Viscoelastic Properties of Epoxy Resins. II. Antiplasticization in Highly Crosslinked Epoxy System

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Synopsis

The effect of the addition of certain low molecular weight compounds to highly crosslinked epoxy resins was investigated. The behavior which is known as antiplasticization, such as increases in modulus and yield strength and the elimination of β-transition, was observed in the highly crosslinked system as well as in the reported cases of thermoplastics—poly(vinyl chloride), bisphenol A polycarbonate, and polysulfone. Chlorinated biphenyl was found to be one of the most effective antiplasticizers examined in the present paper. However, the remarkable reduction in compressive strain at break and impact strength was not recognized for the highly antiplasticized samples. These phenomena have been interpreted on the basis of free volume concept.

INTRODUCTION

It is known that the addition of a low amount of plasticizer to poly(vinyl chloride) results in changes in mechanical properties at a glassy region which is opposite to plasticization such as the increase in tensile strength and the decreases in elongation and impact strength.[1,2] Furthermore, the similarity in behavior of bisphenol A polycarbonate and related polymers has been discussed in a series of papers by Jackson and Caldwell and termed antiplasticization.[3-5] Antiplasticization has also been observed in certain condensation polymers such as polysulfone and phenoxy resin.[6,7]

Concerning crosslinked polymer systems, the study of the compounds showing antiplasticizing effect should be quite important in view of the interaction between three-dimensional network construction and diluents and, further, to elucidate the chemical and physical structure of polymer network. Bisphenol A-based epoxy resin was selected as the matrix material, and three kinds of low molecular weight compounds were examined as antiplasticizers.

The present paper discusses the correlation between the structure of the highly crosslinked polymer matrix and that of low molecular weight compounds and the mechanism of antiplasticization.

EXPERIMENTAL

Materials

Diglycidyl ether of 4,4′-isopropylidenediphenol (bisphenol A) (DGEBA) was prepared from a commercial resin (Epikote 828) by molecular distillation. The oxirane oxygen content determined by the HCl–dioxane method was 9.17% (calculated value 9.41%).

Ethylenediamine (EDA) was reagent grade and used as received. Three kinds of antiplasticizers were employed in the present work—pentachlorobiphenyl (CB), an adduct of 1 mole DGEBA with 2 moles phenol (DGEBA-P) and dibutyl phthalate (DBP). Their structure and properties are shown in Tables I and II.

TABLE I
Structure of Materials

TABLE II
Properties of Materials

Code	Molecular weight	Density	Solubility parameter[a]
Matrix	—	1.195	10.0
CB	(327)	1.541	10.2
DBP	278	1.042	9.85
DGEBA-P	528	1.178	10.5

[a] Calculated from the values of Hoy.[8]

Preparation of Specimens

The epoxide or its mixture with an antiplasticizer was cured with 8.6 phr ethylenediamine at room temperature for 24 hr, followed by heating at 150°C for 5 hr in a draft oven.

The specimens used for the Clash-Berg measurements were of dimensions 0.3 × 0.6 × 6.0 cm. The specimens for the stress–strain measurements in compression were 1.3 × 1.3 × 3.0 cm bars. The specimens for the dynamic mechanical measurements were 0.1 × 0.01 × 2.5 cm strips.

Measurements

Ten-second shear modulus was determined with a Clash-Berg torsional apparatus in a silicon oil bath.   A heating rate of 1°C/min was employed.

Compressive stress–strain measurements were made on an Autograph IS-2000 type stress–strain tester.   Relative rate of motion of the grips was 5 mm/min.

Mechanical loss tangent was measured on a Vibron DDV-II dynamic viscoelastometer (Toyo Baldwin Co.) at 11 Hz and a heating rate of 1°C/-min using an air bath.

RESULTS AND DISCUSSION

Modulus–Temperature Relationship

The modulus–temperature curves measured for the samples antiplasticized with CB are shown in Figure 1.   In this figure, 3×10 sec shear modulus ($\approx E$) was plotted against temperature.   All of the curves of the figure show clearly a glassy region, a transition region, and a rubbery region which are characteristic for highly crosslinked polymeric systems.   Similar curves were also obtained for the samples antiplasticized with DBP or DGEBA-P, respectively.

From these curves, inflection temperature, as defined in a previous paper,[9] and glassy modulus at 25°C were obtained and plotted versus the weight fraction of the antiplasticizers used (Figs. 2 and 3).
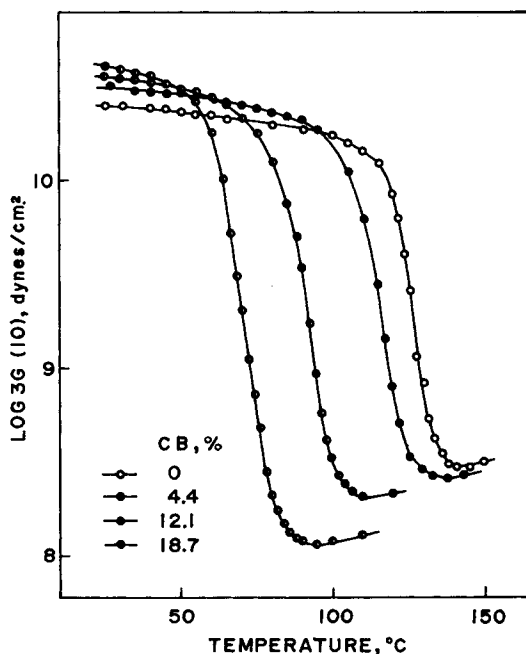

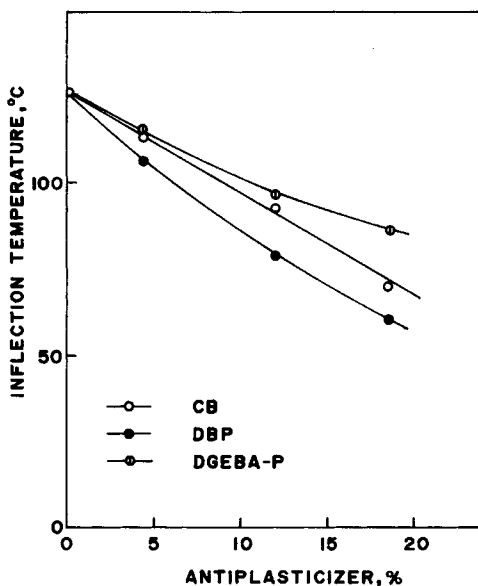Fig. 1. Modulus–temperature curves for antiplasticized epoxy resins.

Fig. 2. Relationship between inflection temperature and antiplasticizer content.
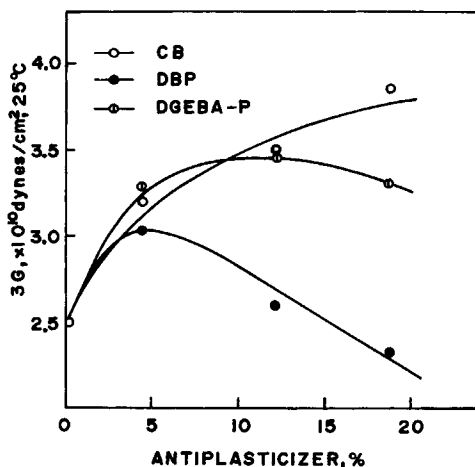

Fig. 3. Relationship between $3\times$ shear modulus and antiplasticizer content.

As shown in Figures 1 and 2, the incorporation of the antiplasticizers lowers the inflection temperature which may be regarded as an ordinary plasticizing or antiplasticizing effect, and DBP was one of the most effective plasticizers examined in the present work. The degree of the decrease in inflection temperature should depend on the glass transition temperature of the added plasticizer.

The rubbery modulus was also depressed. The reduction in the rubbery modulus suggests the decrease of crosslinking density caused by the dilution effect with antiplasticizers.

The most striking effect observed by incorporating the diluents to the crosslinked epoxy resins is recognized in the change of the glassy modulus. Figure 1 shows the curves of modulus versus temperature for the cured epoxy resins diluted with CB, proving an increase in the glassy modulus, while Figure 3 demonstrates the change in glassy modulus at 25°C versus the weight per cent of the antiplasticizers.

In the present paper, the increase in glassy modulus at 25°C upon dilution of the epoxy resins is defined as antiplasticization. One of the best antiplasticizers was found to be CB, which has been known as a quite effective antiplasticizer for polycarbonate, polysulfone, and crosslinked diallyl phthalate resins.[4,10] It should be noted that even DBP has a slight antiplasticizing effect within the 10% dilution level.

Stress–Strain Measurements

Stress–strain tests were made in compression. Materials under compression are much more ductile than when under tension,[11] and whole stress–strain curves can be obtained more easily by compressive tests than by tensile tests for a rather brittle material such as highly crosslinked epoxy resins (Fig. 4). Young's modulus was calculated from the initial linear slope of the stress–strain curves and plotted against the weight fraction of the antiplasticizers used (see Fig. 5). Yield strength, break strength, and compressive strain (%) at break were also obtained, and they are tabulated in Table III.

As shown in Figure 5, the compressive modulus and yield strength are increased by adding the diluents CB and DGEBA-P to the crosslinked epoxy resins. Eighteen percent CB is capable of increasing the compressive modulus 57% as well as the yield strength 28%. DGEBA-P is less effective than CB, but it is still capable of increasing modulus 47% and yield strength 17%. On the other hand, DBP is not so effective in increasing the modulus and strength of the epoxy resin, though a small peak was observed in the modulus–antiplasticizer content curve.

TABLE III
Mechanical Properties from Compressive Stress–Strain Measurements

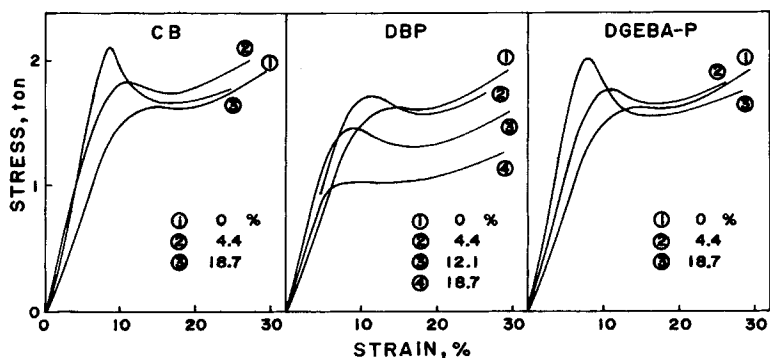| Anti-plasticizer	Weight fraction, %	Modulus, (kg/cm^2) $\times 10^4$	Yield strength, kg/cm^2	Break strength, kg/cm^2	Strain at break, %
——	—	1.39	1150	1330	29.1
CB	4.4	1.82	1210	1310	27.6
	12.1	2.19	1350	1280	24.0
	18.7	2.23	1480	1200	25.7
DBP	4.4	1.76	1140	1200	26.7
	12.1	1.75	980	1040	29.6
	18.7	1.59	720	870	28.8
DGEBA-P	4.4	1.76	1170	1180	26.3
	12.1	2.05	1240	1050	27.7
	18.7	2.06	1340	1160	28.8

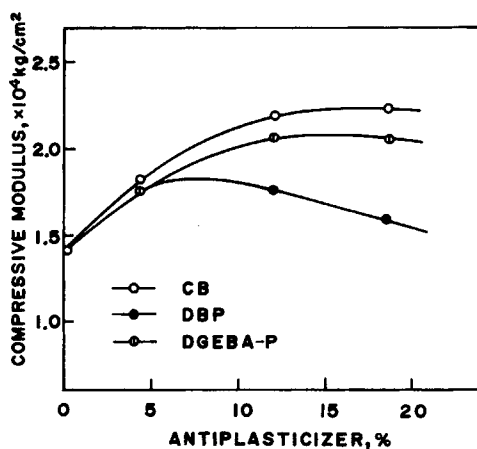Fig. 4. Stress–strain curves for antiplasticized epoxy resins.

Fig. 5. Relationship between compressive modulus and antiplasticizer content.

In comparison with the curves in Figures 3 and 5, the degree of increase in modulus and the amount of antiplasticizer for peak modulus values deviate from the values obtained from those of modulus–temperature measurements.   The reason for this may be the difference in the time scale or the nature of the measurements.

Dynamic Mechanical Measurements

Mechanical loss tangent–temperature data measured at 11 Hz for the samples antiplasticized with CB is shown in Figure 6.   Similar data of lower temperature transition region are also shown for the samples antiplasticized with DGEBA-P or DBP (Fig. 7).   From these curves, the peak values and temperature of the β-transition were obtained and are presented in Table IV.

It should be noted that the magnitude of the β-transition is apparently reduced and the peak temperature of the β-transition shifts slightly to a lower range by the addition of antiplasticizers.   These phenomena are

TABLE IV
Dynamic Mechanical Properties for Antiplasticized Epoxy Resins

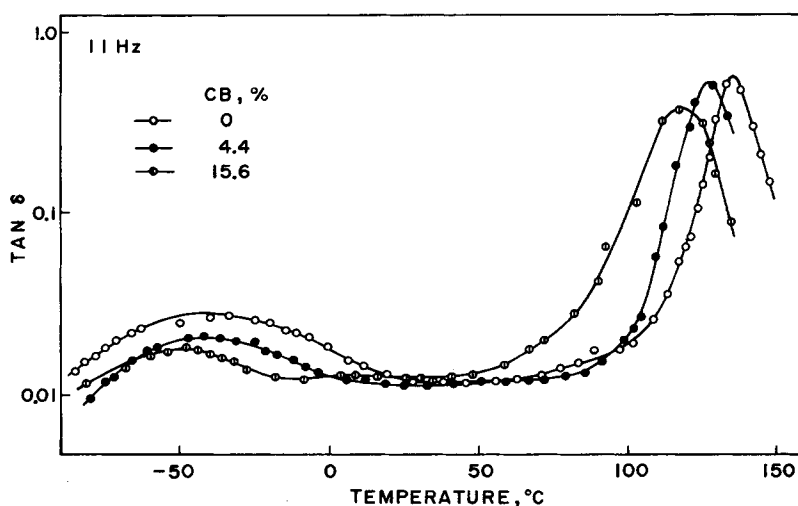| Anti-plasticizer	Weight fraction, %	β-Dispersion		α-Dispersion		Impact strength, kg-cm/cm[a]
		Temp., °C	tan δ	Temp., °C	tan δ	
—	—	−39	0.029	135	0.60	2.38
CB	4.4	−41	0.021	126	0.56	2.38
	15.7	−48	0.018	119	0.38	2.50
DBP	4.4	−43	0.023			
	18.7	—	—			
DGEBA-P	4.4	−42	0.023			
	18.7	−54	0.016			

[a] Izod method.

Fig. 6. Mechanical loss tangent–temperature curves for crosslinked epoxy resins anti-plasticized with chlorinated biphenyl.

quite similar to the observations made with poly(vinyl chloride)–anti-plasticizers or polysulfone–antiplasticizer system.[6,12,13]

These phenomena may be interpreted to be the result of remarkable effects on the short-range motion of the matrix polymer chains with the anti-plasticizer added. The motion of the matrix polymer chains is restricted by the incorporation of the antiplasticizer molecules in the polymer matrix. The shape, size, and polarity of antiplasticizers should be considered in selecting an effective antiplasticizer.[4] However, the fact that an anti-plasticizer, DGEBA-P, having similar structure as the matrix, has a notable antiplasticizing effect reveals that interaction between the matrix and the antiplasticizer may not be the determining factor. That antiplasticization may be caused by the filling of matrix free volume with antiplasticizer seems the most probable explanation. It has been reported that the glassy
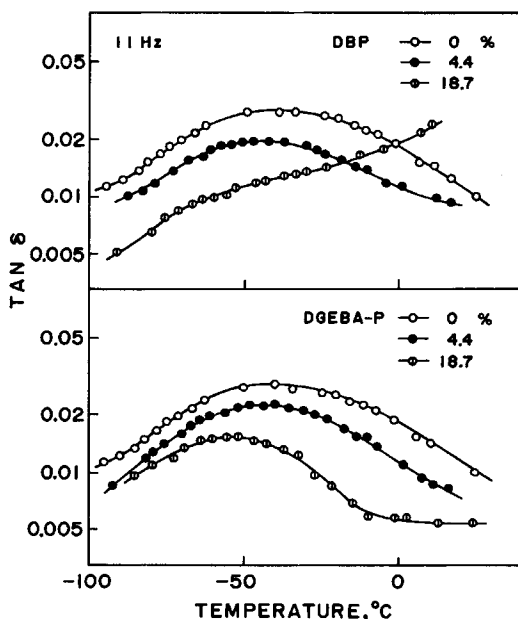
Fig. 7. Mechanical loss tangent–temperature curves (β-transition region) for crosslinked epoxy resins antiplasticized with DBP and DGEBA-P.

modulus of polymeric material is largely affected by its polarity and the amount of its free volume.[9,14]

It has also been reported that for antiplasticized thermoplastics, the reduction or the elimination of low-temperature transition is invariably accompanied by a rapid decrease in impact strength. However, for the antiplasticized three-dimensional system, Izod impact strength was not changed much by the addition of CB up to 18.7%, as shown in the last column of Table IV. The results that antiplasticizer has no effect on the impact strength of epoxy resin may be related to the values of compressive strain at break which should be parallel to the values of elongation at break.

The relation between the impact properties and the elongation of poly-(vinyl chloride) was studied extensively by Pezzin et al.,[15] where the room temperature impact strength was controlled only by the elongation at break, which is similar to our observations.

This is tentatively interpreted to mean that free volume has very little effect on the impact behavior of the highly crosslinked epoxy system. It has been believed that free volume should play an important role in the extraordinarily high impact strength of some thermoplastic polycarbonate,[16] which shows a drastic drop in impact strength upon incorporation of antiplasticizers.[5]

CONCLUSIONS

1. The phenomenon known as antiplasticization, which is defined as increases in modulus and yield strength upon incorporation of a low molec-

ular compound, is also observed in highly crosslinked epoxy systems as well as in thermoplastics such as PVC, etc.

2. For the antiplasticized three-dimensional system, the compressive strain at break and the impact strength remain unchanged within the addition level of 18.7% antiplasticizer.

3. The prime reason for antiplasticization is considered to be the filling of free volume of matrix polymer by antiplasticizer molecules, which may be verified by the decrease in β-transition peak in the loss tangent curve.

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