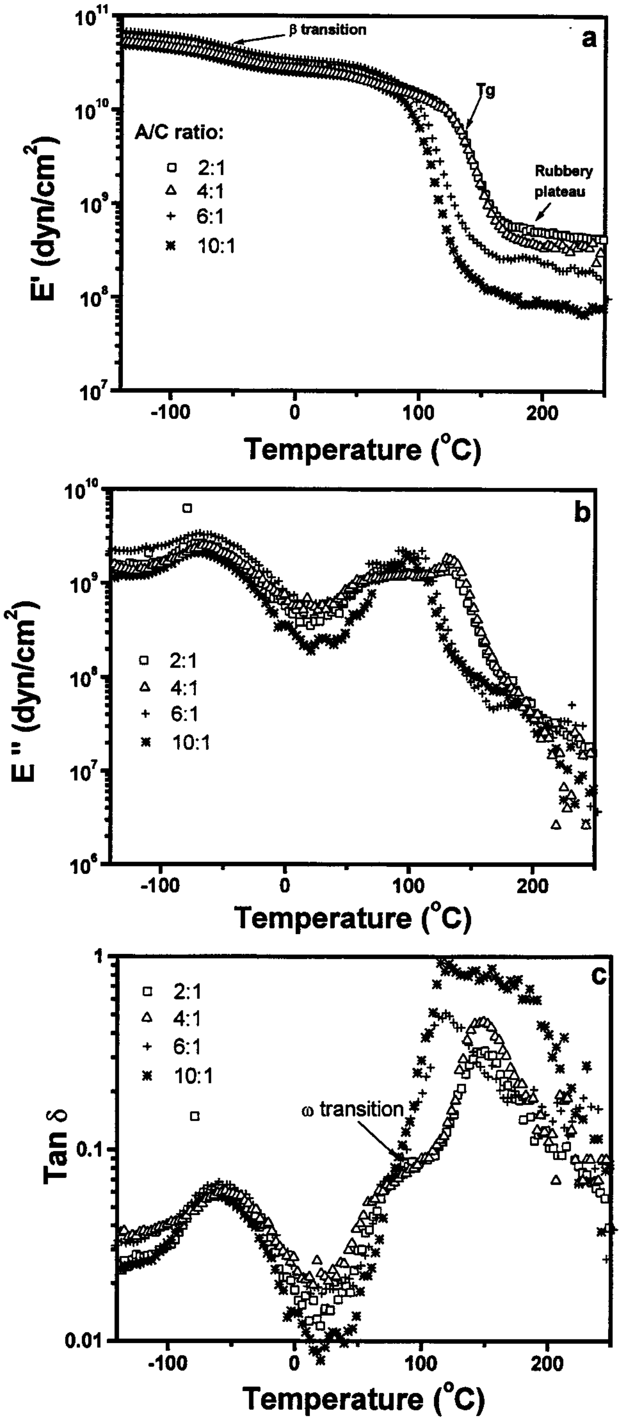

Figure 4. DMTA thermograms of LCTs formed from diepoxide **A**/diamine **C** with different mole ratios.

Samples prepared by curing diepoxide **B** with diamine **C** had poor mechanical properties. However, when a small amount of diepoxide **B** was mixed with diepoxide **A**, the polymer formed had better mechanical properties than that formed by using diepoxide **A** alone (Figure 3). A mole ratio of **A**/**B** equal to 4:1 gave the best results. The tensile modulus and break strength were the largest among all systems studied, but the elongation did not change with the addition of diepoxide **B** (Figure 3). The reason for this is not clear to us.

To study the effect of macroscopic molecular orientation on the mechanical properties of the LCTs, two samples with a diepoxide/diamine mole ratio of 4:1 were cured in a magnetic field. For one sample, only diepoxide

Table 2. Tensile Properties of Selected Samples

sample no.	tensile modulus (GPa)	elongation at break (%)	break strength (MPa)
4 (**A**/**C**, unoriented)	1.44	6.15	15.5
12 (**A**/**C**, oriented)	2.48	10.65	33.4
10 ([**A** + **B**]/**C**, unoriented)	1.85	6.08	20.2
13 ([**A** + **B**]/**C**, oriented)	2.98	11.24	42.5

Table 3. Average Molecular Weight between Cross-Linking Site (M_c) of Final Liquid Crystalline Thermosets

sample no.	2	4	5	6	8	9	10	12
M_c (g/mol)	344	435	905	1911	555	459	956	932

A was used; for the other, the mole ratio of **A**/**B** was 4:1. The measured mechanical properties of the unoriented and oriented polymers are listed in Table 2. The data show that the modulus, break strength, and elongation for both oriented samples were about 2 times as large as the corresponding parameters for unoriented polymer samples. These values are much larger than those of the samples obtained by polymerizing diacrylate liquid crystal monomers in our previous work.[30] The tensile modulus and elongation at break are comparable to those of most commercial epoxy resins, but the break strength is 40−50% smaller.[53] The likely reason for this behavior is the rigidity of the mesogenic core of the monomers, which is nevertheless a basic requirement for the formation of liquid crystals. Using different compounds but the same strength of magnetic field, liquid crystalline epoxy thermosets with higher tensile modulus (~6.5 GPa) was obtained by Benicewicz et al.,[33] but the authors did not report any data on elongation at break and break strength.

The dynamic mechanical properties of epoxy thermosets made from different diepoxide/daimine molar ratios (2/1, 4/1, 6/1, and 10/1) are shown in Figure 4. The lower transition centered around −75 °C, which is called a β relaxation transition, can be attributed to the movement of side chains (either bond bending or stretching) or to the localized movement of the glycidyl ether fragments either between networks or as pendants, though the motions of mesogenic core groups can also have some contribution.[48,54−59] The second more significant transition is a glass transition (T_g) and is characterized by a second maximum in the loss modulus or tan δ in our systems. The transition is affected by the diepoxide/diamine ratio (Figure 4). Between the β and glass transitions, an intermediate ω relaxation appeared in the temperature range from 50 to 125 °C for almost all samples. Traditionally this relaxation has been assigned to unreacted molecular segments or inhomogeneities in the sample arising from dissimilar cross-linking sites.[54,57,60] Therefore, a higher cross-linking efficiency leads to a smaller ω relaxation.

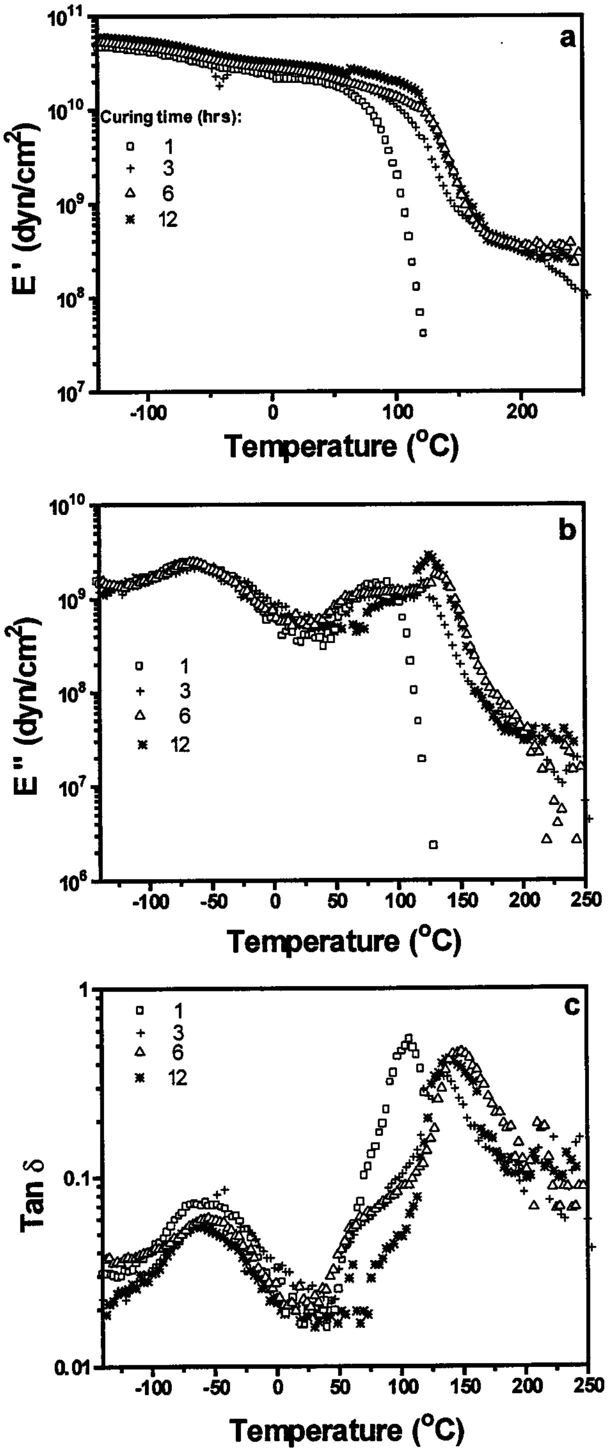

Figure 5. DMTA thermograms of LCTs with a diepoxide **A**/diamine **C** mole ratio of 4:1 and different curing times.

The storage modulus, E', in the plateau region above T_g is proportional to the number of cross-linking density or, alternatively, the chain length between entanglements by the following equation[2,55, 61−64]

$$E' \approx (3\rho RT)/M_c \tag{1}$$

where ρ is the polymer density, which was assumed to be 1.313 g/cm^3, R is the gas constant, T is temperature in kelvin, and M_c is the molecular weight between cross-linking sites. Thus, the M_c values of the final liquid crystalline networks can be calculated from the modulus of the plateau region and are listed in Table 3. For sample with a 2:1 mole ratio, the M_c is 344 g/mol, which is almost the same as $(M_{\text{diamine}} + 2M_{\text{diepoxide}})/3 = 391$, where M_{diamine} and $M_{\text{diepoxide}}$ are the respective molecular weights of diamine cross-linker (184) and diepoxide **A** (494). This suggests that the epoxide groups almost completely reacted with the primary and secondary amino groups. The other samples have larger M_c, indicating smaller cross-linking densities. This is likely due to the increase in self-polymerization of the epoxide groups with the increase in diepoxide/diamine ratio.

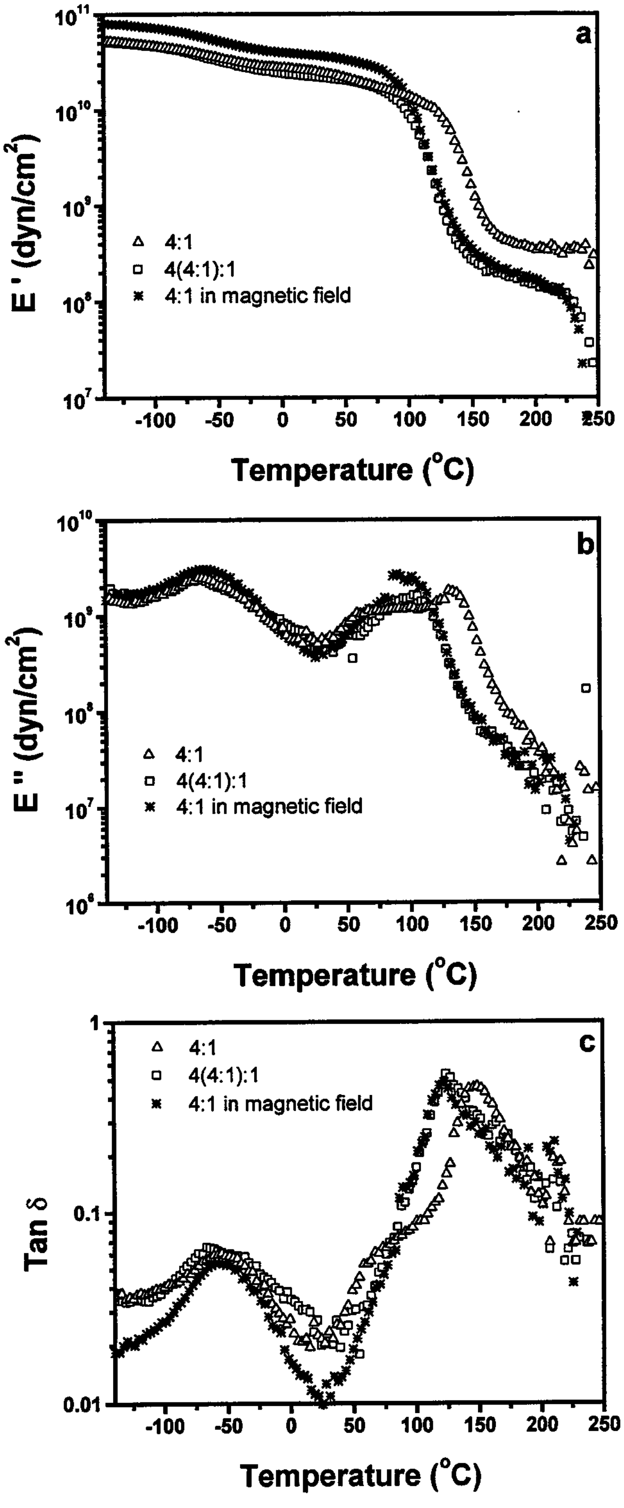

Figure 6. DMTA thermograms of LCTs with diepoxide/diamine mole ratio of 4:1 cured under different conditions. The numbers in parentheses indicated the mole ratio of diepoxide **A**/diepoxide **B**. The other sample did not contain diepoxide **B**.

For the four samples whose DMTA thermograms were studied, the ratio of the cross-linking densities is about 1:0.8:0.4:0.2 (Figure 4a), whereas the corresponding diamine/diepoxide ratios are 0.5:0.25:0.17:0.1. Except for the sample with a 4:1 ratio, the two sets of ratios are nearly the same. The agreement of these ratios indicates that the number of cross-linking inversely correlates with the amount of diepoxide, which is not surprising but is not necessarily predictable either. The trends in Young's modulus noted earlier are almost certainly due to a decrease in cross-linking density; the value of the storage modulus (E') at room temperature in Figure 4 mirrors the trends in Young's modulus. The glass transition temperature also decreases with a decrease in diepoxide, which is expected due to the lower cross-linking density.

To study the effect of curing time on the dynamic mechanical properties, samples with a diepoxide **A**/diamine **C** mole ratio of 4/1 were used. The data in Figure 5 show that the glass transition temperature T_g increases with the increase in curing time, with a corresponding increase in cross-linking density. For the sample cured for 1 h, a plateau was not observed because of insufficient cross-linking. On the other hand, DMTA indicates that curing is nearly complete in about 6 h, which is consistent with the result obtained from the measurement of the tensile properties (Figure 2).

The dynamic mechanical properties of two other samples with a 4:1 diepoxide/diamine mole ratio were studied. For one sample, part of diepoxide **A** was replaced with diepoxide **B** (mole ratio of **A**/**B** = 4:1). For another sample, only diepoxide **A** was used, but the curing was performed in a magnetic field. The replacement of 1/4 of diepoxide **A** with **B** does not change the dynamic mechanical properties significantly in the glassy state but reduces the glass transition temperature and decreases the amount of cross-linking by a factor of 3 (Figure 6). Curing the sample in a magnetic field increases the storage modulus by a factor of about 1.8 from −150 to +70 °C (Figure 6a). This is consistent with the results of the tensile properties (Table 2). Interestingly, the glass transition temperature and the cross-linking density of the oriented sample are smaller than those of the sample cured outside the magnetic field. A possible explanation for this behavior is that the magnetic field aligns the monomer molecules, and the extent of cross-linking is reduced in the curing process.

Conclusions

We have performed a detailed study of the mechanical properties of LCTs prepared from two diepoxides and a diamine under different conditions. Macroscopic orientation of the polymers was achieved by curing the sample in a magnetic field in the nematic phase of the monomers. Compared to samples cured outside the field under the same conditions, the oriented LCTs show an improvement in their tensile modulus, break strength, and elongation at break by a factor of about 2. This is consistent with the result obtained for another type of thermoset at the same magnetic filed strength.[33] More work is in progress to quantify the degree of orientation, to study the optical, IR, and microwave birefringence, and to further improve the mechanical properties.

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