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Characterization of Network Structure of Epoxy Resins by Dynamic Mechanical and Liquid Swelling Tests*

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SUMMARY

A combination of dynamic mechanical and swelling properties has been used to elucidate the structure of epoxy resin systems as a function of time and temperature of cure, concentration of flexibilizer, and curing agent concentration. The dynamic properties of the resin in the rubbery region were used to determine the molecular weights between cross-links. The poor network structure formed with epoxies is shown by the dynamic and swelling tests. The existence of heterogeneity or two phases has been found in the epoxy resin system under certain polymerization conditions. Broad damping peaks may not be due to chemical heterogeneity but may be the result of the curing reaction continuing during the tests.

INTRODUCTION

Although it is known that the properties of epoxy resins depend upon the nature of the curing conditions as well as on the chemical constitution of the materials, very little work has been done to characterize the complex cross-linked network structures that are found in such resin systems. In this work an attempt is made to partially characterize the cross-linked networks of some typical epoxy resins by the use of dynamic mechanical tests and by swell-

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ing and extraction tests using liquids which are good solvents for the uncross-linked resins. Similar tests are the classical methods of characterizing the more perfect but less densely cross-linked networks found in vulcanized rubbers.

An additional complicating factor appears with polymeric systems which are not rubbers but which have glass transition temperatures above room temperature. With such systems the chemical reactions may not be complete under certain curing conditions, but upon heating the sample or on swelling in a liquid, the chemical reactions involved in the cross-linking process may start again. Thus, the final polymer after a dynamic modulus test may not be representative of the original material; therefore, dynamic mechanical tests are especially useful for detecting incomplete cross-linking reactions [1]. Although there are a number of papers on the dynamic mechanical properties of epoxy resins, apparently none of the past work has used this tool to learn something about the network structure of these polymers [2, 3].

The variables included in this work are the effect of temperature and time on the extent of the cross-linking reactions, changes due to postcuring treatments, the effect of flexibilizing agents on the network structure, and the effect of chemical stoichiometry on the perfection of network structures.

EXPERIMENTAL

A. The commercial resins, flexibilizer, and curing agents used in this study are shown in Table 1. The epoxy resins are essentially bis-phenol A-diglycidyl ethers; Epon 815 also contains a monofunctional diluent such as alkyl or aryl glycidyl ether. The epoxy flexibilizer EM207 (Thiokol) is a polyester having a molecular weight of 1500 (as measured by vapor pressure osmometry), and contains an average of 1.3 carboxylic groups per molecule.

The test specimens were cast between parallel glass plates (6 in. \times 6 in.), and the thickness was controlled by spacers. A thickness of 0.030 in. was used for cured resins having a shear modulus G in the range of 10^8 dynes/cm² at 30° above the glass transition; 0.060 in. thick specimens were used for the flexible resins having a shear modulus in the range of 10^7 dynes/cm² at 30° above the glass transition temperature. Variation in thickness of the test specimen was less than 0.001 in. Test samples were cut from the 6 in. \times 6 in. slab into 0.375 in. \times 4 in. \times 0.030 in. or 0.060 in. strips. The edges were sanded smooth to remove machine marks. The cure cycles on the resins were carefully controlled.

B. The dynamic shear modulus and damping (log decrement) were determined by the recording torsion pendulum described by Nielsen [4]. The frequency for the dynamic testing was kept in the

Table 1. Resins and Curing Agents

Resin	Chemical structure	Source	Epoxide equivalent
Epon 815		Shell	175-195 Contains monofunctional diluent
Epon 820	"	Shell	180-195 Contains monofunctional diluent
Epon 826	"	Shell	180-188
Epon 828	"	Shell	185-192
EM207	Carboxylic terminated polyester	Thiokol	mol wt 1500 1.3 carboxylic groups/molecule
Curing agent			
TETA		Fisher	
MDA		Fisher	
Curing agent D	Tri(2 ethyl hexoate) salt of tri(dimethyl amine methyl) phenol	Shell	
Curing agent Z	Aromatic amine mixture	Shell	

range of 1.5-0.5 cps by changing the moment of inertia disk. The sensitivity of the instrument was adjusted during the measurement so as to keep the angle of twist on the sample low. During the measurements, the sample was blanketed with an atmosphere of nitrogen. In the epoxy system, the dynamic modulus test results are sensitive to the rate of temperature change and to the time for which the specimen was held during the torsion test. The dynamic modulus was measured at 5°C intervals. Rate of heating was 1°C/min with a 4-min hold at each temperature. The glass transition temperatures were determined from the maximum in the damping curves.

C. Swelling measurements on epoxy cast resins were made in reagent-grade acetone. Approximately 0.3 g of cured resin was soaked for 14 days in 25 ml of solvent at 25°C. The solvent was replaced after 7 days with fresh solvent. The amount of soluble material was determined by evaporation of the acetone and weighing the residue. The swelling ratio was determined from the relation

$$\text{swelling ratio } q = \frac{\text{volume of swollen polymer}}{\text{volume of unswollen polymer}}$$

The volume of solubles was subtracted from the total polymer volume to obtain a true amount of polymer subjected to swell. The soluble fraction was determined from the relation

$$\text{soluble fraction} = \frac{\text{weight of soluble material}}{\text{weight of initial cured resin}}$$

RESULTS AND DISCUSSION

The cross-linking reactions in the epoxy resin system are dependent upon the type of resin, curing agent, additive, and curing conditions. These many variables make the prediction of physical properties difficult. Several important parameters such as resin composition and time and temperature of cures have been varied, and the dynamic mechanical properties have been measured as a function of these variables.

Figure 1 shows the dynamic mechanical data as a function of time for Epon 815 epoxy resin cured with triethylenetetramine (TETA) in a ratio of 7 parts resin to 1 part curing agent at 25°C. The dynamic modulus curves show the curing reaction continuing for long periods, at least up to 552 hr. The glass transition temperature, T_g , as measured by either the break in the modulus curve or the peak in the damping curve, increases with time. The damping curves are extremely broad; it is shown later that this broadness is due to the continuation of the curing reactions as the test temperature increases above the original curing temperature or the glass

transition of the system and is not due to chemical heterogeneity as in the case of some copolymers [5]. The results indicate that the curing reaction must have been complete at about 100°C, as both the modulus and damping curves for all the specimens shown in Fig. 1 are the same above 100°C.

Figure 2 shows the dynamic mechanical properties of the Epon 815 and TETA cured at various temperatures. Postcuring above 25°C shifts T_g up to at least the curing temperature until the curing reaction is complete at about 80°C; postcuring at temperatures higher than 80°C then does not bring about any further changes. The higher the degree of cure during the postcuring cycle, the sharper

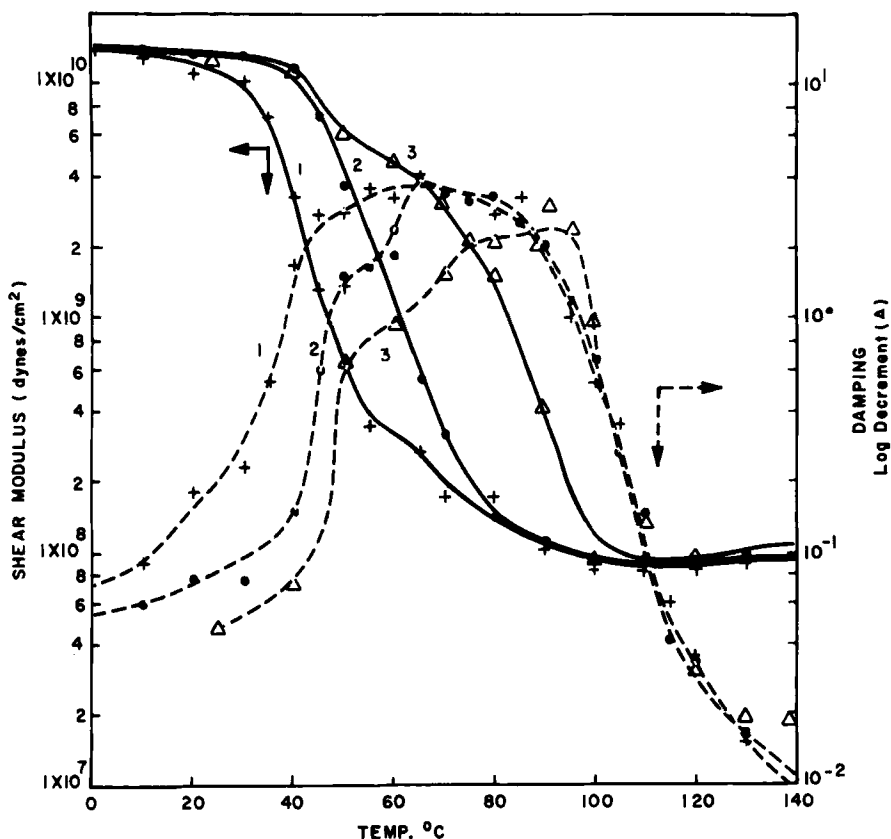


Fig. 1. Dynamic mechanical properties of Epon 815 cured with TETA at 25°C as a function of time. Curve 1 = Epon 815 + TETA (7:1), 24 hr at 25°C; curve 2 = Epon 815 + TETA (7:1), 120 hr at 25°C; curve 3 = Epon 815 + TETA (7:1), 552 hr at 25°C.

is the damping peak. This is to be expected if the broadness of the damping peak is related to chemical reactions taking place during the time required to make the dynamic mechanical test in which the temperature is slowly increasing.

Proof that the epoxy resins can change in structure during a dynamic mechanical test is offered in Fig. 3, in which the test was repeated twice on the same specimen (Epon 815 and TETA 7:1). The two sets of curves differ in the expected manner. Additional evidence of the speed of curing reactions can be obtained by running the dynamic test at some constant temperature above T_g . This is

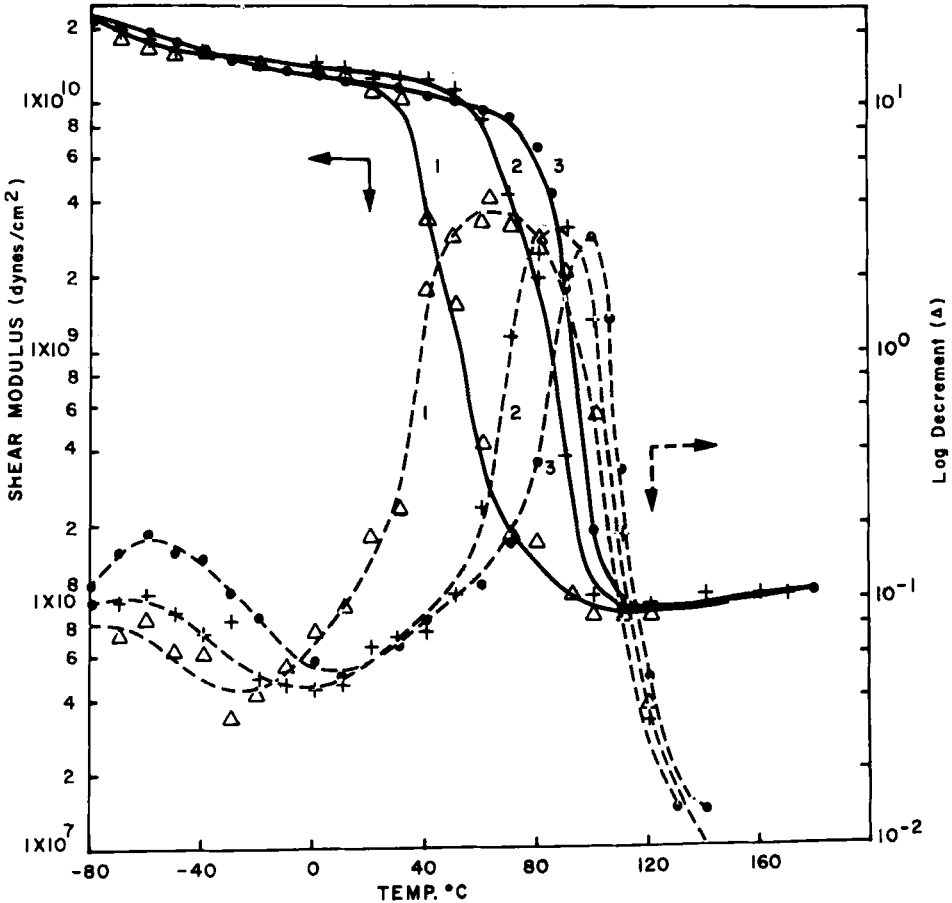


Fig. 2. Cure temperature effect on dynamic mechanical properties of Epon 815 + TETA. Curve 1 = 24 hr at 25°C; curve 2 = 24 hr at 25°C + 18 hr at 40°C; curve 3 = 24 hr at 25°C + 18 hr at 120°C.

illustrated in Fig. 4 for a test run at 90°C on a specimen cured at 25°C. The modulus increases rapidly to a limiting value while the damping increases very rapidly, goes through a maximum, and then slowly decreases. Subsequent raising of the test temperature to 120°C gave values of both damping and modulus that were predicted from previous results at 120°C; there was no change in the dynamic mechanical values over a test period of 3 hr. This constancy of the dynamic values is a good indication that curing reactions were complete.

The effect of chemical stoichiometry, defined as the ratio of epoxy resin to amine curing agent, on the dynamic properties is shown in Fig. 5 for the system Epon 815 and EM207 in a ratio of 1:1 with

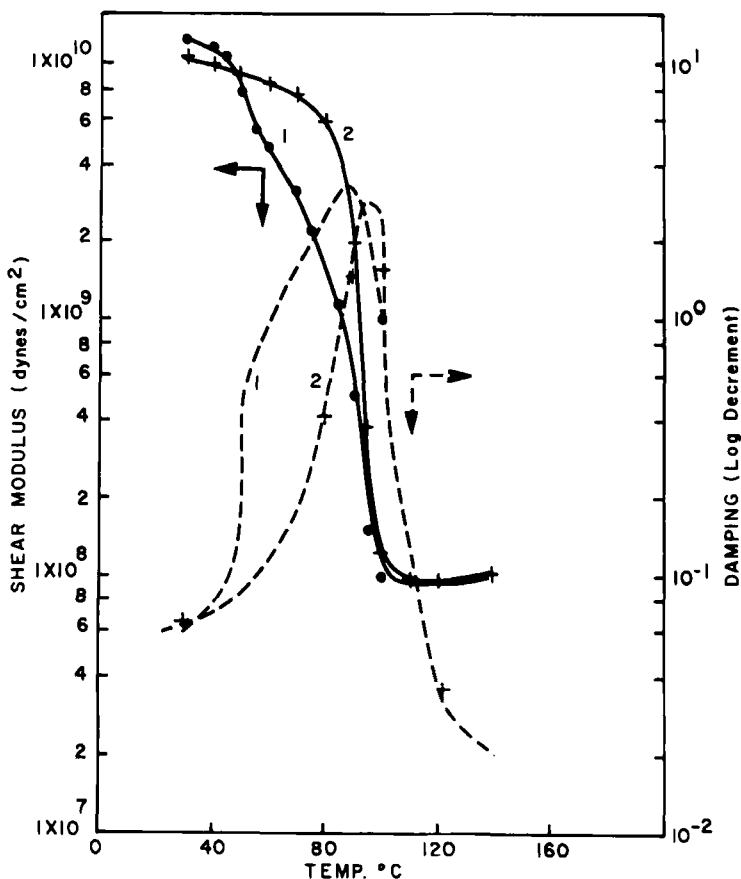


Fig. 3. Changes in dynamic mechanical properties during curing reaction and after complete cure. Curve 1 = first modulus run after curing for 24 hr at 25°C; curve 2 = repeat run on same sample.

TETA as the curing agent. Two levels of amine curing agent were used; a ratio of 6 parts resin to 1 of curing agent gave a resin composition rich in amine, while a ratio of 9 parts resin to 1 of curing agent gave a system rich in resin. The cured resin containing the 6:1 ratio became turbid as it cured at room temperature and gradually became translucent upon postcure at 60 and 100°C. The 9:1 cured resin remained transparent at all cure temperatures. The break in dynamic shear modulus curve is shifted to a lower temperature for the cured resin containing the 6:1 ratio, and the damping shows a double peak for this resin. The glass transition temperature for the resin containing a 9:1 ratio is approximately 20°C higher than that of the 6:1 resin.

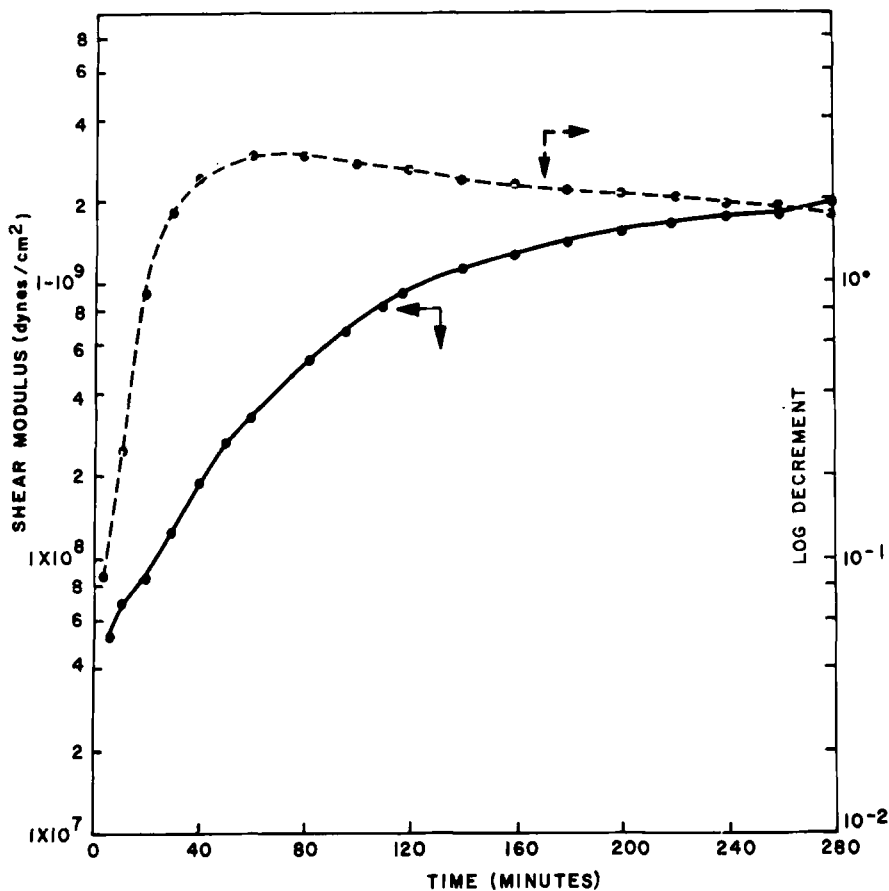


Fig. 4. Mechanical property change during curing reaction at 90°C for Epon 815 + TETA after curing for 24 hr at 25°C.

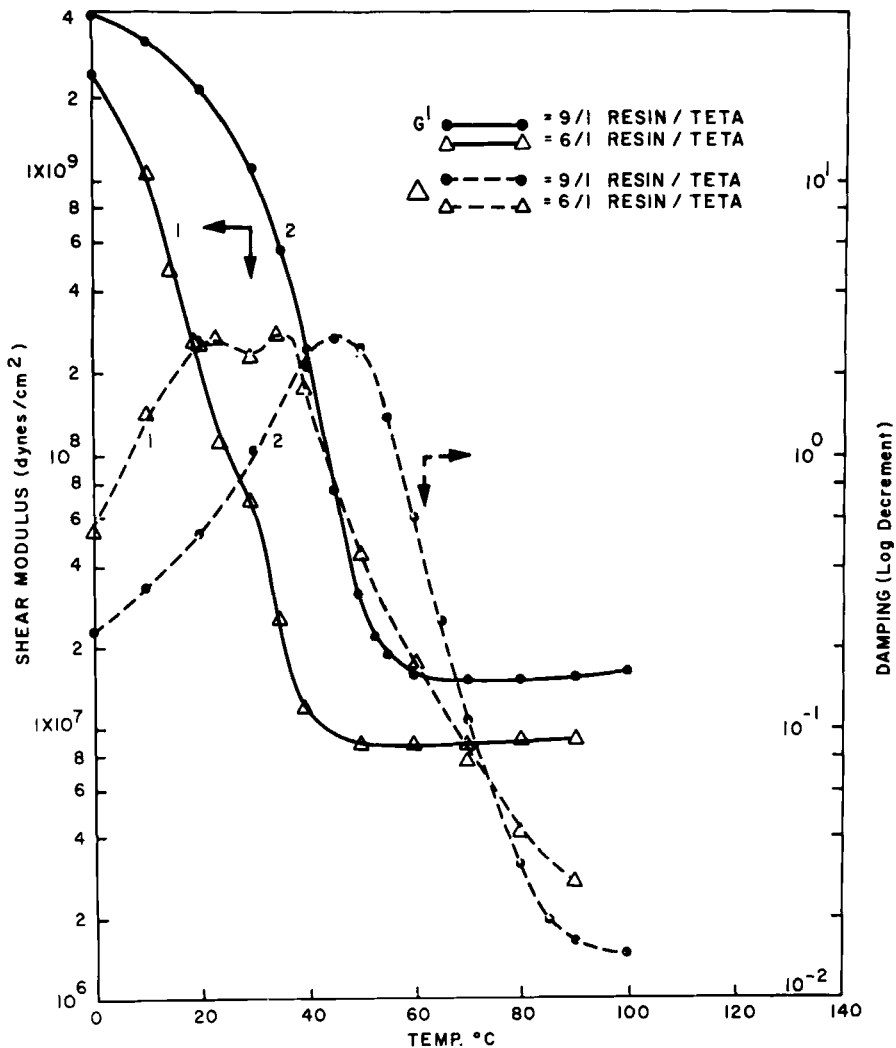


Fig. 5. Dynamic mechanical properties of Epon 815 and flexibilizer (EM207) 1 : 1 with varying ratios of curing agent (TETA). Curing cycle, 24 hr at 25°C and 24 hr at 60°C. Curve 1 = resin/amine curing agent ration 6 : 1; curve 2 = resin/amine curing agent ratio 9 : 1.

Epoxy systems usually show higher modulus for compositions containing high concentrations of curing agent due to the formation of more cross-links or a tighter network. The systems described here show the reverse. The double peaks in the damping curve must arise from two different species, since the broad double peak cannot be attributed to additional reaction of the resin and curing agent; the cure was made at temperatures 60°C above the glass transition to ensure complete reaction. The two phases formed in such a resin system could arise if the initial reaction occurred rapidly to form long linear molecules between the carboxyl groups from the EM207 and amine curing agent and then those molecules cross-linked to form a microgel. After formation of a microgel, the other chemical reactions take place to form a macrogel such as shown in Fig. 6. If a higher modulus particle is embedded in a lower modulus matrix, the modulus of the composite is determined primarily by the modulus of the matrix phase and increases only slowly with concentration of the higher modulus filler phase. Such a composite would account for the lower modulus of the heterogeneous 6:1 cured resin compared with the homogeneous 9:1 resin. Slight differences in chemical composition and polymerization conditions can convert a one-phase epoxy resin into a two-phase system, and these two phases behave differently mechanically.

The presence of two distinct phases was verified by phase contrast and electron microscopy which showed continuous and discontinuous phases. An electron micrograph (Fig. 7) showed the presence of two phases and the three-dimensional structure.

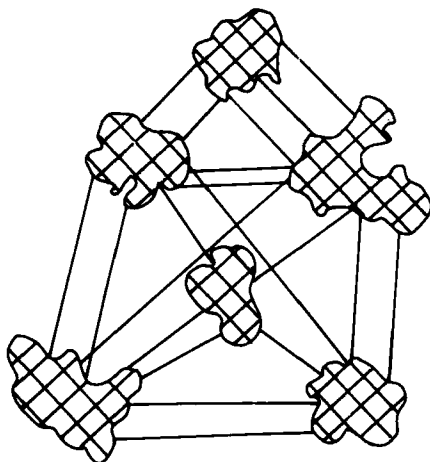


Fig. 6. Representative structure of a two-phase epoxy resin where microgel is formed, then later loosely cross-linked by continuation of reaction.

Larger structures are noted optically with some of the discontinuous particles as large as $5\ \mu$. Cuthrell [6] has shown that many epoxy resin systems contain two phases with floccules in an interstitial fluid. A recent paper by Solomon et al. [7] discussed the possibility of first forming microgel and then macrogel during the cross-linking reactions to give a final heterogeneous network structure such as shown schematically in Fig. 6.

The effect of flexibilizing agents on the network structure of epoxy resins is illustrated in Fig. 8 and Table 2. The flexibilizing agent in this case not only lowers the glass transition temperature, but also lowers the modulus above T_g by reducing the perfection of the network structure. This reduction in the perfection of the cross-linked network will also be shown by the swelling and sol fraction data. Large amounts of monofunctional flexibilizing agent greatly reduce the amount of material tied up by the cross-linked network so that a large percentage of the total polymer is soluble and can be extracted from the cross-linked gel. Because these flexibilizing agents reduce the number of chains tying the network together, the elastic modulus above T_g is greatly reduced.



Fig. 7. Electron micrograph of a 1 : 1 mixture of Epon 815 and EM207 cured with TETA resin/curing agent ratio of 6 : 1 for 24 hr at 25°C and 24 hr at 60°C .

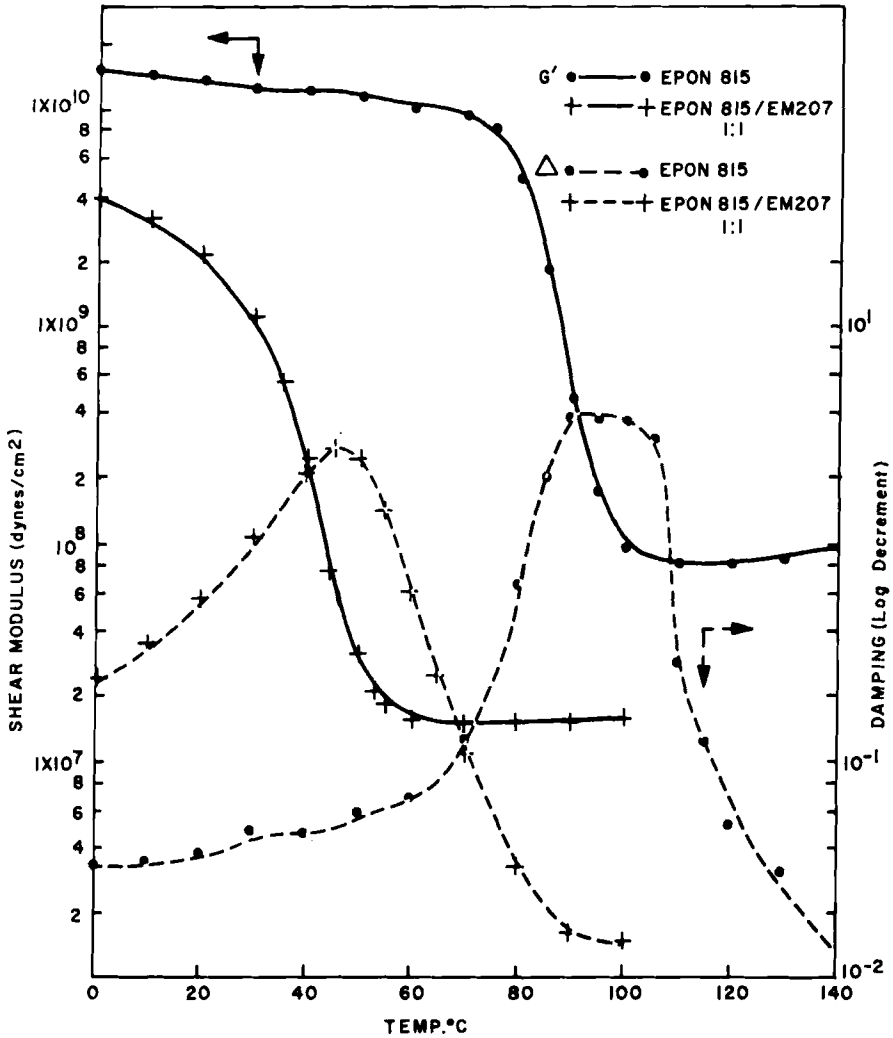


Fig. 8. Effect of flexibilizing agent on dynamic mechanical properties of an epoxy resin. ● — ● Epon 815 + TETA (7:1); + — + Epon 815/EM207 (1:1) + TETA (7:1) cured for 24 hr at 25°C and 24 hr at 60°C.

Table 2. Dynamic Modulus Measurements on Epoxy Resin Systems

Composi- tion No.	Resin system	Cure	T _g , °C	G' at T _g + 30°C	M _c	
					Kinetic	Theoretical
I Epon	815 + TETA (7:1)	24 hr at 25°C 24 hr at 60°C	92	8.6 × 10 ⁷	447	367
II Epon	815/EM207 (90/10)	24 hr at 60°C	84	6.8 × 10 ⁷	554	411
III Epon	815/EM207 (80/20)	24 hr at 60°C	65	4.9 × 10 ⁷	730	496
IV Epon	815/EM207 (70/30)	24 hr at 60°C	60	3.9 × 10 ⁷	905	580
V Epon	815/EM207 (60/40)	24 hr at 60°C	50	3.6 × 10 ⁷	954	615
VI Epon	815/EM207 (50/50)	24 hr at 60°C	26	1.5 × 10 ⁷	1,940	1,950
VII Epon	815/EM207 (40/60)	24 hr at 60°C	30	3 × 10 ⁶	10,700	—
VIII Epon	815/EM207 (30/70)	24 hr at 60°C	10	8.4 × 10 ⁶	3,640	—
IX Epon	815/EM207 Resin/Curing agent 6:1	24 hr at 25°C 24 hr at 60°C 1 3/4 hr at 100°	23, 34	8.8 × 10 ⁶	3,660	—
X Epon	815/EM207 Resin/Curing agent 9:1	24 hr at 25°C 24 hr at 60°C 1 3/4 hr at 100°	45	1.55 × 10 ⁷	2,180	1,790
XI Epon	815 + TETA	24 hr at 25°C 18 hr at 40°C	80, 90	9.4 × 10 ⁷	406	352
XII Epon	815 + TETA	24 hr at 25°C 24 hr at 60°C	93	8.6 × 10 ⁷	448	366
XIII Epon	815 + TETA	24 hr at 25°C 18 hr at 120°C	97°	9.8 × 10 ⁷	397	346
XIV Epon	826 + MDA	6 hr at 165° Molded at 160°	172	1.55 × 10 ⁸	370	335
XV Epon	826 + MDA (solution)	3 hr at 150°	135	9.8 × 10 ⁷	434	346

Dynamic mechanical tests are capable of detecting subtle differences in the structure of polymers of the same overall chemical composition that result from differences in polymerization conditions. An example is illustrated in Fig. 9. Polymers made from Epon 826 resin and methylenedianiline (MDA) curing agent were polymerized in bulk and in solution. The solution-made polymer was partially reacted (B-staged), removed from solvent, and dried, and the cross-linking reaction was then completed in the normal manner in a mold at 160°C and the specimen postcured for 3 hr at 160°C. Figure 9 shows that the final network structure of these polymers was radically different. The solution-polymerized poly-

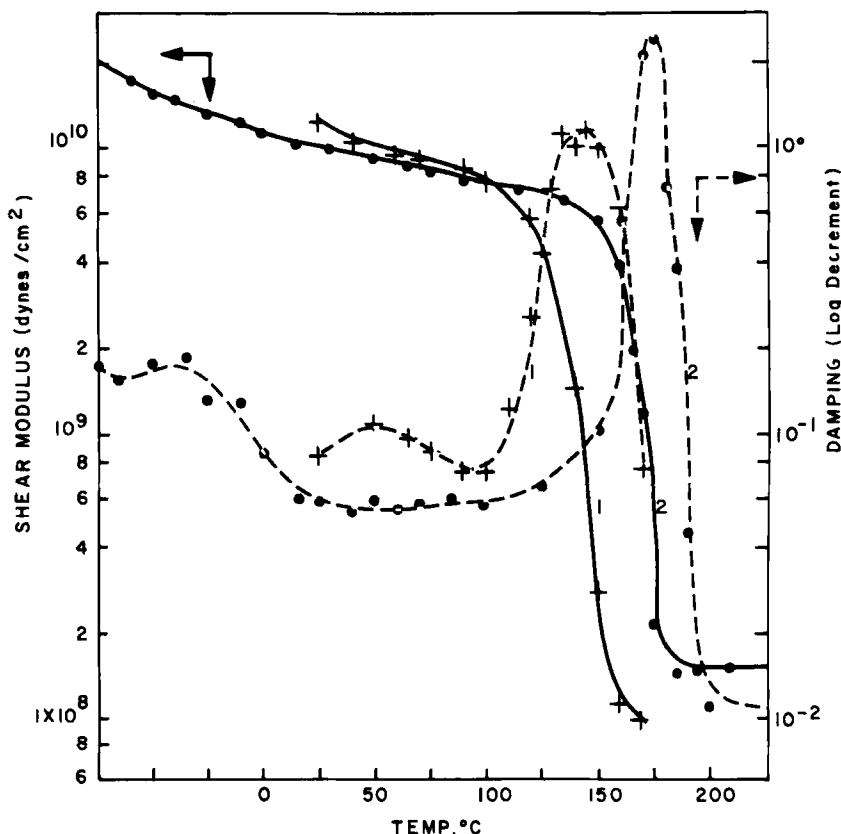


Fig. 9. Dynamic mechanical properties of Epon 826 cured with MDA. Comparison of bulk- and solution-polymerized cures. Curve 1 = Epon 826 + MDA solution polymerized and compression-molded. Resin B-staged, molded at 160°C, and cured for 3 hr at 150°C. Curve 2 = Epon 826 + MDA bulk-polymerized and cured for 6 hr at 165°C.

mer had a lower glass transition temperature and a lower degree of cross-linking, as shown by the lower value of the high-temperature shear modulus. The low-temperature secondary glass transition was shifted from -50°C for the bulk-polymerized polymer to $+50^{\circ}\text{C}$ for the solution-polymerized polymer. The damping peak for the Epon 826 + MDA resin prepared from solution and B-staged is broad and some resemblance to a two-phase system is noted. The modulus shows a behavior similar to resins described in Fig. 5. The dynamic properties of the B-staged resin can be explained on the basis of the presence of microgel which formed during the early stages of polymerization. Large loops were introduced, through the amine acting partly as a difunctional molecule, which were later cross-linked through the tetrafunctionality of the amine. Again, the structure may be something like that shown in Fig. 6.

Additional information about the degree of cross-linking and the perfection of the network structure of epoxy resins can be obtained from swelling and sol fraction measurements. Swelling data for the different resin systems are given in Table 3. For systems in which the chemical composition is held constant but the temperature and time of cure are varied, the amount of swelling and the amount of material that can be extracted are essentially constant. This might seem strange at first, since the dynamic mechanical data show that the cross-linked structure of these materials was radically different. (See, for instance, Figs. 1 and 2.) It is explained by the fact that the swelling liquid is a good plasticizer for epoxy resins, so that as the polymer swelled, its T_g shifted to a temperature below that at which the swelling tests were carried out (25°C), and the chemical cross-linking reactions could continue to completion. Thus, the swelling tests are useless for giving information about the original cross-linked structure of undercured resins. Such tests do, however, give information about completely reacted materials.

Figure 10 illustrates the detrimental effect of monofunctional flexibilizing agents on network structure. (EM207 contains some monofunctional groups, since the number of active carboxyl groups was found to be 1.3 per molecule.) Such agents greatly increase the sol fraction. Small amounts of these agents greatly increase the amount of swelling, but the amount of swelling may level off at higher concentration. The fact that large amounts of material can be extracted indicates imperfect network structures. Even though these materials are more highly cross-linked than normal vulcanized rubbers, more material can be extracted from these epoxies than can be extracted from vulcanized rubbers.

As the elastic modulus above the T_g decreases, the amount of swelling should generally increase as long as the solvent polymer interaction factor does not change significantly. Such a correlation was generally found as the amount of flexibilizer was increased and the curing agent concentration remained constant (Fig. 11).

Table 3. Swelling of Epoxy Resins in Acetone at 26°C

Composi- tion No.	Resin system	Cure	% Solubles	Swelling ratio
I	Epon 815 + TETA 7:1	24 hr at 25°C 24 hr at 60°C	—	1.31
II	Epon 815 + EM207 (90/10)	24 hr at 60°C	1.5	1.38
III	Epon 815 + EM207 (80/20)	24 hr at 60°C	3.0	1.45
IV	Epon 815 + EM207 (70/30)	24 hr at 60°C	6.1	1.53
V	Epon 815 + EM207 (60/40)	24 hr at 60°C	7.2	1.45
VI	Epon 815 + EM207 (50/50)	24 hr at 60°C	12.4	1.48
VII	Epon 815 + EM207 (30/70)	24 hr at 60°C	23.9	1.54
I _A	Epon 815 + TETA 7:1	24 hr at 25°C	1.13	1.36
I _B	Epon 815 + TETA 7:1	40 hr at 25°C	0.55	1.38
I _C	Epon 815 + TETA 7:1	120 hr at 25°C	1.90	1.36
I _D	Epon 815 + TETA 7:1	24 hr at 25°C 18 hr at 40°C	—	1.32
I _E	Epon 815 + TETA 7:1	24 hr at 25°C 18 hr at 120°C	—	1.30

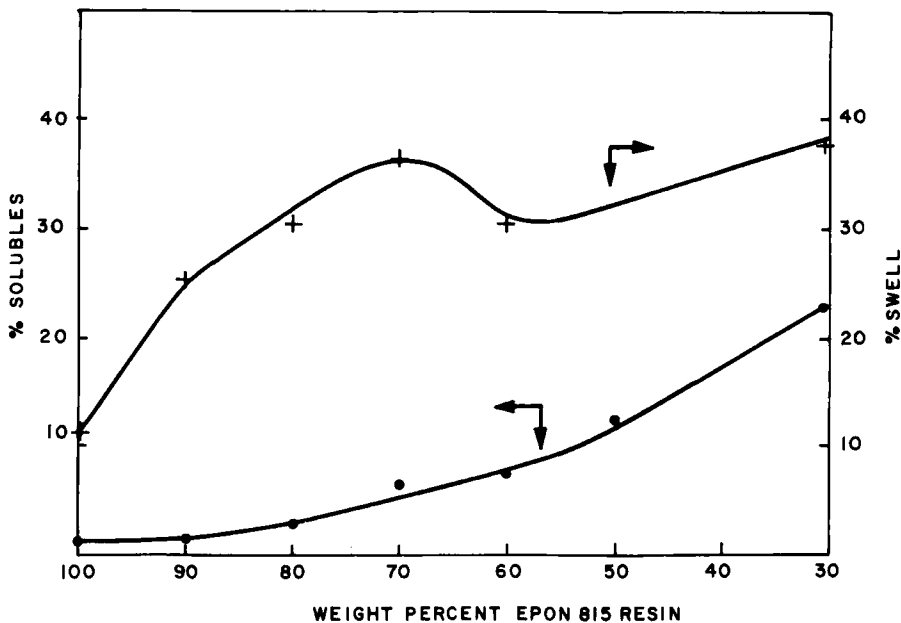


Fig. 10. Swelling of Epon 815 with varying amounts of flexibilizer. Resins cured for 24 hr at 25°C and 24 hr at 60°C.

Table 4 shows the dynamic shear modulus and swelling data for the Epon 815 + EM207 system as a function of curing agent ratios and for two Epon 826 + MDA resins, one prepared from bulk and the other polymerized from solution. In both cases the swelling increased as the modulus above the glass transition decreased. Although there is a general correlation between swelling data and high-temperature modulus data, a unique relationship is not expected because of possible heterogeneity in the cross-linked network. It appears that a combination of swelling and dynamic mechanical tests might be a good tool for detecting and studying heterogeneity in the density of cross-links. This heterogeneity factor has been largely neglected in the past.

The average degree of cross-linking can be characterized by M_c , the molecular weight between cross-links, which can be estimated in four ways:

1. From the elastic shear modulus above the T_g by the kinetic theory of rubber-like elasticity using the equation [8]

$$G = dRT/M_c$$

where G is the shear modulus.

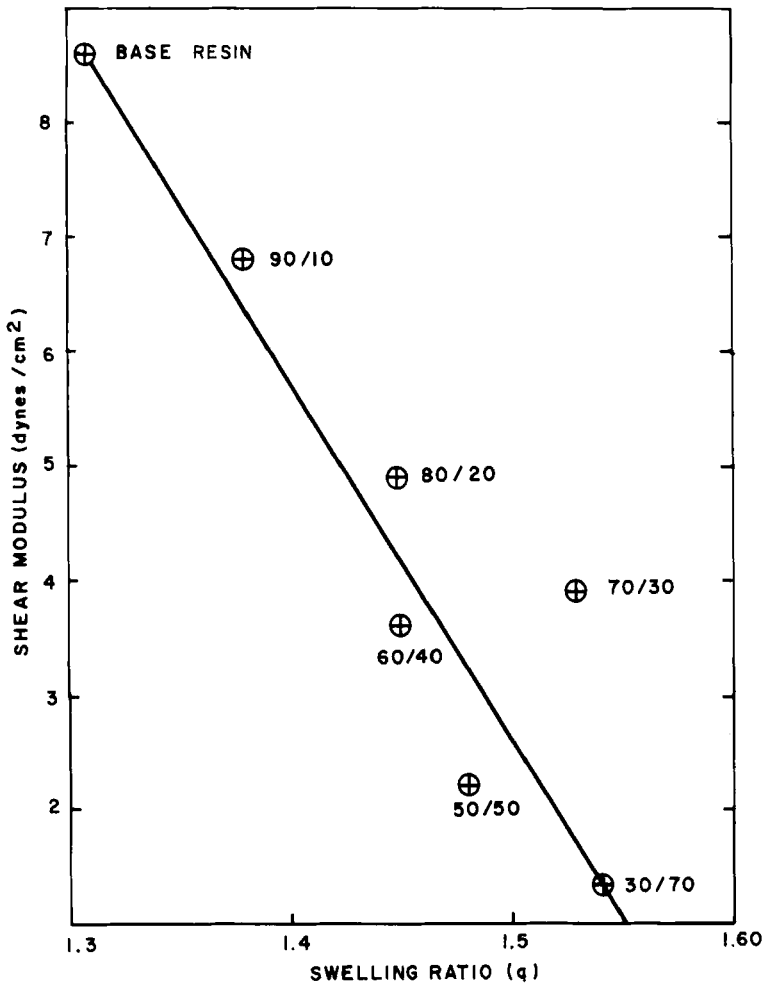


Fig. 11. Shear modulus at $T_g + 30^\circ\text{C}$ vs. swelling ratio for Epon 815 with varying amounts of flexibilizer. Numbers at data points are Epon 815/EM207 ratios.

Table 4. Modulus and Swelling of Epoxy Resins

Resin system	G at T _g + 30°C, dynes/cm ²	% Solubles	% Swelling	Swelling ratio
Epon 815 + EM207 (1:1) 6:1 resin/curing agent	8.8×10^6	30.4	84.9	2.25
Epon 815 + EM207 (1:1) 9:1 resin/curing agent	1.55×10^7	32.2	54	1.80
826 + MDA (solvent)	9.8×10^7	0.1	14.5	1.19
826 + MDA (bulk)	1.55×10^8	0.3	6.1	1.09

2. From the elastic modulus above the T_g using an empirical equation by Nielsen [9]

$$\log_{10} G \doteq 7.0 + \frac{293d}{M_c}$$

where G is the shear modulus in dynes/cm², and d is the density of the polymer.

3. From the chemistry of the systems [10].

4. From swelling tests using the Flory relation [11].

Table 3 compares M_c values calculated by methods 1, 2, and 3. In many cases the agreement between the theoretical chemical values and the empirical equation values is quite good. The values from the kinetic theory of rubber are generally not quite as close to the chemical values as are the empirical values. In the completely reacted systems, good estimates of M_c can generally be calculated from the chemistry of the system.

It appears that the theoretical equations for swelling [11] do not apply to systems as highly cross-linked as epoxy resins. Calculated values of M_c are far too small, i.e., these resins did not swell as much as expected. The observed swelling ratios for the epoxy resins were lower than calculated values of swelling ratio from the Flory relation even when a polymer-solvent interaction parameter of +0.5 was used. The value of +0.5 is the interaction parameter where incipient precipitation will take place with the least amount of swelling possible. Acetone, the solvent used for swelling measurements, would have a polymer-solvent interaction coefficient less than zero or a negative value which would lead to even higher predicted values for the degree of swell. Therefore, swelling data will not yield a suitable value for molecular weight between cross-links.

CONCLUSIONS

1. Dynamic modulus measurements have shown that broad damping is not necessarily related to heterogeneity of the network proper, but can be a manifestation of the curing reaction occurring simultaneously.
2. Slight differences in chemical composition or polymerization conditions can convert a single-phase epoxy resin into a two-phase system with different physical properties.
3. Monofunctional flexibilizing agents greatly reduce the perfection of the network structure and cause reduced elastic moduli above T_g and also give rise to large amounts of extractable material in the polymers.
4. Swelling theory does not hold for highly cross-linked systems; swelling is less than expected.
5. The value of the molecular weight between cross-links, M_c , can be closely approximated from the chemistry of the system if the curing reactions are allowed to go to completion and provided that the reactions follow the principal chemical reactions such as epoxy plus amine. Good estimates of M_c can also be made by using an empirical equation relating M_c to the elastic modulus above T_g .
6. The large sol fraction and "cheesy" fragile nature of the swollen epoxy resins indicate that the network structure of such polymers is much less perfect than normal vulcanized rubbers even though the epoxy resins are the more highly cross-linked.
7. Dynamic mechanical tests are sensitive to changes in the network structure of epoxy resins, and more extensive use should be made of such tests in characterizing these materials than has been the case in the past.

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