

Influence of the introduction of flexible alkyl chains on the thermal behavior and mechanical properties of mesogenic epoxy thermosets

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ABSTRACT: A mesogenic epoxy resin (DGETAM) was cured with a series of curing agents having different lengths of long alkyl chain (n BAB, $n = 4, 8, 12$). Properties of the curings were compared with those of the DGEBA cured with the same curing agents revealing the achievement of a balance between certain levels of thermal properties and excellent mechanical properties. Moreover, some curing systems were prepared with twin mesogenic type epoxy resins (DGE n MA, $n = 4, 6, 8, 10, 12$) having different lengths of alkyl chain as a flexible spacer and the same curing agents (n BABs). Combinations of the same concentrations of chemical structures in the basic units of the network structure were applied, and the thermal and mechanical properties of their curing systems were investigated. The fracture energy of each system increased considerably with the increase of the alkyl chain length that adjoins the two mesogenic groups in the epoxy resins. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44244.

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INTRODUCTION

Epoxy resins are widely used in industrial products such as adhesives, coatings, paints, and electrical insulation materials. Recently, the demand for functional, high-performance resins has increased, especially for use in electronics.

Mesogenic type epoxy resins, which have rigid-rod-like mesogenic core structures, have attracted strong interest for their unique and excellent properties, such as glass transition temperature (T_g), thermal conductivity, fracture toughness, and bonding.^{1–9}

Previously, we reported that the mono-mesogenic-type epoxy thermosets showed strong mechanical properties because of the effects that the orientation of their network chains containing mesogenic groups have on the fracture process.^{4,6} Therefore, the effective orientation induction of mesogenic groups is one of the good choice for the development of toughened network polymer materials.

On the other hand, some twin-mesogenic-type and mono-mesogenic-type epoxy resins with long flexible chains have also been reported.^{10–19} Moreover, we have reported that the former showed superior bonding strength, compared with conventional epoxy resins and mono-mesogenic-type epoxy resins.¹⁰ This is due to the fact that mesogenic groups slip easily as a result of the introduction of a flexible alkyl chain between two rigid mesogenic groups and because of the consequent decrease in

the internal stress. However, the importance of the locations at which flexible alkyl chains are introduced (between two mesogenic groups or everywhere on the network chains) remains unknown.

In this study, mono- and twin-mesogenic-type epoxy resins were cured with a series of curing agents having different lengths of long alkyl chain. The influence of the introduction of flexible chains to the network structure on the thermal and mechanical properties of the cured systems was systematically investigated.

EXPERIMENTAL

Synthesis of the Diglycidyl Ether of Terephthalylidene-Bis-(4-amino-3-methylphenol) (DGETAM)

DGETAM was synthesized by the condensation of terephthalaldehyde and 4-amino-3-methylphenol followed by epoxidation with chloromethyloxirane.⁶

The synthesized epoxy resin adopted a nematic phase in the temperature range 169 to 212 °C: C 169 N 212 I.

Synthesis of Twin Mesogenic Epoxy Monomers (DGE n MA)

DGE n MA ($n = 4, 6, 8, 10, 12$) were synthesized by almost the same pathway and conditions used in a previous article.¹⁰

The phase transition temperatures of these synthesized epoxy resins are shown in Table I. The chemical structures were identified with IR and NMR, respectively.

Table I. Phase Transition Temperature of Twin Mesogenic Epoxy Resin (DGE*n*MA)

Epoxy resin	Phase transition temperature (°C)	
	Heating	Cooling
DGE4MA	C 170 N 179 I	C 125 N 168 I
DGE6MA	C 169 I	C 140 N 153 I
DGE8MA	C 165 I	C 140 I
DGE10MA	C 128 N 133 I	C 102 N 132 I
DGE12MA	C 132 I	C 97 N 105 I

Synthesis of *n*'BAB

n'BAB (*n*' = 4, 8, 12) as curing agents were synthesized by the reaction of α,ω -dibromoalkane (*n*' = 4, 8, 12) and *p*-amino-benzoic acid in DMF in the presence of K_2CO_3 at 80 °C for 10 h.

The melting points of 4BAB, 8BAB, and 12BAB were 207 °C, 187 °C, 136 °C, respectively.

Curing of the Epoxy Resins (DGEBA and DGETAM)

Epoxy monomer (1.50 g) and a stoichiometric amount of curing agent were combined in an aluminum sample container ($35 \times 15 \times 10 \text{ mm}^3$) and cured for 1 h at 175 °C and for 1 h at 185 °C in an isotropic phase. The chemical conversion of the epoxy groups was over 95% in all cured systems.

Curing of the Epoxy Resin (DGE*n*MA)

Epoxy monomer (1.50 g) and a stoichiometric amount of curing agent were combined in an aluminum sample container ($35 \times 15 \times 10 \text{ mm}^3$) and cured for 2 h at 185 °C in an isotropic phase. The chemical conversion of the epoxy groups was over 95% in all cured systems.

Measurement

The synthesized epoxy monomers and cured resins were incorporated into KBr pellets and analyzed by FT-IR spectroscopy (SPECTRUM 100, Perkin-Elmer, Inc.).

Phase transition temperatures were determined using a differential scanning calorimeter (DSC7020, Seiko Instruments, Inc.) at a heating rate of 5 °C/min.

The LC textures of the epoxy monomer and cured resins were analyzed with cross-polarized light from a polarized optical microscope (POM; BH-2, Olympus Co.). The thickness of the polished curings was approximately 40 μm .

A dynamic mechanical analysis of the cured system was completed using a nonresonance forced vibration viscoelastometer (DVE-V4, Rheology Co., Ltd.) in the tension mode. The frequency and amplitude of the vibration were adjusted to 10 Hz and $\pm 5 \mu\text{m}$, respectively. The heating rate was 2 °C/min and the measured temperature range was $-150 \text{ }^\circ\text{C}$ to 250 °C. The sample dimensions were approximately $4.0 \times 30.0 \times 0.3 \text{ mm}^3$.

The tensile test was carried out according to JIS K7113 (one-fifth type). The length, width, and thickness of the specimen were 30, 2, and 2 mm, respectively. The specimen was mounted in an Instron-type tensile machine (AGS-J, maximum load 1 kN;

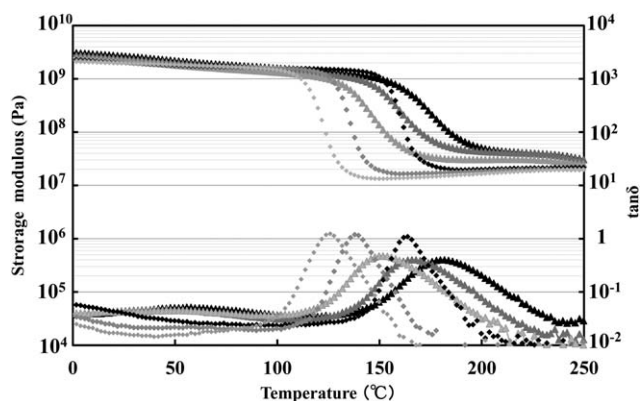


Figure 1. Dynamic mechanical properties of the cured systems. (◆) DGEBA/4BAB, (◆) DGEBA/8BAB, (◆) DGEBA/12BAB, (▲) DGETAM/4BAB, (▲) DGETAM/8BAB, (▲) DGETAM/12BAB.

Shimadzu Corp.) and loaded at a constant test speed (2 mm/min). The fracture energy of each cured system in the tensile test was calculated from the area under the stress–strain curves.

RESULTS AND DISCUSSION

Thermal and Mechanical Properties of DGEBA/*n*'BAB and DGETAM/*n*'BAB

The dynamic mechanical properties of the DGEBA and DGETAM cured with *n*'BAB (*n*' = 4, 8, 12) are shown in Figure 1. Both epoxy-cured systems showed a maximum $\tan \delta$ peak as the T_g value with an increase in the alkyl chain length in the curing agents. However, the T_g of the DGETAM system was always higher than that of the DGEBA system given the same curing agent and alkyl chain length. This suggests that the DGETAM with a rigid mesogenic core had higher thermal stability and maintained the suppressed thermal molecular motion of the whole network structure. In addition, the decrease in the T_g value with an increase in the alkyl chain length of *n*'BAB was smaller than that in the case of DGEBA. This is derived from the self-reinforcement due to the rigid mesogenic groups in DGETAM.

The stress–strain curves of the DGEBA and DGETAM systems obtained by the tensile test are shown in Figure 2. Both epoxy-

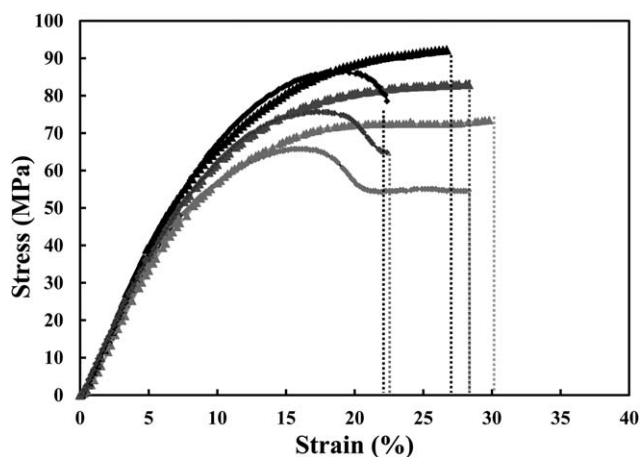


Figure 2. Stress–strain curves of the cured systems. Symbols are the same as in Figure 1.

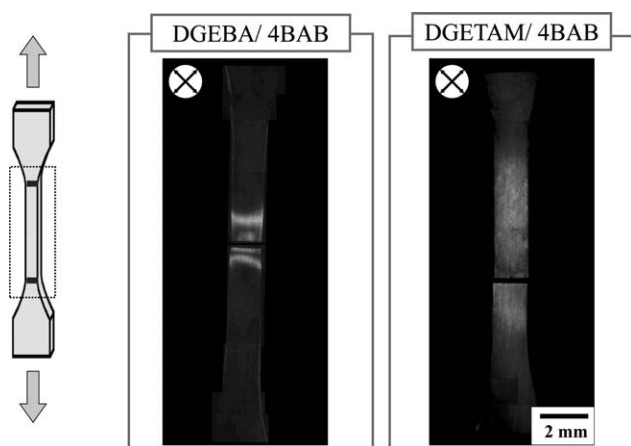


Figure 3. Polarized optical micrographs of the test specimens after the tensile test.

cured systems showed a decreased tensile modulus as the alkyl chain length of n' BAB increased. However, while all DGEBA systems showed a clear yielding point, all DGETAM systems showed a maximum stress just before the fracture. Therefore, their fracture energy calculated from the S-S curve's area became higher in the DGETAM system than in the DGEBA system cured with the same curing agent. To investigate how the different behaviors of the S-S curves of these systems occur, POM images of the DGEBA and DGETAM cured with 4BAB after fracturing are shown in Figure 3. Because both systems showed a dark field over the sample before fracturing, it could be confirmed that they are each composed of an amorphous network structure. However, the fractured samples showed a bright field especially near the broken area in the test specimen, and the area was considerably larger in the DGETAM system. This phenomenon indicates that the sample deformation in the DGETAM system occurred on a larger scale. Similar behavior has already been observed in many epoxy resin systems that have a rigid and planar mesogen core structure. We have also reported that the DGETAM cured with DDM showed high fracture toughness because of the orientation of the mesogenic group on the fracture process.⁴ Because of n' BAB (an aromatic amine with a flexible long alkyl chain) was the curing agent, it is considered that the network chains containing a mesogenic group can easily arrange themselves along the stress direction over a wide range of the test specimens.

The relationships between the alkyl carbon number of a curing agent and the T_g or fracture energies of the DGEBA and DGETAM systems are shown in Figure 4. As previously mentioned, the T_g values of both epoxy systems decreased with an increase in the alkyl carbon number of a curing agent, though the degree of T_g decrement was smaller in the DGETAM system. On the other hand, the fracture energy of the DGETAM systems was always much higher than that of the DGEBA systems, regardless of the difference in alkyl chain length of the curing agent. This is due to the decrease in the tensile modulus derived from the introduction of the long flexible chain to the network chains.

Thermal and Mechanical Properties of DGE n MA/ n' BAB

The effect of the introduced alkyl chain as a long flexible chain on the mobility of the network chains was investigated. Figure 5

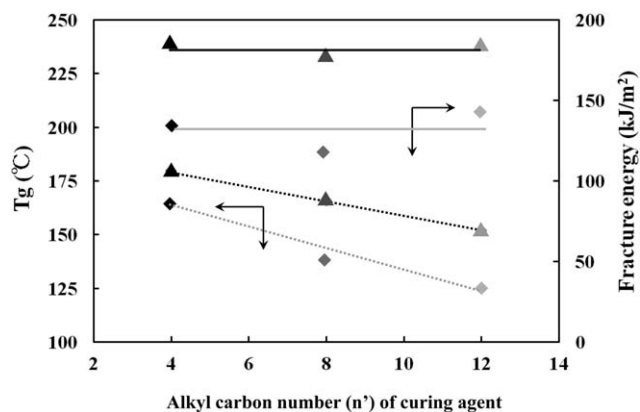
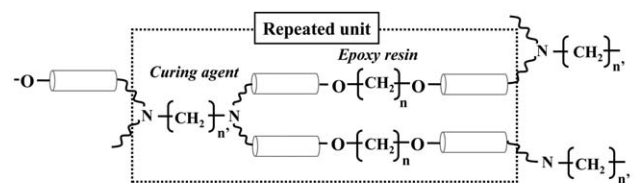


Figure 4. Relationships between the alkyl carbon number (n') of a curing agent and the T_g and fracture energies of cured systems. Symbols are the same as in Figure 1.

shows a series of prepared curing systems. Three types of DGE n MA/ n' BAB system, whose basic structural units had 20, 24, and 28 total carbon numbers, respectively were selected. Simultaneously, the concentration of the mesogenic groups was the same in each series of curing systems. Though these curing systems have the same carbon numbers in the basic structural units if the total carbon numbers are the same, the flexible chain is located in the middle of two mesogenic groups or in the backbone structure in the curing agent. These systems, and the influences of the flexible chain on their thermal and mechanical properties, should be clarified and compared.

The dynamic mechanical properties of DGE4MA/12BAB, DGE6MA/8BAB, and DGE8MA/4BAB are shown in Figure 6. The T_g shown as the peak of $\tan \delta$, was always 120 °C in all these systems, with a total alkyl carbon number of 20 in the basic structural unit. As the temperature increased, the modulus and $\tan \delta$ of all systems exhibited almost the same behavior, and there was no observed influence of the location at which the long alkyl chains were introduced. These results indicate that, in the DMA measurement in which the small-scale deformation was applied, the total carbon number of the basic structural unit dominates the molecular motion in the whole network chain structure and the mobility of the network chain



Carbon number of DGE n MA/ n' BAB systems (Concentration of mesogenic groups)

Epoxy resin	Curing agent		
	4BAB	8BAB	12BAB
DGE4MA	12 (45%)	16	20
DGE6MA	16 (44%)	20	24
DGE8MA	20 (42%)	24	28
DGE10MA	24 (41%)	28	32
DGE12MA	28 (40%)	32	36

Figure 5. Network structures of the DGE n MA/ n' BAB systems.

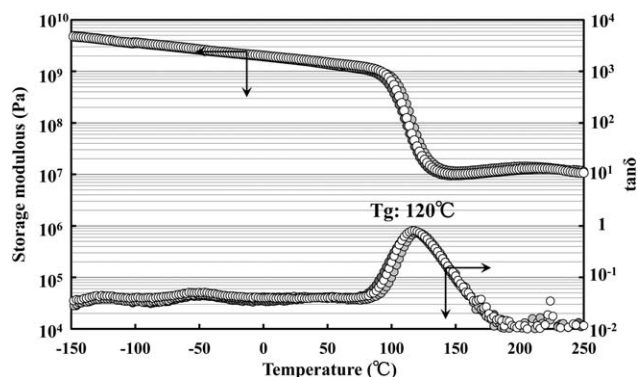


Figure 6. Dynamic mechanical properties of the DGE n MA/ n' BAB systems (total alkyl carbon number: 20). (○) DGE4MA/12BAB, (●) DGE6MA/8BAB, (◐) DGE8MA/4BAB.

is independent of the location of the introduced alkyl long chain.

The stress–strain curves of the DGE4MA/12BAB, DGE6MA/8BAB, and DGE8MA/4BAB are shown in Figure 7. In all systems, though the stress–strain curves showed clear yielding points, the initial modulus at the linear region presented the same values. In the small-scale deformation region, the sample behaved in the same way as a function of the concentration of flexible chains in the network structure, as was the case with DMA measurement. For the originally superior plastic deformability of mesogenic-type epoxy systems, the mesogenic groups in these systems also slipped against each other when the external stress was loaded. The degree of plastic deformation increases with increasing length of the flexible chain that adjoins the two mesogenic groups of epoxy resin. On the other hand, the strain displayed a characteristic change. This result suggests that the deformability of the network chains was strongly affected by the location of the flexible chain even though the total carbon number of the basic structural unit did not change.

The relationship between T_g and fracture energy with increasing alkyl carbon number of the DGE n MA is shown in Figure 8. Regardless of the total carbon number of the basic structural unit (20, 24, 28), the fracture energies of the systems increased

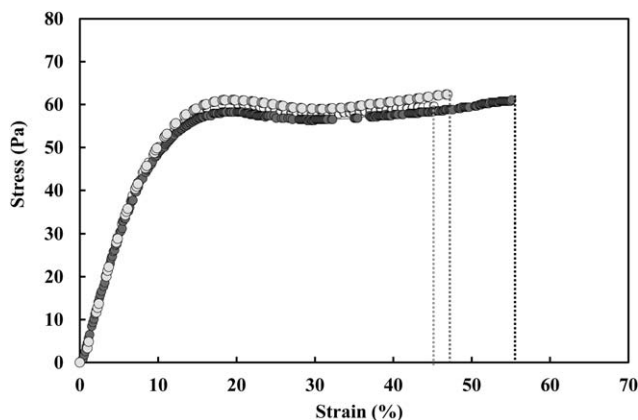


Figure 7. Stress–strain curves of the DGE n MA/ n' BAB systems (total alkyl carbon number: 20). Symbols as in Figure 6.

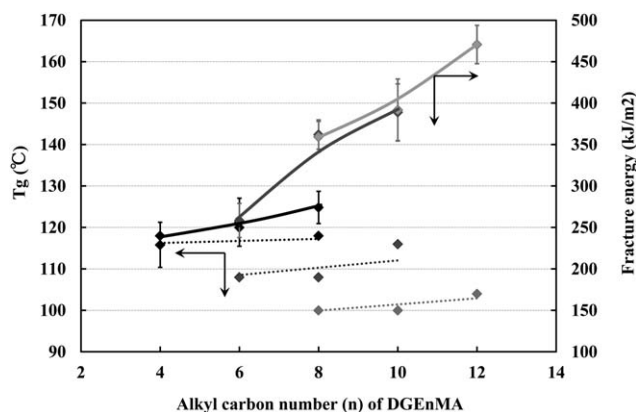


Figure 8. Relationships between alkyl carbon number of DGE n MA and, the T_g and fracture energies of the DGE n MA/ n' BAB systems. (◆): $2n + n' = 20$, (◇) $2n + n' = 24$, (●) $2n + n' = 28$ systems.

vigorously with increasing length of the alkyl carbon number (n) of DGE n MA, though the difference in T_g values was within 10 °C. These results suggest that the introduction of a longer flexible chain between the two mesogenic groups is considerably valuable for the compatibility of the superior mechanical properties and high T_g .

CONCLUSIONS

Given the same total carbon number of the basic structural unit, the modulus and $\tan \delta$ of all systems in DMA exhibited almost the same behavior, and there was no clearly observed influence of the location at which the long alkyl chains were introduced. On the other hand, the degree of plastic deformation increases with increasing length of the flexible chain that adjoins the two mesogenic groups of epoxy resin.

The relationship between T_g and fracture energy with increasing alkyl carbon number of the DGE n MA was discussed. Regardless of the total carbon number of the basic structural unit, the fracture energy of the series of systems increased vigorously with increasing length of the alkyl carbon number (n) of DGE n MA.

The results clarified that the introduction of a longer flexible chain between the two mesogenic groups is considerably valuable for the compatibility of the superior mechanical properties and high T_g .

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