

Viscoelastic Properties of Epoxy Resin. I. Effect of Prepolymer Structure on Viscoelastic Properties

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Synopsis

The intermolecular cyclization reaction is investigated in highly crosslinked epoxy systems, where diepoxides with different mobilities between terminal epoxy groups were crosslinked with ethylene diamine. Based on the measured values of the Clash-Berg 10-sec modulus in the rubbery region, the correlation between the mobility and the cyclization reactivity of the diepoxides is discussed. The epoxide with higher mobility is found to have a higher rubbery modulus than that with lower mobility, as was expected. This is tentatively explained by the difference in the reactivity of the formation of the 11-membered ring. Dynamic mechanical measurements were also run on a forced vibration apparatus. The higher β -transition peak of the polymer of bisphenol-A diglycidyl ether was interpreted in terms of its higher free volume as well as lower density and lower glassy modulus. The higher modulus in the glassy region of ethylene glycol diglycidyl ether-ethylenediamine was explained on the basis of hydrogen bonding.

INTRODUCTION

This work is part of a study to elucidate the correlation between physical properties and chemical structure in highly crosslinked polymer systems.

The properties of crosslinked polymers are well known to be markedly affected by physicochemical properties such as chemical structure of network and degree of crosslinking, the latter being influenced by the extent of inter- and/or intramolecular joint reaction with starting prepolymers or polymers. Moreover, the mobility of ring units involved in crosslinked network chains was revealed to have a significant effect on the glass transition temperature and viscoelastic properties of polymers as observed in crosslinked diallyl succinate-type polymers.¹

Therefore, in the present paper, four kinds of diglycidyl ethers (see Table I) with different chain mobilities between terminal epoxy groups were prepared and crosslinked with ethylenediamine, and the shear modulus and dynamic mechanical properties were obtained as a function of temperature for the crosslinked polymers derived therefrom.

We wish to discuss the influence of the cyclization reactivity reflecting the mobility of the diepoxides employed upon the network structure and mechanical properties based on the measured viscoelastic properties.

EXPERIMENTAL

Materials

Diglycidyl ether of resorcinol and catechol (DGER and DGEC) were experimental resins which were prepared by the reaction between a corresponding dihydric phenol and a large excess of epichlorohydrin in the presence of sodium hydroxide, followed by repeated fractional distillations. Both epoxides are crystalline at room temperature.

Diglycidyl ether of ethylene glycol (DGEEG) was prepared according to the method described in the literature² and purified by repeated fractional distillations.

Diglycidyl ether of 4,4'-isopropylidene diphenol (bisphenol-A) (DGEBA) was obtained from a commercial resin (Epikote 828) by molecular distillation.

The oxirane oxygen content was determined by the HCl-dioxane method³ and is given in Table I.

Ethylenediamine (EDA) was reagent grade and was used without further purification.

Preparation of Specimens

Epoxides were cured at room temperature with ethylenediamine for 24 hr, followed by heating at 150°C for 5 hr in a draft oven. A small excess of the curing agent was used to assure complete reaction of the epoxy groups. Formulations for curing are as follows: DGER, 13.5 phr EDA; DGEC, 13.5 phr EDA; DGEEG, 16.6 phr EDA; DGEBA, 8.6 phr EDA.

The extent of cure was checked by infrared spectroscopy for the cured films; a noticeable absorption peak due to epoxy groups at 915 cm^{-1} could not be found for any of the films.

The specimens used for the Clash-Berg measurements were machined into rectangular strips ($0.6 \times 0.3 \times 5.0$ cm) from cast plates. The specimens for dynamic mechanical measurements were carefully cut into $0.1 \times 0.01 \times 2.5$ cm strips from cast films and kept dry in a desiccator.

Measurements

Shear modulus-temperature measurements and dynamic mechanical properties-temperature measurements were carried out over a wide temperature range in order to cover the entire viscoelastic spectrum from the glassy high modulus to the rubbery plateau region. Shear modulus was determined accurately with a Clash-Berg torsional apparatus in a silicone oil or methanol bath with a repeatability of $\pm 10\%$. In the present work, 3×10 sec shear modulus ($\approx E$) was plotted against temperature.

TABLE I
Epoxy Prepolymers

Code	Structure	Oxirane oxygen, %	
		Found	Calcd.
DGER		13.86	14.41
DGEC		13.25	14.41
DGEEG		17.63	18.26
DGEBA		9.17	9.41

Dynamic property mean the mechanical loss tangent and was measured on a Vibron DDV-II dynamic viscoelastometer (a forced vibration apparatus) at 3.5 to 110 Hz and a heating rate of 1°C/min using an air bath.

RESULTS

The shear modulus-temperature curves are shown in Figure 1. In this figure, all modulus-temperature curves show clearly a glassy region, a transition region, and a rubbery region, which are typical for highly cross-linked systems.

The inflection temperature, T_i , was defined as the temperature where

$$\log 3G = \frac{\log 3G_{\text{glassy}} + \log 3G_{\text{rubbery}}}{2}$$

and is obtained by manipulation as shown in Figure 2. Glassy modulus, $3G_1 = 3G$ at $T = T_i - 50$, rubbery modulus $3G_2 = 3G$ at a minimum point, and ω , the width of the transition region in degrees, were determined from these curves. These parameters are listed in Table II. From the equation of rubber elasticity, a front factor was calculated for each system⁴:

$$G = \Phi z c R T$$

where Φ = front factor, z = number of network chains per crosslinking molecule (4/2), c = moles of amine molecule per cc, R = gas constant, T

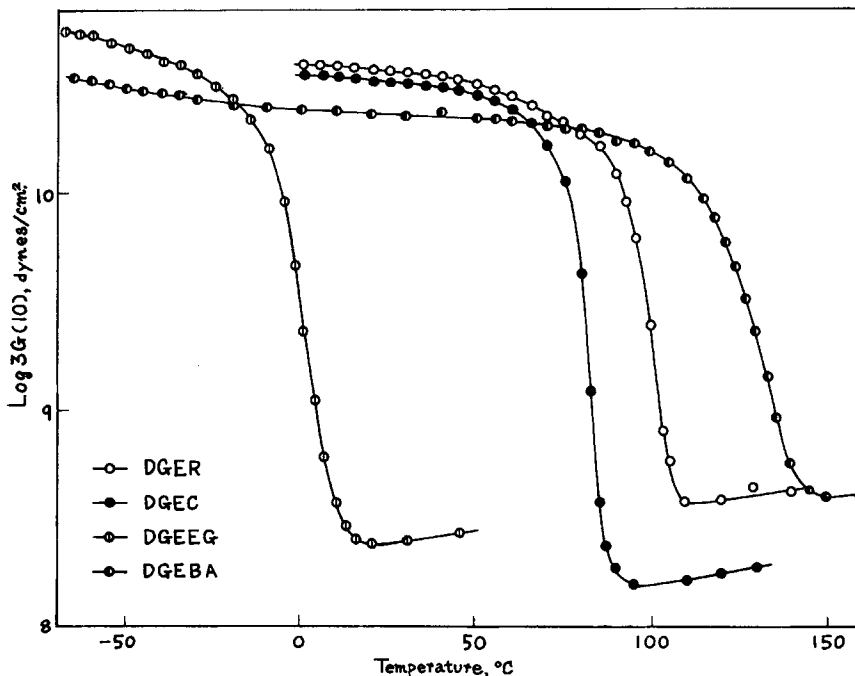


Fig. 1. Modulus-temperature curves for crosslinked epoxy resins.

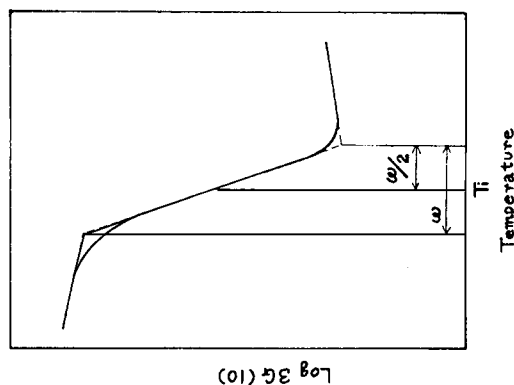


Fig. 2. Inflection temperature determination.

= absolute temperature. The calculated front factors are listed in Table III.

Mechanical loss tangent data represented by 11-Hz curves are shown in Figure 3. From these curves, we can inspect the information concerned with molecular motions in each system by assigning dispersions. Table IV presents these dispersions. Transition temperature is defined as a peak temperature in the loss tangent-temperature curves. From the shift of loss tangent peak by varying frequency, the apparent activation energy ΔE for the segmental motions in the glass transition region was calculated. The values of ΔE are also presented in Table IV.

TABLE II
Viscoelastic Parameters from Modulus-Temperature Curves

Epoxide	Hardener	T_i , °C	ω	Glassy modulus $3G_1$ at $T_i - 50$	Rubbery modulus $3G_2$
DGER	EDA	102	15	3.11×10^{10}	3.88×10^8
DGEC	EDA	84	10	3.25×10^{10}	1.56×10^8
DGEEG	EDA	0	19	4.72×10^{10}	2.48×10^8
DGEBA	EDA	129	29	2.03×10^{10}	4.10×10^8

TABLE III
Front Factor for Crosslinked Epoxy Resins

Epoxide	$3G_2$ found	T_r , °K	Specific gravity at T_r	Front factor
DGER	3.88×10^8	386	1.25	0.81
DGEC	1.56×10^8	370	1.26	0.34
DGEEG	2.48×10^8	293	^a	0.72d
DGEBA	4.10×10^8	423	1.15	1.31

^a Could not be measured.

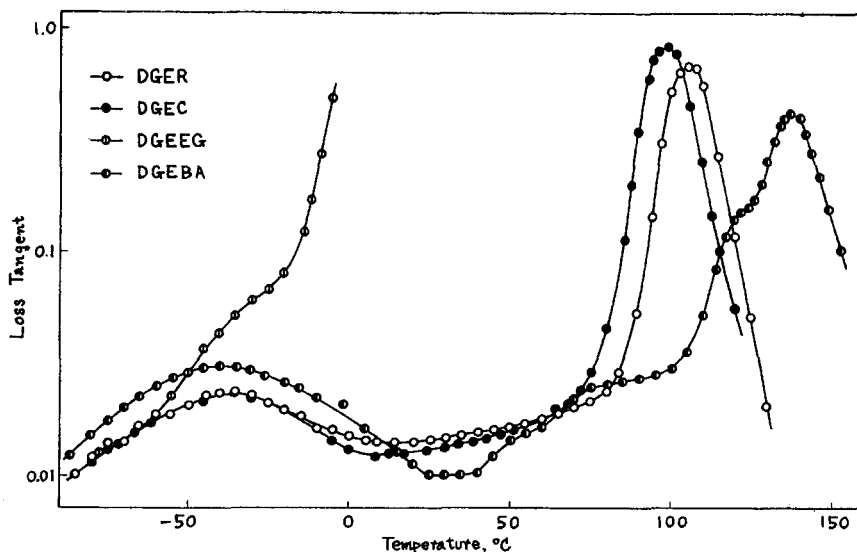


Fig. 3. Mechanical loss tangent-temperature curves for crosslinked epoxy resins.

TABLE IV
Transitions of Crosslinked Epoxy Resins (11 Hz)

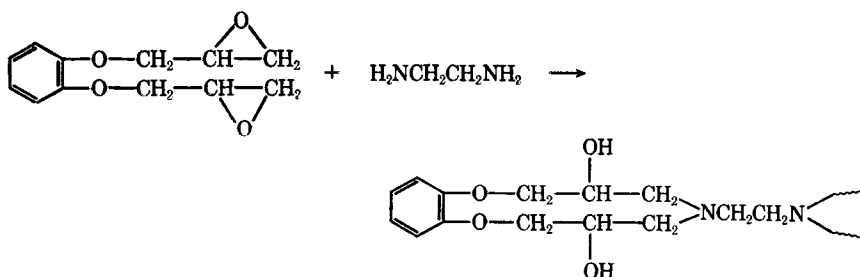
Epoxide	β -Transition, °C	α -Transition, °C	Apparent activation energy, kcal/mole
DGER	-37	110	191
DGEC	-38	98	172
DGEEG	-35	(0)	—
DGEBA	-42	138	191

DISCUSSION

Cyclization Reaction of Diepoxides

Modulus in Rubbery Region

The modulus in the rubbery plateau region is well known to be a direct measure of the degree of effective crosslinking in crosslinked polymer systems. The DGER-EDA resin has a higher rubbery modulus, more than double, than the DGEC-EDA polymer. The rubbery modulus for the two systems should be similar in view of their structural similarity as diepoxy prepolymer. Accordingly, it was attempted to explain the difference in rubbery modulus in terms of their crosslinking densities; in other words, the cyclization reaction between an amino group of EDA and both epoxy groups in DGEC may lead to the formation of an 11-membered ring as shown below, resulting in a decrease in effective crosslinking density:



In the DGEC-EDA system, the 11-membered ring was easily constructed by a Stuart-type molecular model, which shows several stable conformations, whereas in the DGER-EDA system, the formation of a similar type of ring was found to be difficult because of remarkable strain.

The DGEEG-EDA system is also assumed to form a similar stable 11-membered ring according to the mobile characteristic of the prepolymer chains, and actually the stable 11-membered ring structure can be derived easily within the molecular framework. However, a higher rubbery modulus was found for this system, indicative of less contribution of ring formation to the crosslinking reaction than the other epoxide. The free rotation at the carbon-carbon bond in the ethylene glycol unit of the prepolymer may diminish the probability of taking ring conformations at the occurrence of the reaction with EDA. This becomes evident by comparing the difference in mobility of the $-\text{O}-\text{C}-\text{C}-\text{O}-$ chain in both DGEEG and DGEC, as shown below:



Obviously, the former has a more flexible C-C chain than the latter, which has a fixed double bond of the benzene ring. The synthesis and characterization of a model compound containing the 11-membered ring is in process in this laboratory.

Front Factor

We obtained a front factor value for the DGEBA-EDA similar to that obtained by Katz and Tobolsky (1.31 versus 1.36).⁴ The front factors for DGER, DGEC, and DGEEG resins are smaller than unity, which suggests that the chains of segments involved in the network are not stretched. Furthermore, the front factor is considered to be a measure of cyclization reactivity as suggested by the low value for the DGEC resin.

Inflection Temperature

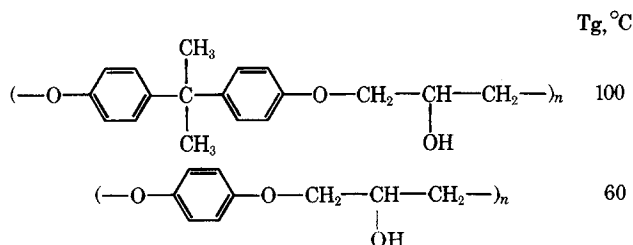
The inflection temperature T_i has been thought to be within a few degrees of the glass transition temperature for amorphous polymers.⁵ The order of

T_i , DGEBA > DGER > DGEC, is in agreement with the results obtained elsewhere.

The difference in T_i between the DGER and DGEC systems can be explained by the effect of symmetry of the diphenoxy group upon the glass transition temperature, as illustrated by the following examples of polyethylene phthalates⁶:

	$T_g, ^\circ\text{C}$
polyethylene terephthalate	69
polyethylene isophthalate	51
polyethylene phthalate	17

The difference in T_i between the monophenylene and bisphenylene polymers is easily understood from the data of the phenoxy-type resins shown below⁷:



DGEBA-EDA has the highest inflection temperature, highest front factor, broadest transition region, and somewhat lower glassy modulus. These results should be attributed to its bulky and rigid bisphenol-A structure, as described later. The width of the transition region, ω , is a measure of plurality of molecular motions of chains involved in the network matrix. The wider transition region of the DGEBA resin can be interpreted as a more complexed nature of the motion on the bisphenol-A unit.

Modulus in the Glassy Region

As may be seen from the results shown in Figure 1, the largest glassy modulus is given for DGEEG and the smallest, for DGEBA, and those of both DGER and DGEC are between the two and comparable to each other.

Heijboer⁸ reported that polarity is the most effective means for increasing the modulus in the glassy region. This is understandable, as the modulus in the glassy region is determined primarily by van der Waals forces, and these forces are increased to a greater extent by an increase in polarity. Here, we take a parameter from the theory of liquid solubility, known as solubility parameter, the square root of the cohesive energy density, to express the level of polarity. Thus, the order of glassy modulus is in good

agreement with that of the solubility parameters calculated after Hoy's values⁹ (see Table V).

The order is also proportional to the calculated concentrations of hydroxyl groups introduced in each crosslinked polymer at complete consumption of epoxy and amine compounds, that is, to the concentration of hydrogen bonding. The presence of three types of hydrogen bonding in amine-cured epoxides, OH—O (hydroxyl), OH—O (ether), and OH—N, was pointed out by Harrod.¹⁰ The effect of the presence of hydrogen bonding on the viscoelastic properties of polymer in the glassy region is not clearly understood

TABLE V
Polarity of Crosslinked Epoxy Resins

Epoxide	Solubility parameter	Hydroxyl content, mole/g
DGEEG	12.0	9.78×10^{-3}
DGER	11.2	7.92×10^{-3}
DGEC	11.3	7.92×10^{-3}
DGEBA	10.0	5.40×10^{-3}

yet. However, the presence of hydrogen bonding in the crosslinked epoxy resins seems to play an important role in diminishing intermolecular distance, therefore in increasing glassy modulus.

Mechanical Dispersions

All of the dynamic mechanical curves show clearly an α -transition as well as a β -transition. The β -transition was first recognized by Kaelble¹¹ and was also observed by other investigators hereafter.^{12,13} The reason for the β -transition has been ascribed to segmental motion of the hydroxyl ether portion in the network, probably a crankshaft-type rotation.^{14,15}

In comparing all the polymer systems, lower density, lower glassy modulus, and a higher β -transition peak were observed for the DGEBA-EDA. These results can be interpreted as a result of a larger free volume of the DGEBA-EDA, due to the rigid bisphenol-A structure.

A shoulder at 123°C in DGEBA-EDA loss tangent curve may be a sign of heterogeneity caused by microgel formation in the curing process as proposed by Kenyon and Nielsen.¹⁶ The values of the apparent activation energy for the glass transition seem to have a similar relation to the values of the α -transition temperature.

The shape and depth of the β -transition peak of DGER and DGEC are similar, and no other peak was observed. The contribution of the 11-membered ring to viscoelastic properties is apparently not recognized for DGEC-EDA. The reason for this is that the 11-membered ring formed is pendant and not included in the main chains, and does not contribute significantly to the segmental motions of the networks. However, lower temperature measurement (lower than -100°C) should be necessary to investigate further the segmental motions of the 11-membered ring.

CONCLUSIONS

1. The primary effect of changing the mobility between terminal epoxy groups in epoxy prepolymers is to effect a different degree of cyclization reactivity during the crosslinking reaction. Thus, the diglycidyl ether of catechol—an epoxide of low mobility—gives a high degree of 11-membered ring formation; on the other hand, the diglycidyl ether of ethylene glycol—an epoxide of higher mobility—has a less cyclized structure.

2. The polymer from the diglycidyl ether of bisphenol-A has the highest front factor, which suggests the lowest degree of cyclization.

3. The polymer from the diglycidyl ether of bisphenol-A appears to have a higher free volume than the other systems. This may be verified by a lower glassy modulus, lower density, and higher peak of β -transition in the loss tangent curve.

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