Viscoelastic Properties of Epoxy Resins. III. Effect of Molecular Weight of Antiplasticizers in Highly Crosslinked Antiplasticization System

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Synopsis

Antiplasticization, defined as an increase in glassy modulus of polymers upon dilution with low molecular weight compounds, was studied for highly crosslinked epoxy resins. A series of oligomers with average molecular weight 500–4000 was incorporated with epoxy resins for elucidating the effect of their molecular weight on antiplasticization. The antiplasticization was found to be dependent on the molecular weight of the oligomers used. It was most evident when the lowest molecular weight oligomer was incorporated, and seems to be suppressed by increasing molecular weight of the oligomers. These results were discussed in correlation with the behavior of dynamic mechanical properties and the changes in specific volume as a function of the epoxy resin and diluents.

INTRODUCTION

Antiplasticization has been defined as an increase in glassy modulus of polymers upon incorporation of low molecular weight compounds and explained as the filling of free volume by the added low molecular weight compounds.[1] Recently, an increasing number of articles relating to the antiplasticization of polymers has been published, which were mainly devoted to that of thermoplastics such as poly(vinyl chloride), polycarbonate, polysulfone, etc.[2-5]

As regards to the antiplasticization in thermosetting resins, the study of their characteristic behavior in antiplasticization should be quite helpful to elucidate the structure of three-dimensional networks.

An extensive study on the structure and dimension of antiplasticizable compounds in polycarbonate and related polymers was conducted by Jackson and Caldwell.[6] For highly crosslinked epoxy resins, polychlorobiphenyl and phenol-endcapped glycidyl ether of 2,2-bis(4-hydroxyphenyl)propane were found as effective antiplasticizers.[1]

In the present paper, we wish to discuss the effect of molecular weight or molecular size of diluents on the antiplasticization of epoxy resins using oligomers with different molecular weights or molecular weight distributions. The oligomers were a series of phenol-endcapped diepoxides of 2,2-bis(4-hydroxyphenyl)propane, which was chosen because of the ease in obtaining homologs with different molecular weights and their excellent compatibility with the crosslinked matrix.

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A purified diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane–ethylenedi-amine resin was used as the polymer matrix.

EXPERIMENTAL

Diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane (DGEBA) used in this work was obtained by molecular distillation of a commercial epoxide. Its oxirane oxygen content by the HCl–dioxane method was 9.17% against the calculated value 9.41%. Ethylenediamine (EDA) was reagent grade and was used without further purification.

TABLE I
Structure and Properties of Materials

Matrix

Diluents

	n^a	Softening point, °C[b]	Density at 25°C
Matrix	—	—	1.196
DGEBA-P1	0.1	viscous liquid	1.178
DGEBA-P2	2	80	1.196
DGEBA-P3	9	119	1.188

[a] Approximate average value.
[b] Ring-and-ball method, ASTM E28-51T.

Three kinds of diluents were prepared by the reaction between corresponding epoxy prepolymers and phenol in the presence of a basic catalyst, followed by distilling off excess phenol under vacuum. Their structure, properties, and gel permeation chromatograms are shown in Table I and Figure 1, respectively. Their gel permeation chromatograms show that they are mixtures of homologs with different molecular weights. The principal constituent of DGEBA-P1 is a compound where $n = 0$ in the formula of Table I and whose molecular weight is 528. The M_n values of DGEBA-P2 and DGEBA-P3 are estimated as 1100 and 4000, respectively, from the obtained epoxide equivalent weight of their original epoxy prepolymers. The molecular weight corresponding to the peak in the molecular weight distribution curve of DGEBA-P3 is shown to be 5600 from extrapolation of the effective carbon number–elution volume relationship.[7] The higher density of DGEBA-P2 than that of DGEBA-P3 may be explained as a phenomenon of packing or self-filling effect where lower molecular weight oligomers fill the free volume of higher molecular weight ones in the solid state.[8]

The epoxide with or without a diluent was cured with a stoichiometric amount (8.6 phr) of ethylenediamine at room temperature for 40 hr, then postcured at 150°C for 5 hr.

Ten-second shear modulus was determined over a broad temperature range with a Clash–Berg torsional apparatus in a silicon oil bath. A heating rate of 1°C/min was used, and the specimens were of dimensions 0.3 × 0.6 × 6.0 cm. Compressive properties were measured on an Autograph IS-2000 type stress–strain tester using 1.5 cm ϕ × 3.0 cm sized bars. The relative rate of compression of the grips was 5 mm/min. Mechanical loss tangent was determined with a Vibron DDV-II dynamic viscoelastometer at 11 Hz and a heating rate of 1°C/min in an air bath. The specimens for the measurements were 0.1 × 0.01 × 2.5 mm strips. Specific gravity of the diluents and cured resins was measured by a flotation method.
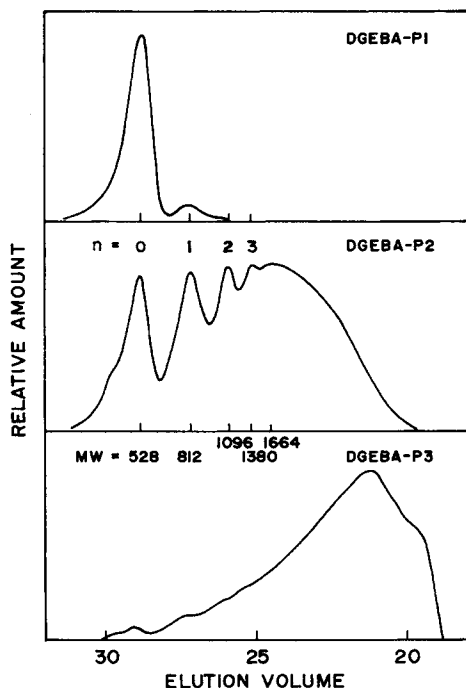

Fig. 1. Gel permeation chromatograms for diluents.

RESULTS AND DISCUSSION

Modulus–Temperature Relationship

Plotted in Figure 2 are 3 × 10 sec modulus ($\approx E$)-versus- temperature curves for the samples cured in the presence of DGEBA-P1. All of the curves show clearly three regions of viscoelastic behavior—a glassy region, a transition region, and a rubbery region—which are characteristic for highly crosslinked polymer systems. Similar curves were also obtained for the epoxy resins incorporated with DGEBA-P2 or DGEBA-P3, respectively. From these curves, flexural
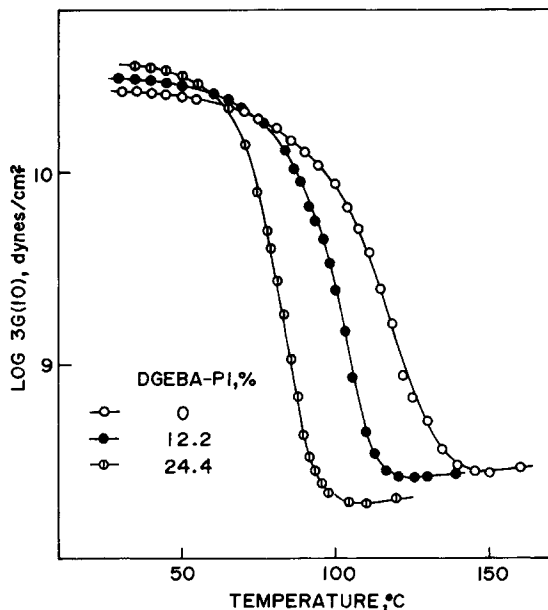
Fig. 2. Modulus–temperature curves for antiplasticized epoxy resins.

temperature T_i and glassy modulus at 25°C were obtained and plotted against the weight fraction of diluents (Figs. 3 and 4).

Upon dilution with DGEBA-P1, the transition region of the epoxy resins shifted to lower temperatures and the modulus in the rubbery regions was seen to decrease, which is considered to be an ordinary plasticizing or dilution effect. The antiplasticizing effect is recognized eminently in the increase in glassy modulus. Figure 3 shows that DGEBA-P2 still has the antiplasticizing effect, though less effective than DGEBA-P1 at the same level of dilution. DGEBA-P3, the diluent with the largest molecular weight of the used has not shown any antiplasticizing effect in the glassy modulus observation.

Concerning the inflection temperature T_i, the addition of DGEBA-P1 and DGEBA-P2 is shown to lower it. DGEBA-P1 is most effective in decreasing T_i. The inflection temperature of the diluted epoxy resins should reflect the glass transition temperature of the epoxy resin and diluents, and also should be a function of the extent of crosslinking of epoxy resins matrix in the presence of the diluents. Within the present dilution level, the extent of epoxide reaction in the diluted systems may not be very much different from that in the undiluted ones, because T_i–diluent concentration curves stay linear.

Stress–Strain Tests

Stress–strain tests in compression were made. The parameters such as Young's modulus, yield strength, break strength, and break strain obtained from the measured stress–strain curves (Figs. 5 and 6) are tabulated in Table II. The compressive modulus and yield strength are plotted against the contents of diluents in Figures 7 and 8.

As may be seen in Figures 7 and 8, DGEBA-P1 is shown to increase the modulus and yield strength of the epoxy resins, while giving little effect on the ultimate compression.
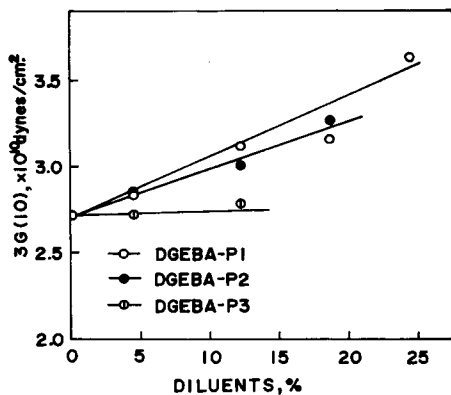
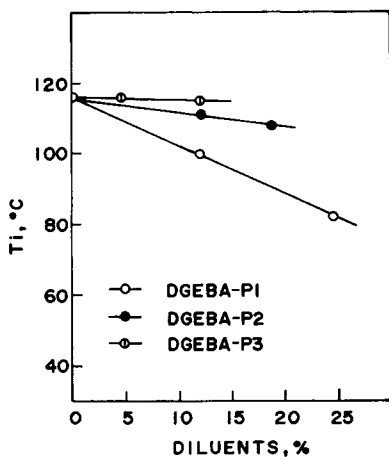Fig. 3. Relationship between 3× shear modulus and diluent content.

Fig. 4. Relationship between inflection temperature and diluent content.

DGEBA-P2 is still an antiplasticizer but less effective than DGEBA-P1 in increasing the compressive modulus, whereas the yield strength remains almost constant at a dilution level of up to 18.7% DGEBA-P2. The highest molecular weight diluent, DGEBA-P3 has no antiplasticizing effect upon compressive modulus. The measured yield strength rather seems to decrease with increase in the amount of DGEBA-P3 (Figs. 6, 7, and 8). The effect of the molecular weight of diluents in antiplasticization is again recognized in the stress–strain measurements.

Dynamic Mechanical Measurements

Mechanical loss tangent–temperature data were measured at 11 Hz for the epoxy resins with or without diluents (Fig. 9). Crosslinked epoxy resins are known to have a local transition (β-transition) in a low-temperature region in some viscoelastic or dielectric spectra. The β-transition of crosslinked epoxy resins has been ascribed to the crankshaft motion of their hydroxy ether portion.[9] Generally, the magnitude of the β-transition of polymeric materials is thought to have a close relation with the free volume at the glassy state.
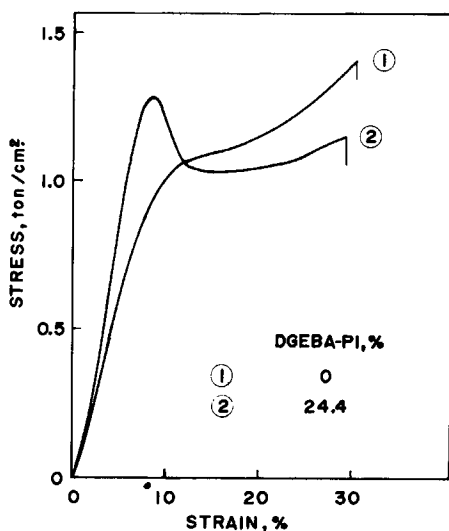
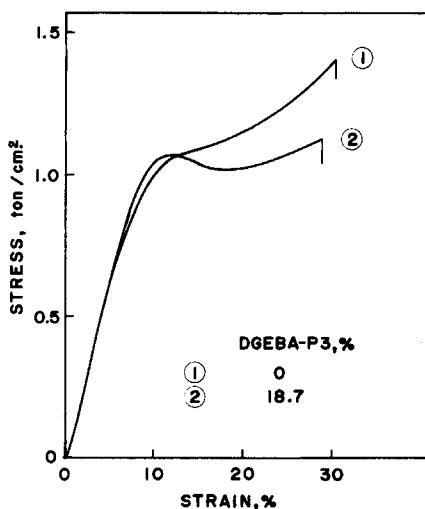Fig. 5. Stress–strain curves for antiplasticized epoxy resins.

Fig. 6. Stress–strain curves for diluted epoxy resins.

As recognized in Figure 9, the magnitude of the β-transition is apparently suppressed, and its peak temperature shifts slightly to lower temperatures as a result of dilution with DGEBA-P1. This is in good agreement with the characteristic behavior of the antiplasticization found in both thermoplastic and thermosetting system.[1,10,11]

On the other hand, the magnitude and the peak temperature of the β-transition for the diluted epoxy resin with 18.7% DGEBA-P3 are almost same with those obtained for the epoxy resin cured without diluent, indicating no remarkable interaction between DGEBA-P3 molecules and network matrix. One possible explanation for this behavior is given by formation of the DGEBA-P3 phase separated from the crosslinked matrix due to its insufficient compatibility.

TABLE II
Mechanical Properties from Compressive Stress–Strain Tests

Diluent	Weight fraction, %	Modulus, (kg/cm²) × 10⁴	Yield strength, kg/cm²	Break strength, kg/cm²	Strain at break, %
—	—	1.49	1140	1350	30.5
DGEBA-P1	4.4	1.65	1150	1300	29.9
	12.1	1.96	1180	1140	27.3
	18.7	2.09	1250	1080	27.1
	24.4	2.09	1280	1140	29.4
DGEBA-P2	4.4	1.57	1140	1250	26.0
	12.1	1.74	1150	1400	30.5
	18.7	1.96	1140	1260	30.9
DGEBA-P3	4.4	1.49	1120	1330	30.3
	12.1	1.49	1110	1320	33.1
	18.7	1.49	1090	1310	(23.4)

However, the possibility of the phase separation may be disregarded because no transition was observed around the softening point ($\approx T_g$) of DGEBA-P3 on the loss tangent–temperature curve of epoxy resin–DGEBA-P3 system.
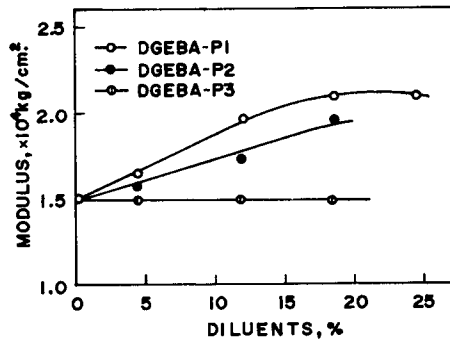

Fig. 7. Relationship between compressive modulus and diluent content.
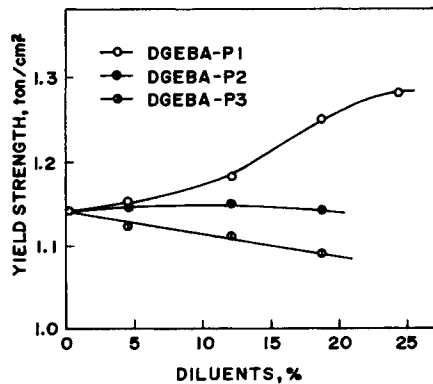

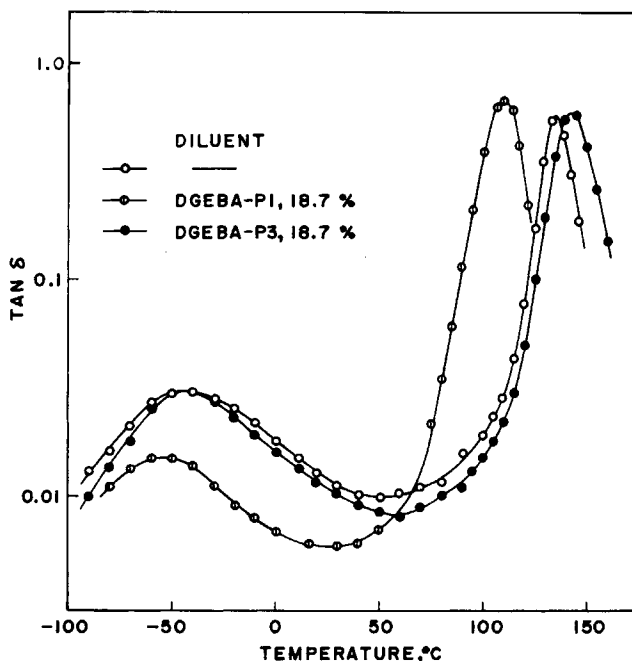Fig. 8. Relationship between yield strength and diluent content.

Fig. 9. Dynamic mechanical loss tangent–temperature curves for crosslinked epoxy resins.

Apparently, the antiplasticization phenomenon is highly correlated with the low-temperature transition of the systems where the movement of local groups should be restricted by its interaction with the diluents added. The highest molecular weight diluent, DGEBA-P3, may be dimensionally too bulky to be confined in the free volume or the available space in the network matrix.

The critical molecular weight of the diluents, in giving rise to antiplasticization, may be highly correlated with the size or dimension of available space caused by the imperfect crosslinking in the matrix.

Specific Volume Measurements

In order to know the mode of interaction of the diluents in the epoxy resins matrix, specific volume measurements were made for the present diluted systems.

In Table III are shown the calculated specific volume V_{cal}, the observed specific volume V_{obs}, and the apparent specific volume of polymer matrix, V_{app}. V_{cal} is obtained by assuming the volume additivity holds for the epoxy resin–diluents systems,

$$V_{cal} = W_d V_d + W_m V_m \qquad (1)$$

where W denotes weight fraction, V is specific volume, and the subscript d and m refer, respectively, to diluent and matrix polymer.

The apparent specific volume of the polymer is calculated on the assumption that the observed changes in specific volume of a polymer–diluent mixture are

due to the changes in the specific volume of polymer, as expressed by eq. (2):

$$V_{app} = \frac{V_{obs} - V_d(1 - W_m)}{W_m}.$$ (2)

As shown in Table III, the specific volume of the antiplasticized system, the epoxy resin–DGEBA-P1, is smaller than the calculated volume. The apparent volume shrinkage is 0.76% for the resin with 24.4% DGEBA-P1.

In Figure 10, V_{cal}, V_{obs}, and V_{app} are plotted against the weight fraction of the diluents. V_{app} is seen to decrease linearly with an increase in DGEBA-P1, which is similar to the results obtained by Wyzgoski and Yeh[3] for the polycarbonate–polychlorobiphenyl system. The decrease in apparent specific volume may be attributed to the decrease in free volume of the systems.

The behavior of V_{obs} and V_{app}, the slight decrease from V_{cal} for the epoxy resin–DGEBA-P2 may be explained by the low amount of effective low molecular weight component in DGEBA-P2, and perhaps by the fact that DGEBA-P2 itself is a self-filling or self-antiplasticizing system.[8]

The slight increase of V_{obs} over V_{cal} for the epoxy resin–DGEBA-P3 mixtures may be caused by bubble involvement in cured resins because of extremely high viscosity of the uncured mixtures. Therefore, the actual volume changes in the systems should be negligibly small. The transparency of the resins remains at the same level with the undiluted epoxy resin, which may erase the possibility of the formation of the DGEBA-P3 phase.
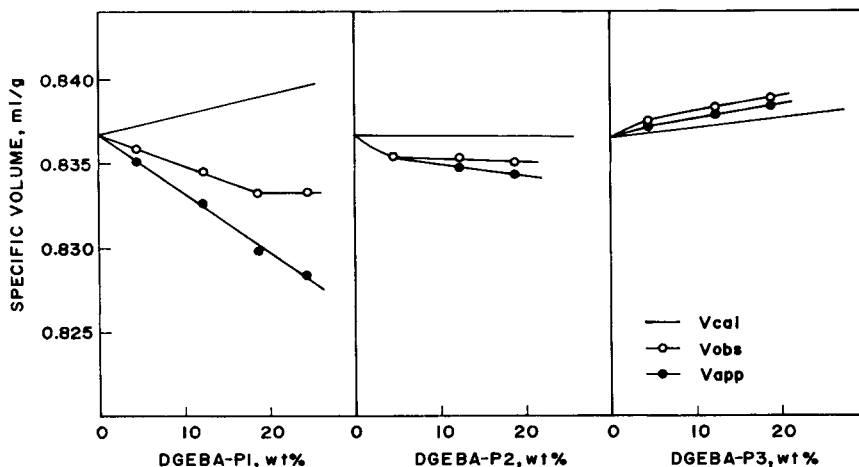

Fig. 10. Relationship between specific volume and diluent content for crosslinked epoxy resins.

CONCLUSIONS

Antiplasticization in highly crosslinked epoxy resins seems to be largely affected by the molecular weight or size of diluents as well as their structure and polarity as studied in the previous paper.[1] By increasing the molecular weight of the diluents, phenol-endcapped epoxy oligomers, antiplasticization of the diluted epoxy resins is seen to be suppressed. The diluent DGEBA-P3, with average molecular weight 4000, has substantially no antiplasticizing effect upon the observed glassy modulus, yield strength in compression, β-transition in dy-

TABLE III
Specific Volume Measurements

Diluent	Weight fraction, %	V_{cal}, ml/g	V_{obs}, ml/g	V_{app}, ml/g
—	—	—	0.8367	—
DGEBA-P1	4.4	0.8372	0.8359	0.8353
	12.1	0.8382	0.8346	0.8326
	18.7	0.8390	0.8333	0.8298
	24.4	0.8397	0.8333	0.8283
DGEBA-P2	4.4	0.8367	0.8353	0.8353
	12.1	0.8366	0.8353	0.8350
	18.7	0.8366	0.8351	0.8344
DGEBA-P3	4.4	0.8369	0.8375	0.8373
	12.1	0.8373	0.8384	0.8379
	18.7	0.8376	0.8389	0.8383

namic mechanical measurements, and changes in specific volume. The dimensions and construction of network involved in the crosslinked polymer matrix and the chemical structure and molecular weight of antiplasticizable diluents should be highly related to each other. More advanced study in this line may lead to the elucidation of the behavior of diluents incorporated in highly crosslinked epoxy resins.

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