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**MONSANTO/WASHINGTON UNIVERSITY
ONR/ARPA ASSOCIATION**

**CROSSLINKING-EFFECT ON PHYSICAL
PROPERTIES OF POLYMERS**

Lawrence E. Nielsen

May 1968

**PROGRAM MANAGER
ROLF BUCHDAHL**

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MONSANTO RESEARCH CORPORATION

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FOREWORD

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CROSSLINKING-EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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A B S T R A C T

A review is made of the theoretical and experimental results of the effect of crosslinking on the physical properties of polymers. Both rubbers and rigid polymers are considered. Topics covered include: Types of network structures, methods of characterizing crosslinked polymers, swelling behavior, glass transitions, elastic moduli and dynamic mechanical properties, creep, stress-strain behavior, thermal properties, and anisotropic networks. The review is written from the practical viewpoint of the experimental scientist who is using crosslinked polymers but who is not an expert on the theory of crosslinking. Areas are pointed out where adequate scientific background information is lacking.

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INTRODUCTION

Many of the polymers used in composite systems and in other applications are crosslinked or thermoset polymers. How do such crosslinked polymers differ in properties from the better understood linear or thermoplastic polymers? This review paper will attempt to answer this question.

In spite of their intractable nature once they are formed and the difficulty of fabricating highly crosslinked polymers, such materials have some outstanding properties that make them ideal for many applications. The properties include:

1. Excellent dimensional stability and low creep rates.
2. Resistance to solvents.
3. In many cases high heat distortion or softening temperatures.

Crosslinked structures can be made in essentially two ways: 1. The tying together of long linear polymer molecules to give an infinite network structure. 2. The building up of low molecular weight multifunctional molecules to give higher molecular weight branched structures and eventually continuous cross-linked structures. An example of the first type is the vulcanization of rubber, while condensation polymerizations containing some tri- or tetra-functional molecules are examples of the second type.

In addition to vulcanized rubbers, typical crosslinked polymers include: phenol-formaldehyde resins, melamine resins, crosslinked polyester resins, and epoxy resins.

The theory of gelation and crosslinking is described in detail in the classical work of Flory (1) and others (2, 3). Infinite network structure or gelation does not occur until the polymerization reaction has progressed to a critical value which is determined by

$$b_c = \frac{1}{f-1} \quad (1)$$

b_c is the critical value of the branching coefficient b which is defined as the probability that a given functional group of a crosslinking agent will lead along a chain to another crosslinking unit. f is the functionality of the crosslinking agent. If $f = 3$, $b_c = \frac{1}{2}$. The branching coefficient b is related to the extent of the polymerization reaction. For instance, in the special case of polyesters formed by reacting a difunctional acid with a mixture of di- and trifunctional alcohols in stoichiometric amounts, the branching coefficient is related to the extent of reaction p by

$$b = \frac{p^2 \rho}{1 - p^2 (1 - \rho)} \quad (2)$$

where ρ is the ratio of hydroxyl groups (reacted and unreacted) belonging to the trifunctional alcohol to the total number of hydroxyl groups in the mixture. Thus, if the mixture contains just the acid and trifunctional alcohol ($\rho = 1$), gelation should occur when the extent of reaction is $p = (\frac{1}{2})^{\frac{1}{2}} = 0.707$. Of course, gelation is nowhere near complete at this extent of reaction, and the gel contains many molecules not attached to the network structure. In the crosslinking of long chain polymers by a crosslinking agent such as in the case of vulcanization of rubber, gelation

starts when there is one crosslinkage for each two of the original polymer molecules. Thus very little crosslinking agent can bring about gelation. In actual systems, the simplicity of the theoretical models and the basic assumptions of the theories may not be realized, so at best, the resulting mathematical equations are only approximate and over simplified.

WAYS OF CHARACTERIZING CROSSLINKED NETWORKS

Since crosslinked networks can have a great variety of structures, it is important to have techniques to characterize these structural parameters such as the crosslink density or the molecular weight of chains between crosslinks, the distribution in the length of chains between crosslinks, the perfection of the network, and the amount of polymeric material not attached to the network. Figure 1 symbolically illustrates a few of the possible types of network structures that might be expected. Networks can be regular, highly irregular, tightly crosslinked, loosely crosslinked, highly imperfect with intramolecular loops and many free ends and molecules trapped in the network but unattached to it, or combinations of the above. The crosslink junctures can be trifunctional or tetrafunctional. Thus, compared to characterizing the distribution in molecular weights of a linear polymer, the characterization of the structure of a crosslinked polymer is much more complex and difficult. To make matters even worse, the available techniques are not as good as those used to determine the molecular weights of linear soluble polymers. Therefore, the best that can be done with most crosslinked systems is to get some kind of an average density of crosslinks and a measure of the perfection of the network.

Methods of studying network structures include:

1. Chemical methods
2. Swelling solvents
3. Elastic moduli above the glass transition temperature
4. Creep (for rubbers)
5. Mechanical damping (for rubbers)
6. Shift in glass transition temperature.

If one knows the concentration of a crosslinking agent, and if it reacts completely according to one's hypotheses about the nature of the chemical reaction, it is possible to estimate the average molecular weight $\bar{M}_c$ of polymer between crosslinks. Generally, however, these chemical methods give only approximate estimates.

In the past, most of the effort has been to characterize the network structure of rubbers or polymers above their glass transition temperature T_g . Less effort has been concentrated on characterizing highly crosslinked polymers beyond the practical range of vulcanized rubbers or where the available theories tend to become invalid. Practically nothing has been done to characterize materials in the rigid state below their T_g where most properties are insensitive to the nature of any crosslinked network that might be present.

If an uncrosslinked polymer is soluble in a liquid, then the same polymer when crosslinked will swell in the liquid. The theory of the swelling behavior of lightly crosslinked polymers in liquids is fairly complete (1). Three types of data can be obtained from swelling measurements: 1. The amount of polymer that is not incorporated into the network structure and, therefore, can be extracted

as a sol fraction. 2. The molecular weight of the sol fraction. 3. The amount of swelling of the gel fraction. Swelling is generally expressed as a swelling ratio q defined as follows:

$$\text{Swelling ratio} = q = \frac{\text{Volume of swollen gel}}{\text{Volume of unswollen gel}}.$$

The soluble part of the material or sol fraction is defined as

$$\text{Sol fraction} = \frac{\text{Weight of soluble material extractable}}{\text{Initial weight of material}}.$$

The three quantities characterizing a crosslinked polymer are theoretically not independent. However, in most practical situations we do not know enough about the crosslinking reactions and their kinetics to apply theory properly, so all three quantities should be measured.

The swelling of a crosslinked polymer in a liquid can be related to the number average molecular weight of the polymer between crosslinks by:

$$-\left[\ln(1-v_2) + v_2 + \chi v_2^2 \right] = \left(\frac{V_1}{\bar{v} M_c} \right) \left(1 - \frac{2M_c}{M} \right) (v_2^{\frac{1}{3}} - v_2/2). \quad (3)$$

where v_2 is the volume fraction of polymer in the swollen polymer in equilibrium with the pure solvent, i. e., v_2 is the reciprocal of the equilibrium value of the swelling index; $v_2 = 1/q$. V_1 is the molar volume of the solvent, $\bar{v}$ is the specific volume of the polymer (reciprocal of its density), M is the molecular weight of the polymer before crosslinking, and M_c is the number average molecular weight of polymer between crosslinked junctions. χ is a term characterizing the interaction between the solvent and the polymer. χ is negative for good solvents, and incipient precipitation is approached for

high molecular weight polymers at $\chi = + 0.5$. Table I lists some χ values for typical polymer-solvent systems.

TABLE I
Polymer-Solvent Interaction
Parameter χ

<u>Polymer</u>	<u>Solvent</u>	<u>Temp. °C</u>	<u>χ</u>	<u>Ref.</u>
Polystyrene	Toluene	27	0.44	a
Polystyrene	Methyl ethyl ketone	25	0.51	b
Polyvinyl Chloride	Tetrahydrofuran	27	0.14	a
Polyvinyl Chloride	Dioxane	27	0.52	a
Polyvinyl Chloride	Tributyl phosphate	53	-0.65	a
Polyvinyl Chloride	Methyl ethyl ketone	25	0.47	b
Nat. Rubber	Benzene	25	0.44	b
Nat. Rubber	Carbon tetrachloride	20	0.28	a
Nat. Rubber	n-hexane	25	0.43	b
Polymethyl methacrylate	Benzene	25	0.41	b
Polymethyl methacrylate	Chloroform	25	0.33	b

a. Brandrup & Immergut, "Polymer Handbook," Interscience, New York, 1966.

b. Bristow & Watson, Trans. Faraday Soc., 54, 1742 (1958).

For typical vulcanized rubbers, q is of the order of 10 in good solvents, and M_c is about 5000. Typical thermoset polymers have M_c much less than 5000, and the swelling equation is not expected to be quantitatively accurate in this case. However, for any given polymer-solvent system the generalization should still hold that as M_c gets smaller, the swelling should be less. Thus, even in highly crosslinked systems, swelling measurements are of value in characterizing the network structure.

Equation 3 can be used to estimate M_c , the number average molecular weight between crosslinks. A possible method of determining the distribution of molecular weights between crosslinks is to measure the swelling of a polymer as a function of pressure (4). The variation of swelling with applied pressure P is:

$$-P = \left(\frac{RT}{V_1}\right) \left[\ln(1 - v_2) + v_2 + \chi v_2^2 + \left(\frac{V_1}{\bar{v} M_c}\right) (v_2^{\frac{1}{3}} - v_2/2) \right]. \quad (4)$$

However, accurate determinations of distributions in M_c are difficult by this procedure because of the inherent low sensitivity of equation 4 and the complex mathematical conversion of experimental results into a distribution function of M_c .

The kinetic theory of rubber (1,5-7) relates the equilibrium elastic modulus at temperatures well above T_g to the density of crosslinks by:

$$G = \left(\frac{\bar{r}^2}{r_0^2}\right) \frac{dRT}{M_c} \left(1 - \frac{2M_c}{M_n}\right). \quad (5)$$

G is the shear modulus of elasticity, d is the density, T is the absolute temperature, R is the gas constant, $\bar{M}_n$ is the molecular weight of uncrosslinked

polymer, $\frac{\overline{r^2}}{r_0^2}$ is the ratio of the mean square distance between network junctures to the mean square end-to-end distance of network chains in free space. The term $\overline{r^2}/r_0^2$ is often neglected since this ratio is generally about 1.0. Equation 5 applies fairly well for crosslinked rubbers if the measurements are carried out slowly enough that near equilibrium is achieved. For fast measurements, especially those on very lightly crosslinked rubbers, the measured modulus values are greater than those predicted by equation 5. At least part of this higher value is due to chain entanglements, which act as temporary crosslinks. The term $2M_c/\overline{M}_n$ is a correction for polymer chain ends not effectively tied into the network; if $\overline{M}_n$ is large or if the degree of crosslinking is moderate, this term can be neglected. Equation 5 can also be approximately given by:

$$G \doteq \frac{dRT}{M_c} \doteq nRT \doteq 2 C_x RT \doteq \frac{\nu RT}{N} \doteq 2\rho dRT \quad (6)$$

where n is number of moles of network chains per unit volume of polymer, C_x is the number of moles of tetrafunctional crosslinking agent per unit volume of polymer, ν is the number of crosslinked chains per unit of volume, N is Avogadro's number, and ρ is the number of moles of crosslinks per gram of final polymer. This equation implies that

$$n = 2 C_x = d/M_c = \frac{\nu}{N} = 2\rho d \quad (7)$$

but Tobolsky (8) suggests that a more accurate equation is

$$n = C_x [2X + 3 (1 - X)] \quad (8)$$

where $(1 - X)$ is the mole fraction of crosslinking agent. Around 20°C , the shear modulus is about

$$G \cong 2.5 \times 10^{10} \frac{d}{M_c} \cong 5 \times 10^{10} C_x. \quad (9)$$

In a later section the effect of very high degrees of crosslinking on elastic moduli will be discussed. Although the kinetic theory of rubber no longer is valid in this case, the elastic moduli still appear to be nearly independent of the chemical structure of the network and to depend primarily upon the tightness of the network structure only. Thus, even at very high degrees of crosslinking, the elastic moduli at high temperatures are still a good empirical method of characterizing crosslinked materials.

Other methods of characterizing network structures that will also be discussed in later sections include the shifting of the glass transition temperature to higher values, the reduction in the creep of rubbery materials, and the change in the mechanical damping behavior of rubbery polymers. These methods are largely empirical and relative in nature, although some attempts have been made to put the shift in glass transition on a good theoretical foundation. In spite of the lack of a good theoretical justification, these methods are useful because of their sensitivity and ease of measurement, especially if they are calibrated for each system by other techniques such as swelling or modulus measurements.

EFFECTS OF CROSSLINKING ON THE GLASS TRANSITION

Crosslinking increases the glass transition temperature T_g of a polymer (9-13). At low degrees of crosslinking, the shift in T_g is very small, but

at high degrees the shift is very large and is sensitive to relatively small changes in M_c . In most systems the shift in T_g is not independent of the chemical composition of the polymer, and this is a complicating factor (10).

As more and more crosslinking agent is incorporated into the network structure, the chemical composition of the polymer gradually changes. The crosslinking agent can be considered as a type of copolymerizing unit. Thus, the shift in the glass transition temperature is made up of two nearly independent effects:

1. The degree of crosslinking or $1/M_c$ and
2. The copolymer effect.

The crosslinking effect always increases T_g and seems to be largely independent of chemical composition while the copolymer effect can either increase or decrease T_g depending upon the chemical nature of the crosslinking agent.

A number of studies have been made relating the degree of crosslinking to the shift in T_g (9,10,12,13). The different studies do not agree very well with each other. However, by averaging the results, rough estimates of M_c can be made from the shift in T_g by the following equation:

$$T_g - T_{g0} = \frac{3.9 \times 10^4}{M_c} \quad (10)$$

where T_{g0} is the glass transition temperature of the uncrosslinked polymer. In using this equation, it must be remembered that it accounts only for the shift due to crosslinking; the shift due to the copolymer effect must be separately accounted for.

DiMarzio (15) and more recently DiBenedetto (16) have derived from theory an equation relating the shift in the glass transition temperature to the degree of crosslinking. DiBenedetto's equation is:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{\left[\frac{\epsilon_x}{\epsilon_M} - \frac{F_x}{F_M} \right] X_c}{1 - \left(1 - \frac{F_x}{F_M} \right) X_c} \quad (11)$$

where T_{g0} is the glass transition temperature of a polymer of the same chemical composition as the crosslinked polymer except the crosslinks themselves are absent; the copolymer effect on T_g due to the crosslinking agent is accounted for in T_{g0} , so equation 11 predicts only the shift in T_g due to crosslinking. $\frac{\epsilon_x}{\epsilon_M}$ is the ratio of the lattice energies for crosslinked and uncrosslinked polymers, while F_x/F_M is the ratio of the segmental mobilities for the same two polymers. X_c is the mole fraction of monomer units which are crosslinked in the polymer. For most polymers it is expected that the mobility of a crosslinked unit is essentially zero, so $F_x/F_M = 0$. The ratio ϵ_x/ϵ_M can be approximated by

$$\frac{\epsilon_x}{\epsilon_M} \approx \frac{d_M}{d_x} \frac{(M_0)_x}{(M_0)_M} \left(\frac{\delta_x}{\delta_M} \right)^2 \quad (12)$$

where the d 's are the densities of the crosslinked and uncrosslinked polymers, $(M_0)_M$ is the molecular weight of an uncrosslinked monomer unit, $(M_0)_x$ is the molecular weight of a crosslinked monomer unit, while δ_x and δ_M are the solubility parameters of crosslinked and uncrosslinked polymer, respectively. DiBenedetto (16) has estimated that $\epsilon_x/\epsilon_M \approx 1.2$ for the styrene-divinyl benzene system, and a similar value should hold for many other crosslinked systems, so that equation 11 can be approximately given in such cases by

$$\frac{T_g - T_{g0}}{T_{g0}} \approx \frac{1.2 X_c}{1 - X_c} \quad (13)$$

At low concentrations of crosslinking agent,

$$\frac{X_c}{1 - X_c} = \frac{2}{n_c} \quad (14)$$

Thus, from equations 11, 12, and 14,

$$T_g - T_{g0} = \frac{2 d_M (M_0)_x}{d_x (M_0)_M} \left(\frac{\delta_x}{\delta_M} \right)^2 \frac{T_{g0}}{n_c} \doteq \frac{2 T_{g0}}{n_c} \quad (15)$$

The theoretical equation 15 has essentially the same form as the empirical equation 10. However, equation 15 does depend somewhat on the structure of the polymer. The part depending upon the ratios of densities, monomer molecular weights, and solubility parameters should be roughly 1.0 or a little greater in many cases. Except for the term T_{g0} , equation 15 has the same form as another empirical equation (13):

$$T_g - T_{g0} \doteq \frac{788}{n_c} \quad (16)$$

where n_c is the average number of atoms in the polymer backbone between crosslinks. There are not enough good experimental data available to decide which equation is best with any degree of confidence, however, equations 13 and 15 are probably to be preferred to the empirical equations.

EFFECT OF CROSSLINKING ON DYNAMIC MECHANICAL PROPERTIES AND UPON ELASTIC MODULI

Typical dynamic mechanical behavior of polymers as a function of temperature is illustrated in Figure 2. At low frequencies of vibration, say one cycle per second or less, the damping peak and the drastic drop in the modulus occur at

about the same temperature as the glass transition. The damping peak is shifted to higher temperatures as the test frequency is increased; typical results are about 7°C shift for each factor of ten increase in the frequency (14).

Typical data on a highly crosslinked material such as phenol-formaldehyde plastics are given in Figure 3 (11). These results show that crosslinking has little effect on the modulus of a polymer below T_g , i. e., at temperatures well below the damping peak, where the material is rigid. However, at temperatures above the damping peak, the modulus is strongly dependent upon the extent of crosslinking. The increase in modulus is much more than what would be predicted by the kinetic theory of rubber.

In addition to the changes in modulus at high temperatures, Figure 3 shows that the damping peak (which is associated with the glass transition region) is shifted to higher temperatures and is greatly broadened as crosslinking increases. It is not known whether or not this broadening is inherently due to crosslinking or if it is due to heterogeneity in the crosslinked structure. Possibly if there were no distribution in the lengths of chains between crosslinks, the transition region would remain fairly sharp as in a linear polymer (9). In some highly crosslinked systems the transition region is so broadened and shifted to such high temperatures that it is impossible to tell whether or not a glass transition exists before decomposition takes place to obscure the experimental results.

Dynamic mechanical tests are a rapid and very sensitive measure of crosslinking at temperatures above T_g . The kinetic theory of rubber shows that the modulus can be used to measure crosslinking, but for lightly crosslinked rubbers, the mechanical damping may be a much more sensitive indicator of

crosslinking (17,18). In the present state of the art, damping is a relative not an absolute, method of measuring crosslinking. However, when it is calibrated for a given system, damping is a rapid and sensitive method of measuring M_c . Figure 4 shows how the damping differs for a very lightly vulcanized rubber and a highly crosslinked rubber (18). In many respects, the damping of a very lightly crosslinked rubber resembles that of a non-crosslinked polymer. The reasons for this are not clearly understood but is believed to be related to trapped entanglements (19). Figure 5 is a calibration curve relating damping above T_g to the swelling of a rubber in a good solvent. Damping decreases as M_c decreases. This would be expected if one assumes that a perfectly elastic system should not dissipate any energy as heat, i. e., its damping should be zero. The mechanical damping is a very convenient method of measuring the degree of crosslinking of rubbers since it requires only a few minutes in contrast to swelling measurements, which generally require several days.

At very high degrees of crosslinking that are characteristic of thermoset polymers, rubber theory no longer is applicable, and equation 5 is not valid at moduli much greater than 10^8 dynes/cm². An empirical approach such as that used by Tobolsky (8,20-23) is then needed to relate elastic moduli to degree of crosslinking. Fortunately, a unique relationship seems to hold which is nearly independent of the chemical composition of the polymer as long as the modulus is measured at temperatures well above the glass transition temperature. This effect of high degrees of crosslinking on modulus is illustrated in Figure 6 for a series of polyethyl acrylate-tetraethylene glycol dimethacrylate (TEGDM)

copolymers in which the TEGDM acts as a crosslinking agent (22). An equation that appears to give a reasonable estimate of the degree of crosslinking for highly crosslinked polymers is:

$$\log_{10} G \cong 7.0 + \frac{293 d}{M_c} \cong 7.0 + 585 C_x \quad (17)$$

The equation holds at temperatures about 30°C above T_g or higher. Its valid range is believed to be roughly 2×10^7 to at least 2×10^9 dynes/cm². Figure 7 shows that in the range of shear moduli from 10^7 to 10^8 dynes/cm² equation 17 and the kinetic theory of rubber give comparable values. At higher degrees of crosslinking, the kinetic theory gives values which are too low. Equation 17 is at best a rather crude empirical relationship, but better experimental data or advances in our theoretical knowledge are required to improve upon it.

Generally the glass transition of a crosslinked polymer will not go much higher than the curing temperature or the temperature at which the polymer was formed even if the T_g would be expected to be much higher (11, 24). This is because most chemical reactions essentially stop at temperatures below T_g . Thus, most crosslinking reactions stop when the reaction has proceeded to the point where T_g is raised to the temperature at which the reaction is being carried out. If the temperature is raised, the reaction can again continue and can be detected by modulus measurements. In measuring the modulus as a function of temperature, the modulus will decrease near T_g , and if further reaction takes place, the modulus will soon start to increase in contrast to the normal decrease as the temperature is raised. Thus, dynamic mechanical tests are useful in studying the extent of crosslinking reactions as functions of time and temperature.

Recent theoretical (25) and experimental (24,26) results indicate that the network structure of many crosslinked polymers such as epoxy resins is not the simple homogeneous type generally assumed. Rather, the polymer can consist of highly crosslinked microgel particles embedded in a less highly crosslinked matrix. This two-phase network structure can be seen by microscopic techniques and also by dynamic mechanical tests. Figure 8 compares the damping behavior of a two phase epoxy resin with a homogeneous polymer of similar over-all chemical composition (24). The microgel phase and the matrix phase clearly show up as two peaks in the broad damping curve, while the homogeneous polymer has a single narrower peak.

CREEP

In creep tests the elongation or deformation of a specimen is measured as a function of time under the action of a constant load. It is well known that crosslinking greatly reduces the creep of a rubbery material, but surprisingly little quantitative data are available in spite of the great practical importance of the subject. The effect of crosslinks is especially pronounced at long times; at very short times crosslinking has a much smaller effect on the creep of rubbers since entanglements can act as temporary crosslinks in decreasing the elongation. Figure 9 illustrates the tremendous sensitivity of creep to the extent of crosslinking as measured by swelling ratio and sol fraction (18). Even very imperfect network structures with low degrees of crosslinking and high sol fractions greatly reduce creep. The creep rate decreases as crosslinking increases, but even with rubbers of very low swelling ratio, creep appears to go on forever at a slow rate (27,28). From theory it might be expected that

creep should be proportional to $q^{5/3}$ (1). This dependence of creep on the $5/3$ power of the swelling ratio is not found to hold accurately experimentally and should be considered as only a first approximation.

Plazek (29) has carried out very accurate creep work on natural rubber as a function of crosslinking. In addition to the general effects discussed above, he found that for a given degree of crosslinking, data at different temperatures could be superimposed by the usual W-L-F shift factors which were developed for noncrosslinked polymers (30). Furthermore, curves for different degrees of crosslinking could be superimposed to give a master creep curve by horizontal and vertical shifts of the creep curves. The vertical shift is given by

$$\log \left(\frac{E_e (M_c)}{E_e (M_c^0)} \right)$$

where $E_e (M_c)$ is the long time equilibrium modulus of a rubber with a degree of crosslinking corresponding to M_c while $E_e (M_c^0)$ is the equilibrium modulus of a reference rubber with crosslinking represented by M_c^0 . The horizontal shift along the time axis is also a function of the degree of crosslinking.

Although many creep measurements have been made on crosslinked polymers in the glassy state, these creep tests have generally been of an

engineering nature and little of scientific value can be obtained from them. The degree of crosslinking has been unknown, and the effects of crosslinking have been obscured by the presence of fillers. However, it appears that crosslinking has no major effect on creep of polymers at temperatures well below their glass transition region. In rigid brittle polymers, molecular motions are so frozen-in that the additional restrictions of crosslinks are hardly noticeable. However, at high loads, at very long times, or at temperatures not far below T_g , crosslinking should reduce creep.

The creep of rigid polymers is strongly dependent upon the elastic modulus of the polymer, the mechanical damping, and the difference between T_g and the ambient temperature. Some thermoset materials such as phenol-formaldehyde and melamine resins have high moduli, low mechanical damping, and high glass transition temperatures. All of these factors tend to reduce creep and creep rate, so these types of polymers generally have low creep and very good dimensional stability. On the other hand, some epoxy and polyester resins have much greater creep; they often have shear moduli less than 10^{10} dyne cm^2 because of low temperature secondary glass transitions. In addition, because of their chemical structure and low curing temperatures, many epoxy resins have relatively low glass transition temperatures.

For these reasons, typical epoxy resins may have considerably greater creep than the more highly crosslinked phenol-formaldehyde resins.

STRESS-STRAIN BEHAVIOR

The effect of crosslinking on stress-strain properties of rubbers and polymers above their glass transition temperatures is well established. However, at temperatures below T_g , little is known, and the evidence is somewhat contradictory.

Many examples of polymers above their T_g have been shown to follow the same general trends illustrated in Figure 10 (31-35). The elongation to break ϵ_B decreases as crosslinking increases. $\epsilon_B = (\lambda_B - 1)$ where λ_B is the extension ratio at break. The tensile strength first increases with crosslinking, goes through a maximum at low degrees of crosslinking, and then progressively decreases. Theory suggests that the extension ratio to break λ_B should be proportional to the square root of the reciprocal of the density of effective crosslinks ν_e (32, 36). Experimentally it has been found in some cases that indeed $\lambda_B \propto \frac{1}{\nu_e^{\frac{1}{2}}}$, (37) but in other cases, the relation is not accurately followed. Theories (32, 38, 39) predict that up to the maximum value the tensile strength σ_B should be proportional to $\nu_e^{\frac{2}{3}}$ or to ν_e . Experimentally, this is found to be roughly correct, but some experimental data on tensile strength may be proportional to $\nu_e^{\frac{1}{2}}$ rather than to $\nu_e^{\frac{2}{3}}$ or ν_e (40).

Although the stress-strain behavior of rubbers shows pronounced variation with crosslinking, these mechanical properties would also be expected to reveal other factors characterizing the network structure. Network structures are not perfect and contain many ineffective intramolecular crosslinks in the form of polymer loops or branches. Loops become especially numerous if the crosslinking reaction is carried out in the presence of an inert diluent. These loops manifest themselves during mechanical tests by decreased modulus and strength (41). Case (42) has developed a theory which predicts how other network characteristics should affect stress-strain properties. This theory indicates that rubbers containing trifunctional branched crosslinks should have greater elongations to break than equivalent rubbers containing tetrafunctional crosslinks. The theory also predicts that rubbers with regularly spaced crosslinks should have greater elongations to break than rubbers containing randomly spaced branch points. Although intramolecular loops are ineffective in carrying an applied load, interpenetrating loops on the other hand can increase the number of effective crosslink points and can help carry an applied load (43).

Smith (44, 45) has proposed the "failure envelope" as a convenient way of compressing a great deal of stress-strain data into a single

diagram. A typical fracture envelope is illustrated in Figure 11 (45). In such a diagram the logarithm of the tensile strength is plotted against the logarithm of the elongation to break. The failure envelope is nearly independent of the temperature or rate of testing if the curves are reduced to a common reference temperature by multiplying the tensile strength by T_0/T , i. e., by the ratio of the reference temperature to the actual temperature, both in degrees absolute. Lowering the temperature or increasing the rate of testing (decreasing the time for the test) moves the experimental data in a counterclockwise direction around the failure envelope. Polymers in the rubbery state are at the bottom of the diagram or to the right side while rigid polymers are at the top. The tensile strength is calculated on the basis of the original cross sectional area, not the actual area at point of fracture. The same fracture envelope is obtained in constant load creep rupture tests as in conventional stress-strain tests.

Figure 12 illustrates the effect of degree of crosslinking on failure envelopes. As expected from the previous discussion, crosslinking shifts the envelope up and to the left. Master curves for all degrees of crosslinking in the rubbery state can be obtained by dividing the

tensile strength by the effective crosslink density to take care of the necessary vertical shift due to modulus changes. The curves for different degrees of crosslinking can then be superimposed to give a single curve (37). Another method of obtaining master curves for all degrees of crosslinking is to plot $\log \lambda_B \sigma_B \left(\frac{T_0}{T} \right)$ against $\log E_e \epsilon_B \left(\frac{T_0}{T} \right)$, where E_e is the long time equilibrium modulus of the rubber (45).

Unambiguous data on the effect of crosslinking on the stress-strain properties of rigid polymers are very scarce. However, in most cases changing the degree of crosslinking has little effect. For long chain rigid polymers such as polystyrene, a little crosslinking may increase the tensile strength, but high degrees of crosslinking drastically decrease tensile strength and make the polymer very brittle. For example, with styrene crosslinked by divinyl benzene, the tensile strength increases from 6700 psi with no crosslinking to 7400 psi at 4 percent divinyl benzene; the tensile strength then drastically decreases to 1000 psi at 25 percent divinyl benzene (46). Theoretically one would expect tensile strength to increase with crosslinking because weak Van der Waals' bonds are being replaced by strong covalent bonds. The decrease in tensile strength may be due to sub-microscopic cracks developing from internal stresses which result from shrinkage

or thermal changes after the mobility of molecular segments has been decreased by crosslinking.

For thermoset polymers such as phenol-formaldehyde polymers, the tensile strength rapidly increases with degree of crosslinking (or cure). Such low molecular weight materials are extremely brittle until the molecular weight has been built up by the curing reaction. However, above a certain stage of cure, the stress-strain properties become insensitive to the amount of crosslinking. At very high degrees of cure, the tensile strength may drop off somewhat. In all systems, but especially so with conventional thermoset polymers, the chemical structure of the polymer changes simultaneously with the degree of crosslinking. It is often impossible to decide whether it is the chemical changes or the crosslinking that is the cause of the observed effects. Radiation can sometimes be used to crosslink polymers, but often radiation simultaneously causes other effects, such as degradation, which confuse the interpretation of data (47). Figure 13 shows how various properties of a melamine resin (a typical thermosetting polymer) change with the degree of cure (48). Although the strength and heat distortion temperature greatly increase with crosslinking, the modulus remains nearly constant.

Strength properties can be discussed in terms of a modified Griffith crack theory (14, 49, 50). For most test specimens the following equation is applicable:

$$\sigma_B = \left(\frac{2E\gamma}{\pi C} \right)^{\frac{1}{2}}$$

In this equation C is the length of the flaw or crack which eventually leads to the fracture of the rigid material, and γ is the surface energy or plastic work function term. The surface energy term γ is the energy required to produce a square centimeter of new surface during the fracture process; it generally consists of several factors: 1. The surface energy of the material, which is low for polymers. 2. The plastic work and molecular orientation that take place at the tip of the growing crack. This last term can be very large compared to the surface energy (50, 51).

Very little information is available on how crosslinking affects flaw size C and surface work γ . At least in some cases, however, crosslinking decreases the surface energy for fracture and at the same time decreases the flaw size (52). These two factors tend to counteract one another, so it is possible for the tensile strength to increase with crosslinking if the flaw size decreases at a faster rate than the surface energy term.

The strength and toughness of a material are increased by an increase in the surface area generated during fracture. Thus, rough fracture surfaces and many cracks rather than a single fracture crack can be desirable. This may be the reason why the experimental surface work term increases in going from a pure crosslinked resin to a laminated fabric structure containing the resin (53).

EFFECT OF CROSSLINKING ON OTHER PROPERTIES

Crosslinking has a pronounced effect on the specific volume of a polymer and on the thermal coefficient of expansion (9, 10, 54, 55,). For both rubbers and rigid polymers, the specific volume decreases nearly linearly with increasing density of crosslinks.

$$\bar{v} = \bar{v}_0 - k\rho \quad (18)$$

where $\bar{v}$ is the specific volume of the crosslinked polymer, $\bar{v}_0$ is the specific volume of the uncrosslinked polymer, k is a constant, ρ is the number of moles of crosslinking agent per gram of crosslinked polymer. A similar equation holds approximately for the coefficient of thermal expansion:

$$\alpha = \alpha_0 - k'\rho. \quad (19)$$

The coefficients of thermal expansion for the crosslinked and uncrosslinked materials are α and α_0 , respectively, and k' is an empirical constant. Different equations hold for the specific volume and the thermal

expansion above and below T_g , i.e., the values of k and k' are different above and below T_g . As mentioned earlier, crosslinking simultaneously increases T_g and broadens the transition region making it less and less distinct as crosslinking progresses.

As might be expected, crosslinking greatly reduces the degree of crystallinity and the melting point of crystallizable polymers (56). The effect is greater than expected if the crosslinking agent is considered just as a comonomer. The added restrictions on chain mobility introduced by the crosslinks also reduces melting points and crystallinity.

Crosslinking increases thermal conductivity slightly (57, 58). The effect is not great even at high degrees of crosslinking; however, it is expected since the flow of heat tends to be greater along covalently bonded chains than in directions perpendicular to chains where the forces are only weak Van der Waals' forces. Crosslinking has the effect of replacing some of the Van der Waals' forces by covalent ones.

Crosslinking can cut down the absorption and swelling of polymers in liquids and vapors which have some affinity for the polymer. This is illustrated in the case of water absorption in a melamine resin in Figure 13 (48). The absorption of water decreases as the extent of cure increases. The volume of a polymer increases roughly the same

amount as the volume of liquid absorbed (59). Thus, if too much liquid is taken up, the polymer may be fractured into many pieces unless the degree of crosslinking is high enough to greatly suppress the swelling (23, 60, 61). This fracture process may be one of the causes of deterioration of many composite materials by water.

Most thermoplastic polymers can be welded or made to adhere to themselves by using heat or solvents along with some pressure to make good contact between the two pieces of polymer. Even small amounts of crosslinking greatly reduce the ease of welding two pieces of the same material together. This field of autohesion has been extensively studied by Voyutskii (62).

Most of the discussion so far has been related to what might be called isotropic crosslinking. However, anisotropic network structures can also be formed. One way of forming anisotropic networks is to partially crosslink a rubber; then the rubber is stretched and the crosslinking is continued to completion. Such a process essentially superimposes two types of networks in one polymer. Such materials show properties due to crosslinking similar to what has already been discussed except that anisotropic network polymer may show somewhat different properties

in different directions. The modulus of anisotropic rubbers is increased in the direction parallel to the direction of stretch while the elongation to break is decreased in the direction of the original stretch (63-65). Swelling tends to be greater in the direction perpendicular to the original direction of stretch. Several papers on the theory and experimental results of anisotropic networks have been published (66-68).

SUMMARY

Crosslinked network structures can be very complex and varied, and our tools for studying and characterizing such structures are not adequate. The techniques for studying high degrees of crosslinking and crosslinking in the solid state are especially poor. For this reason, clear-cut data showing how crosslinking affects various physical properties is limited, and more good scientific work is needed both for developing techniques and for determining the relation of physical properties to crosslinking.

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Figure: 1

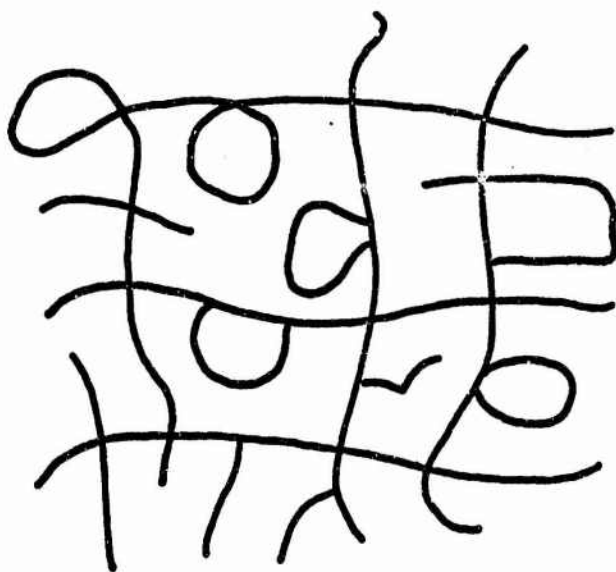
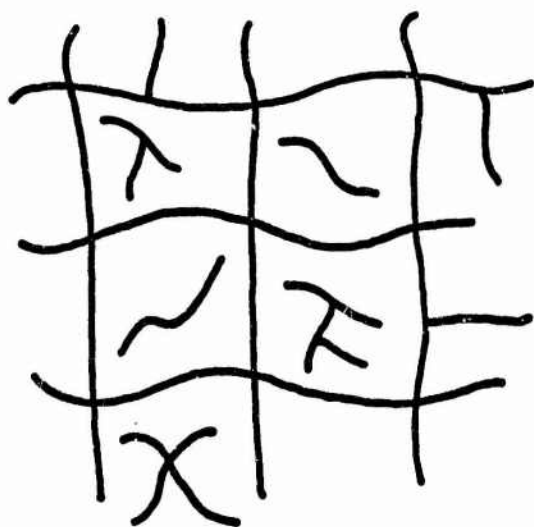
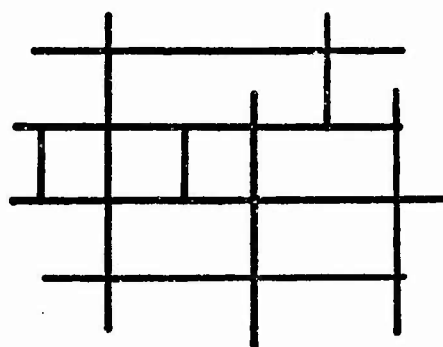
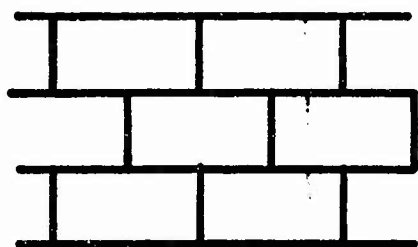
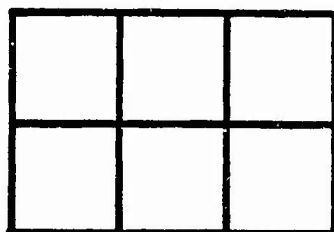
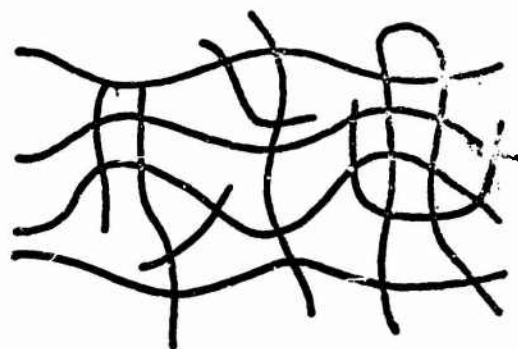
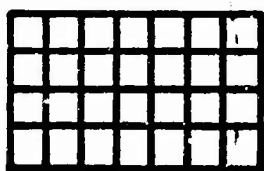


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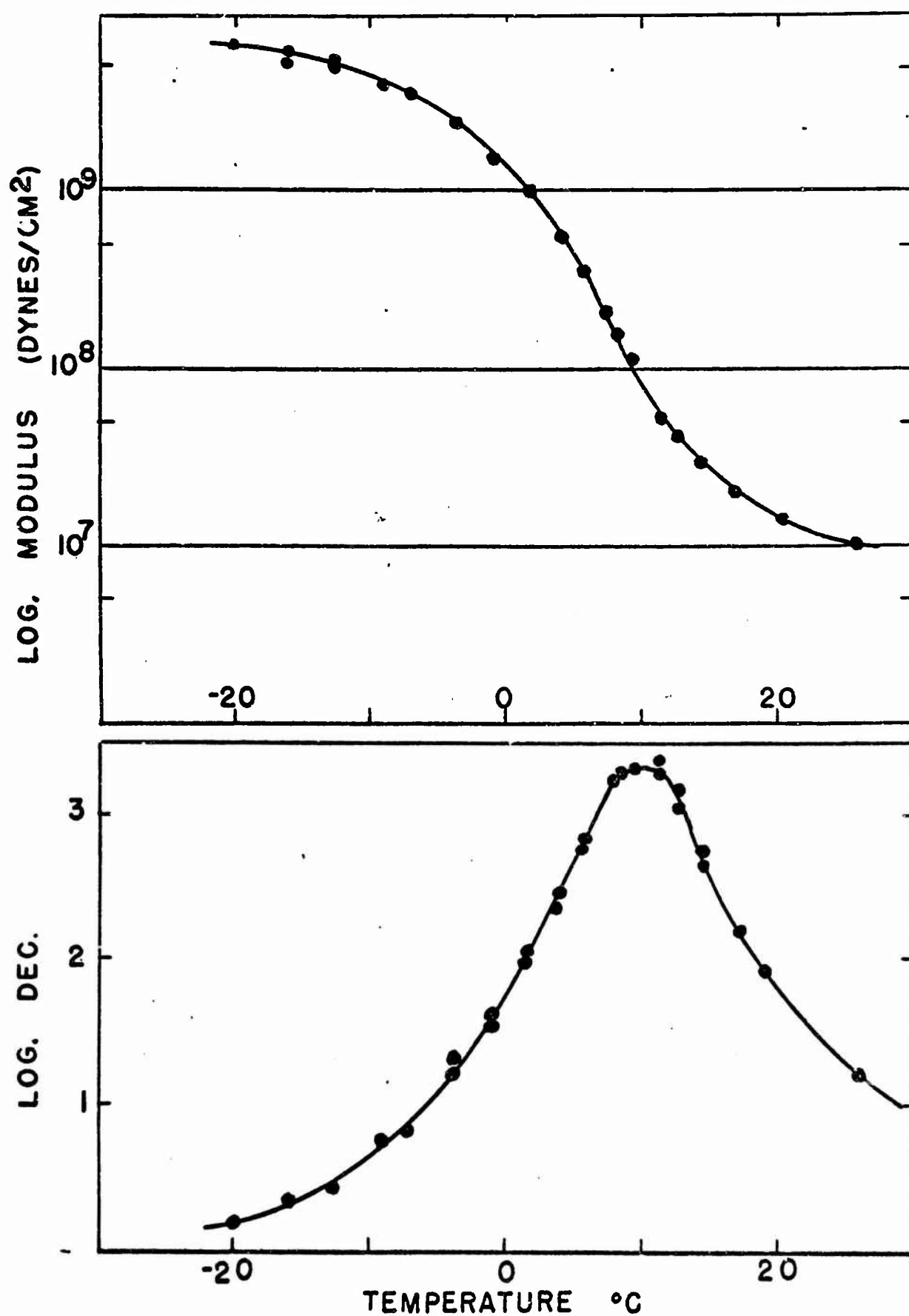
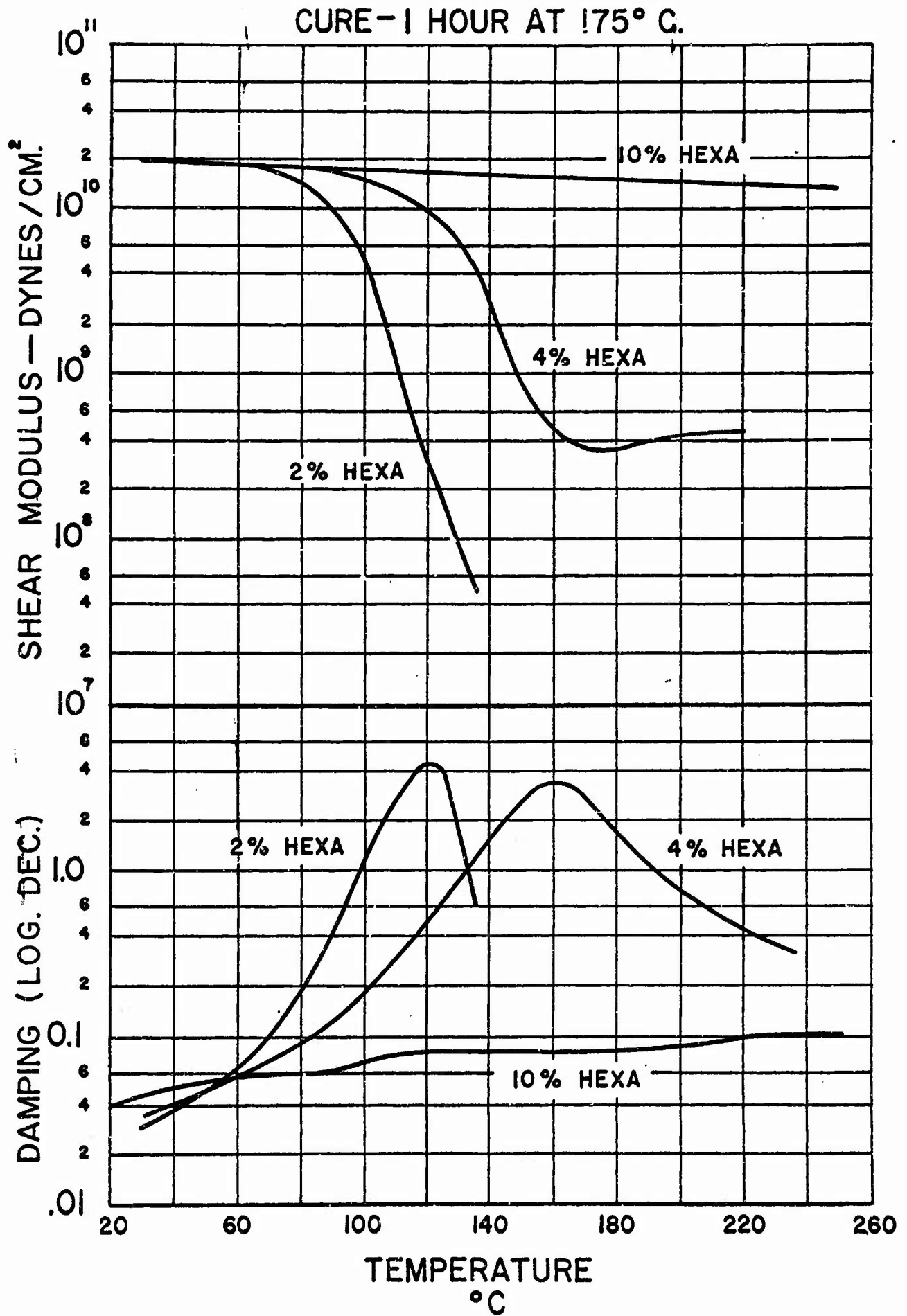
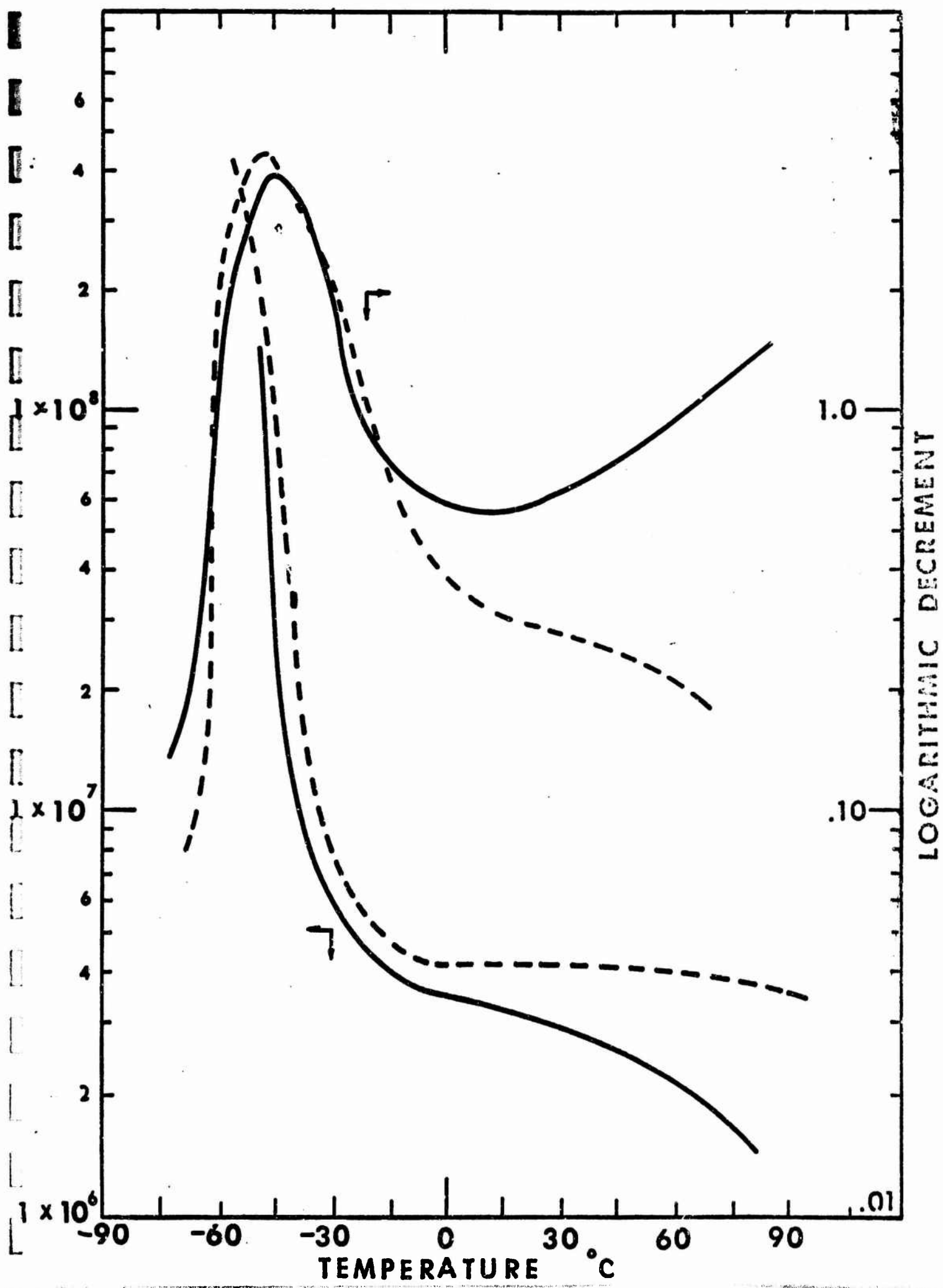


Figure 3





DAMPING (LOG. DECREMENT) AT 50°C

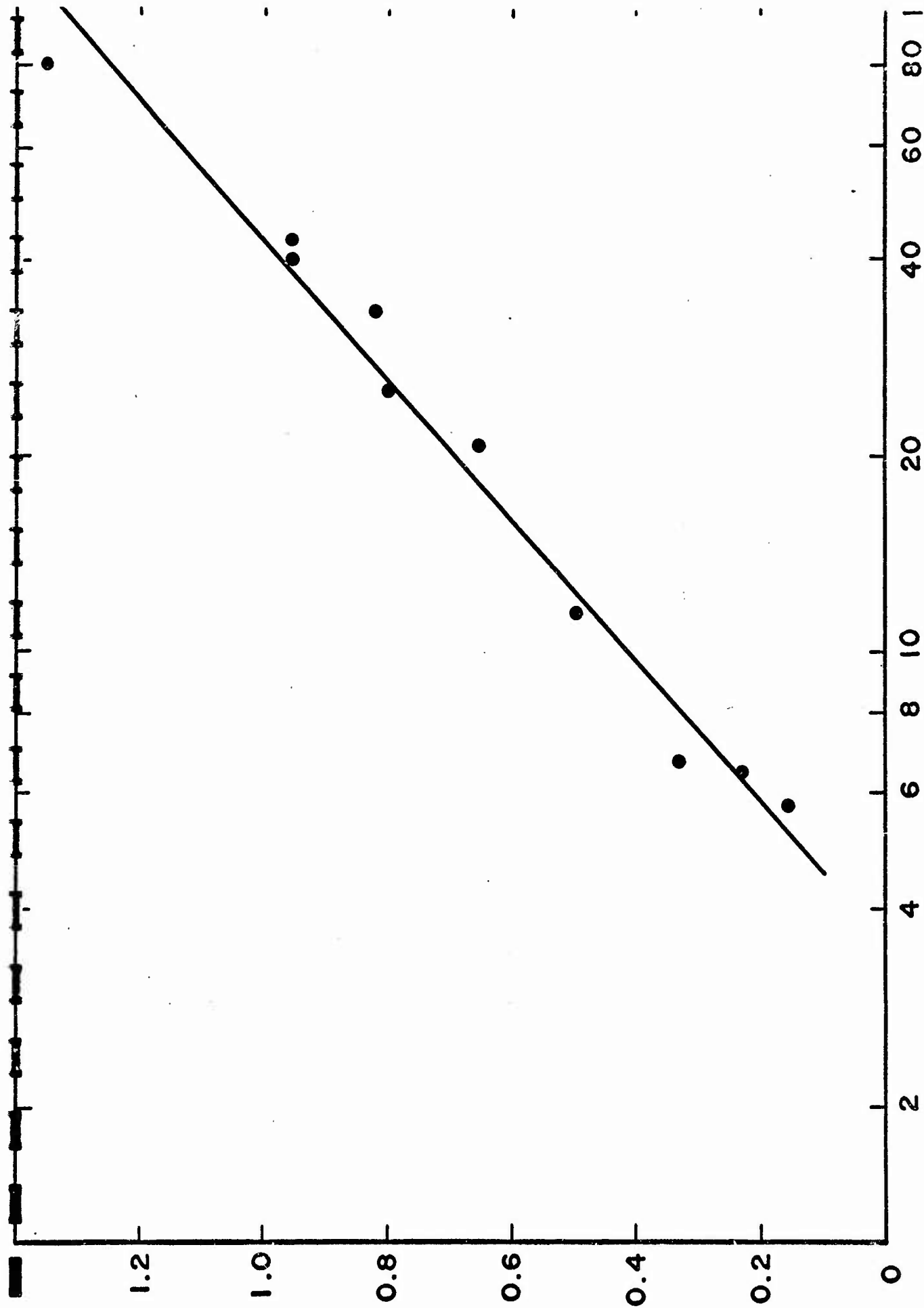


Figure 6

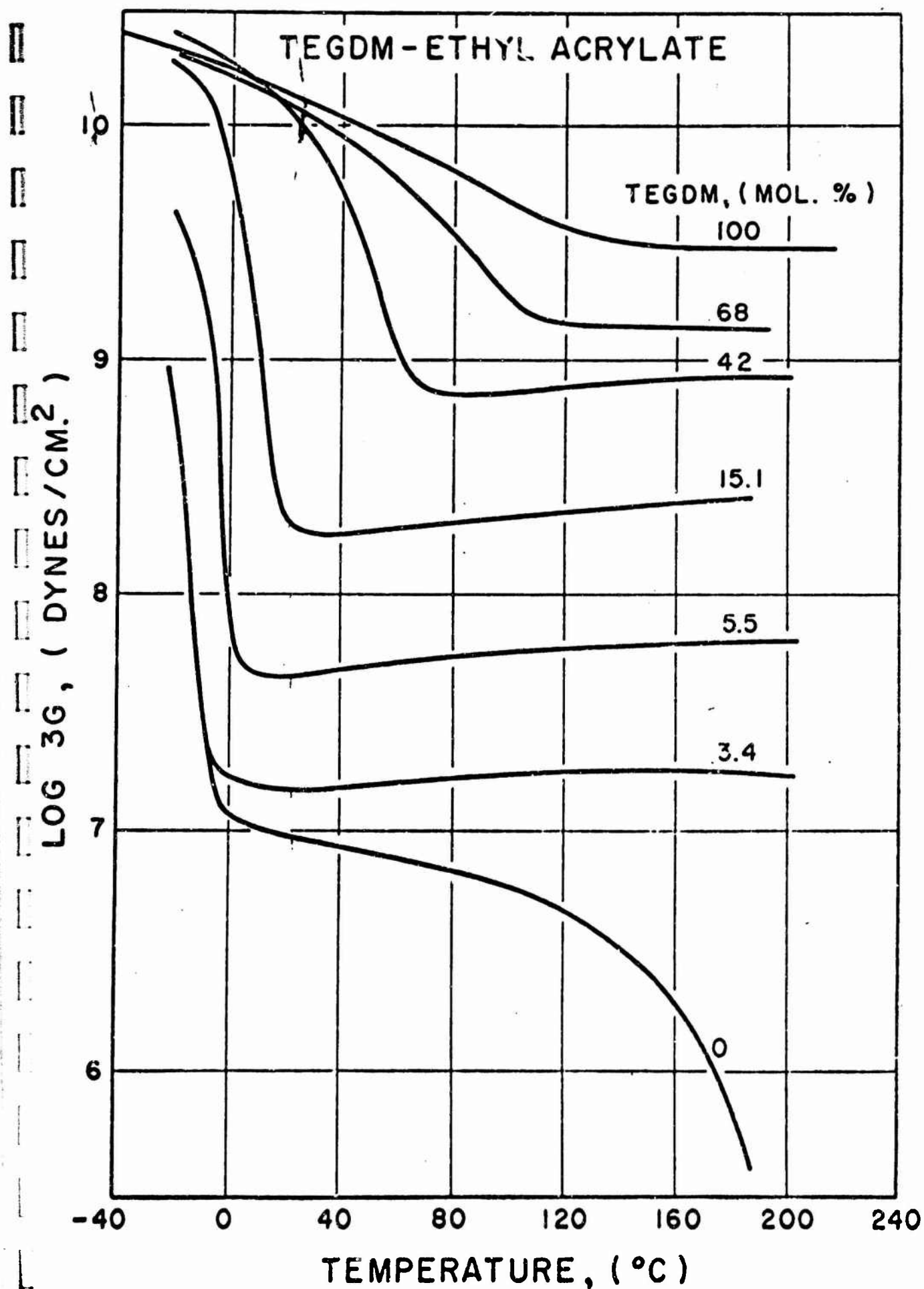


Figure 7

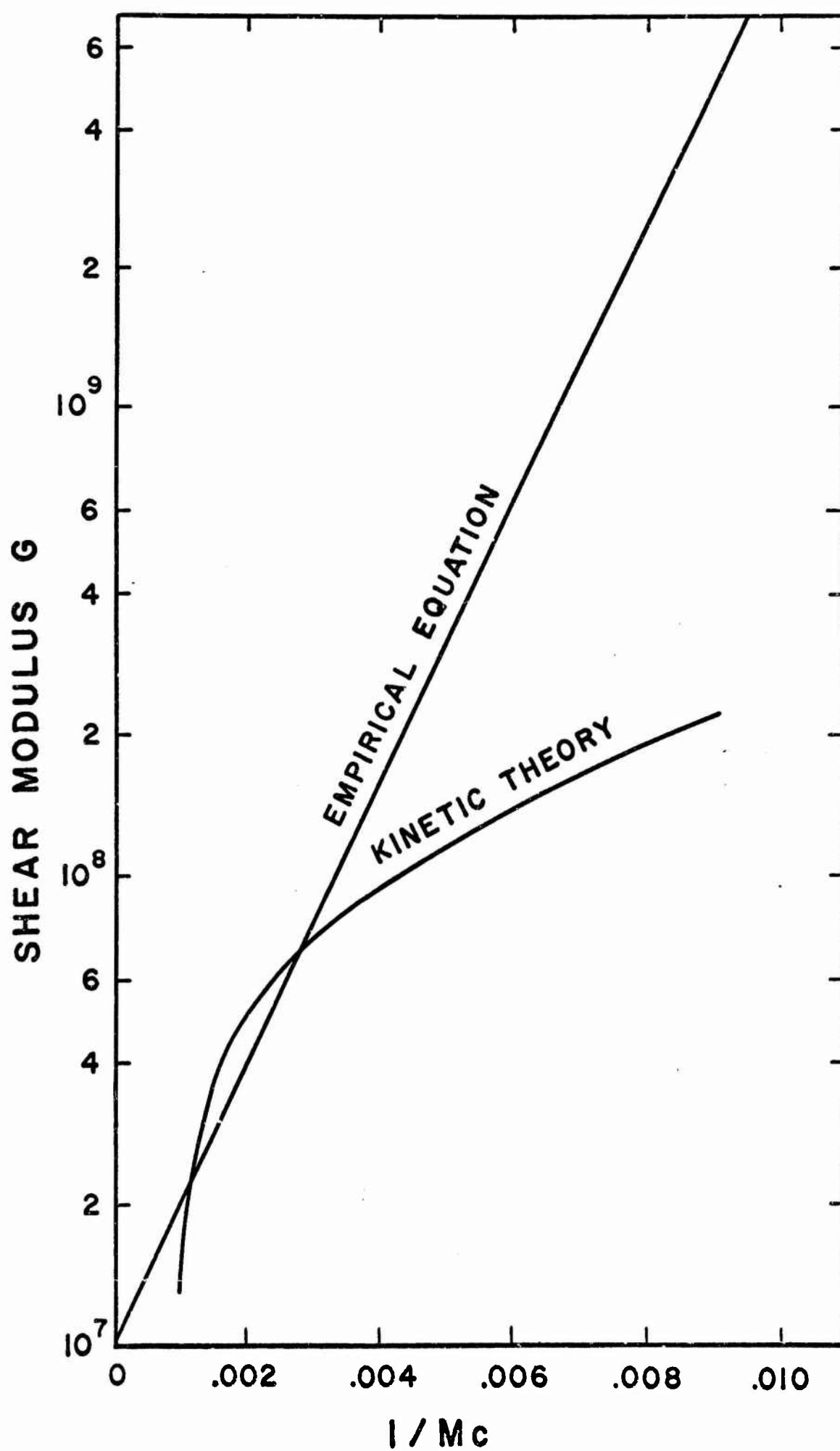
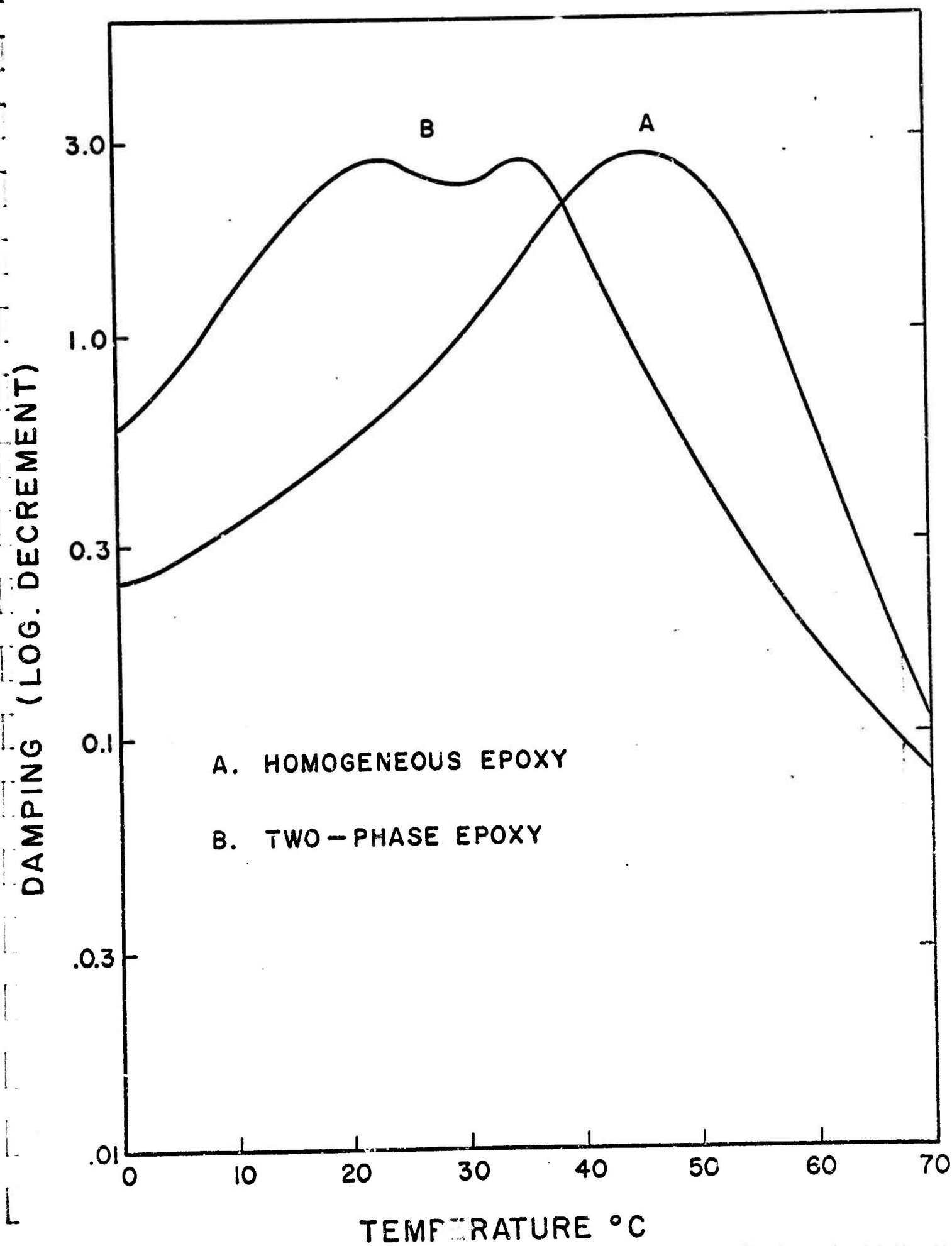


Figure 8



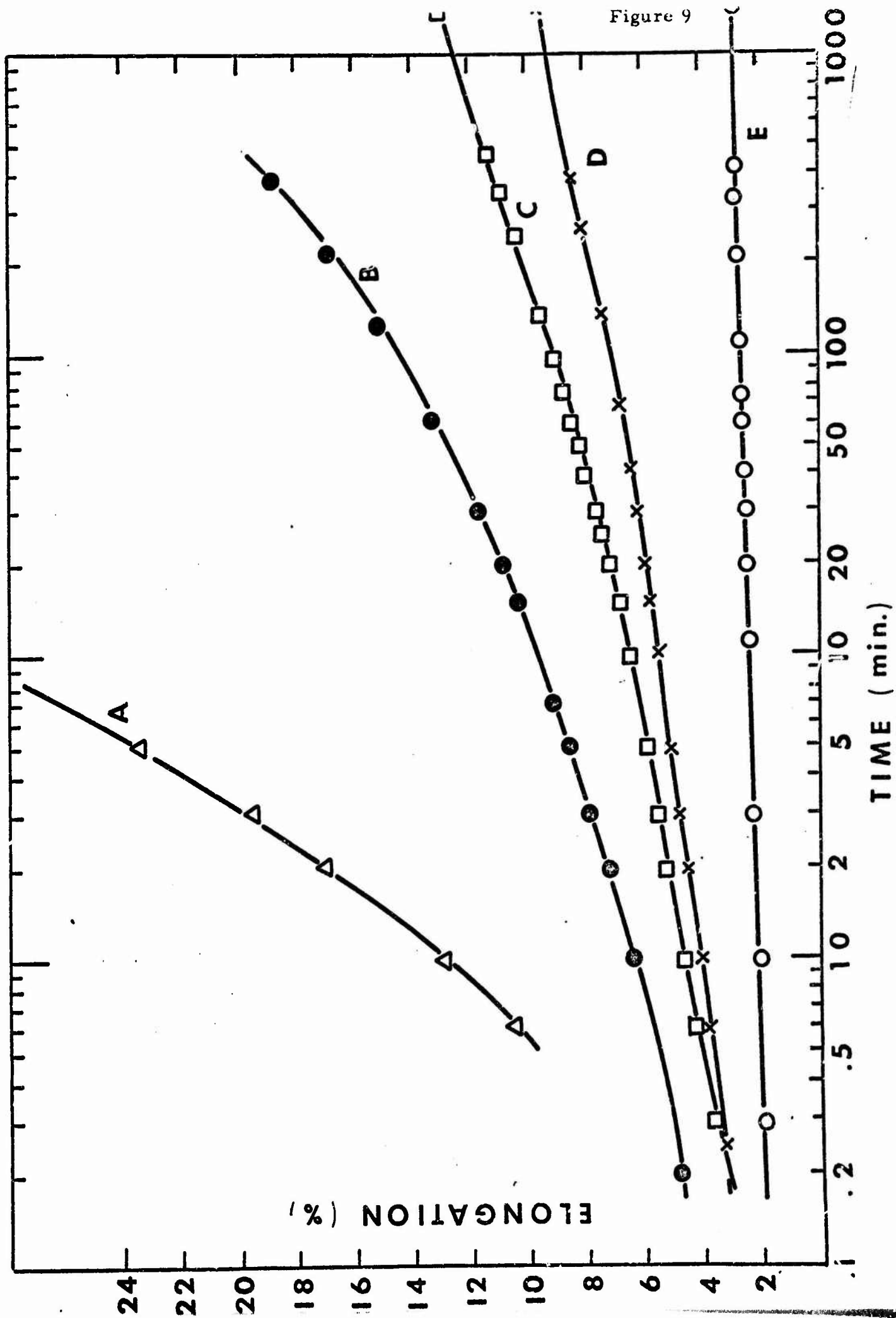
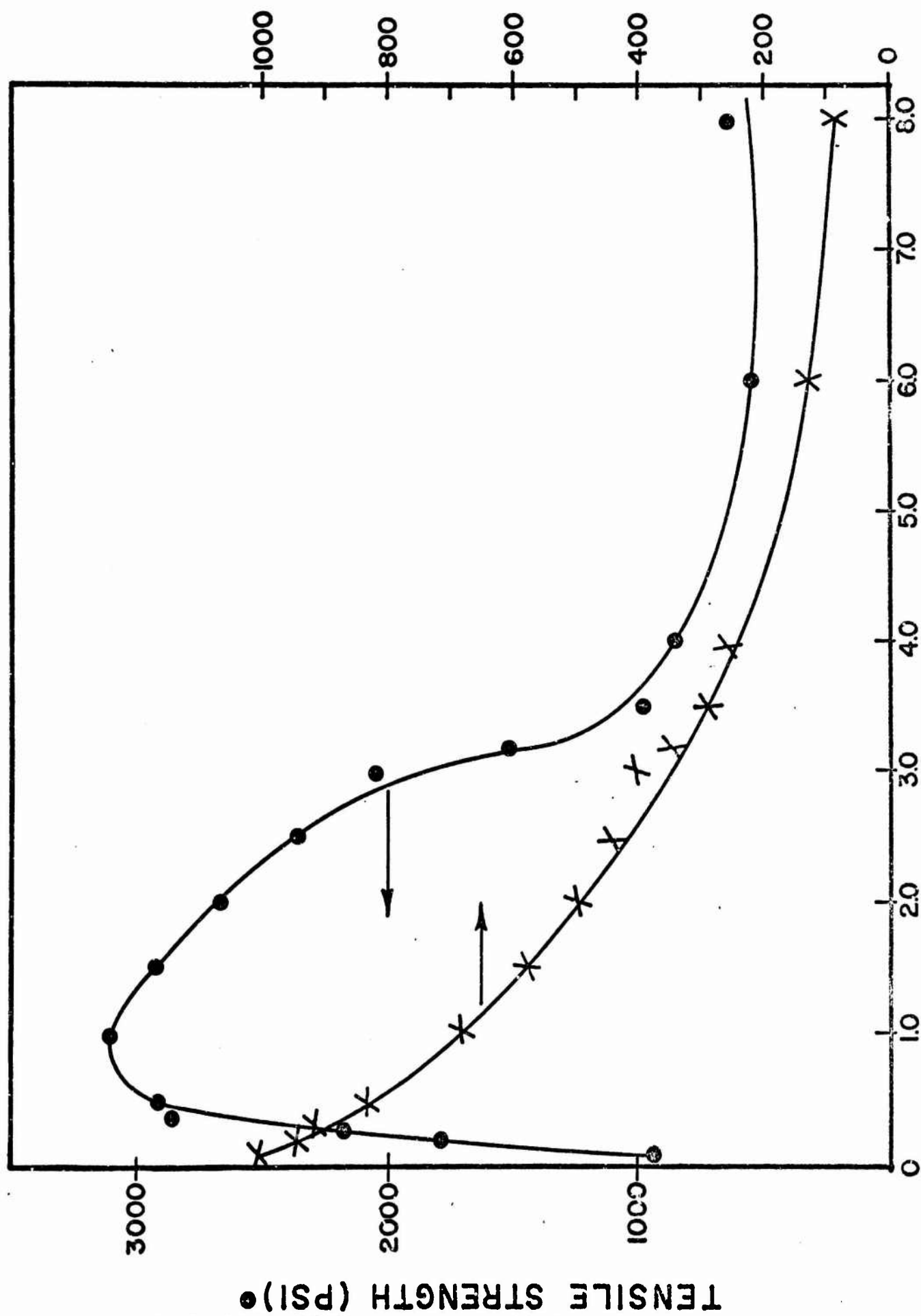


Figure 10



CONCENTRATION OF CROSS LINKING AGENT

Figure 11

FRACTURE ENVELOPE FOR SBR VULCANIZATE

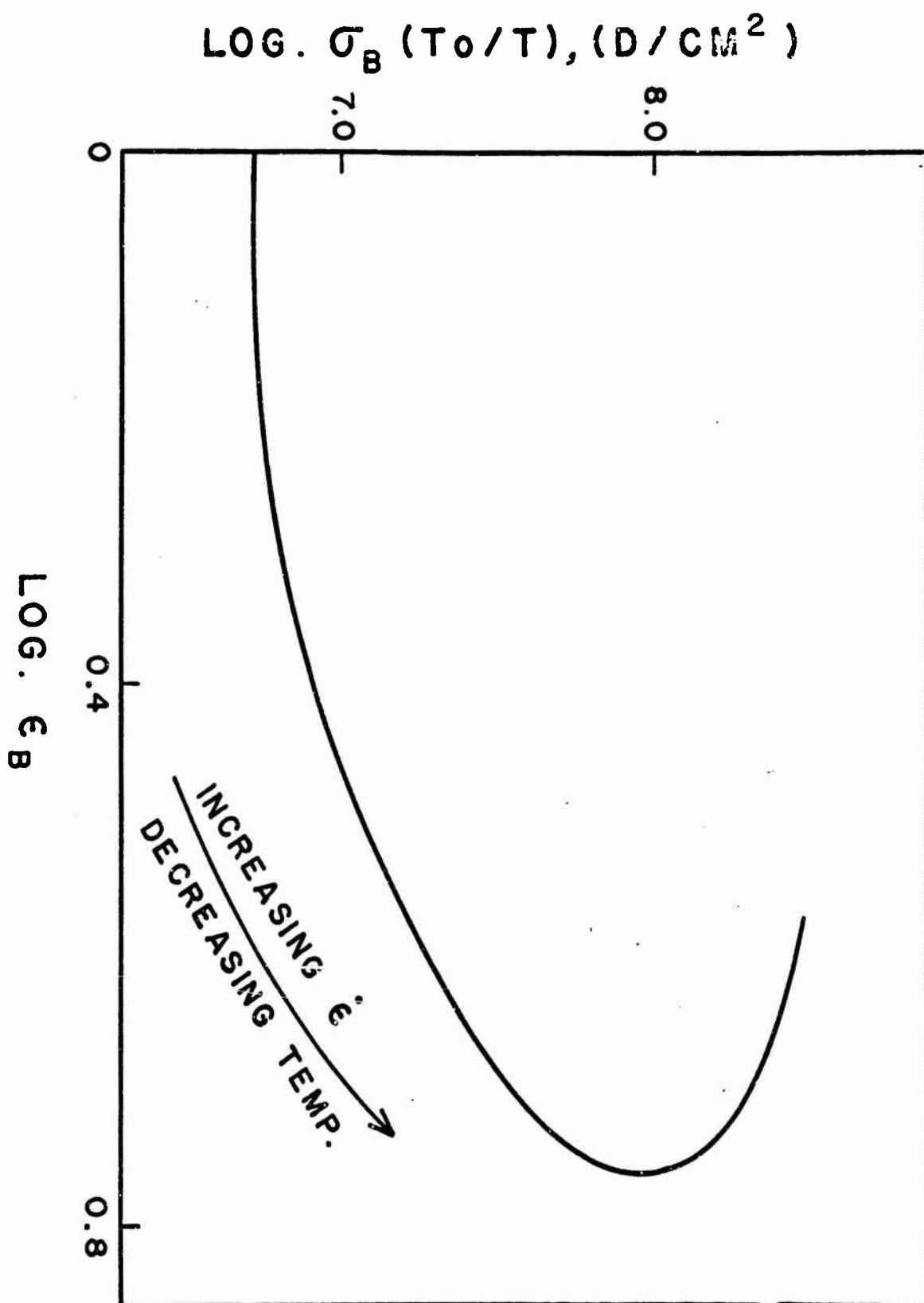


Figure 12

$\text{LOG} . \sigma_B (T_0 / T)$

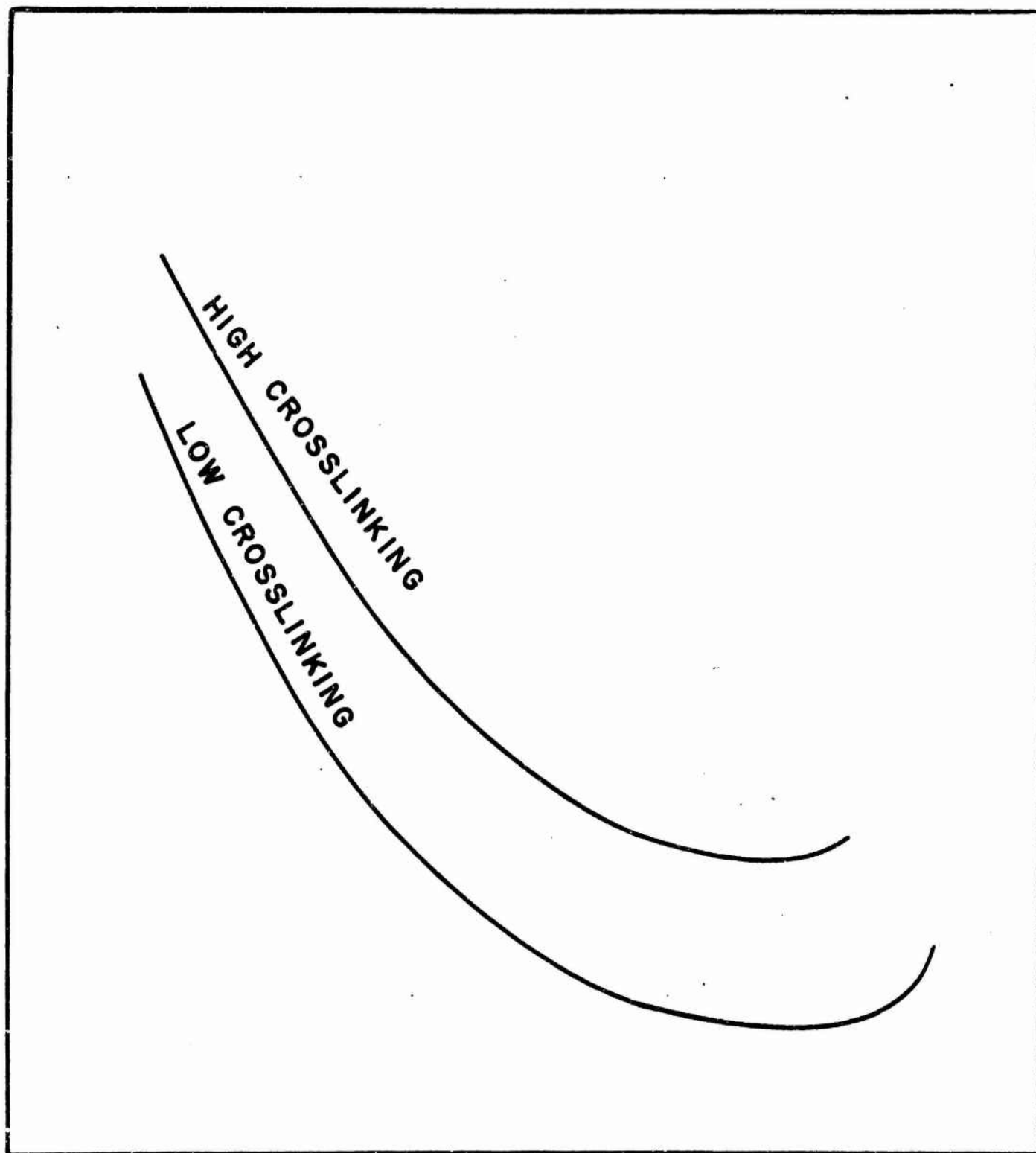
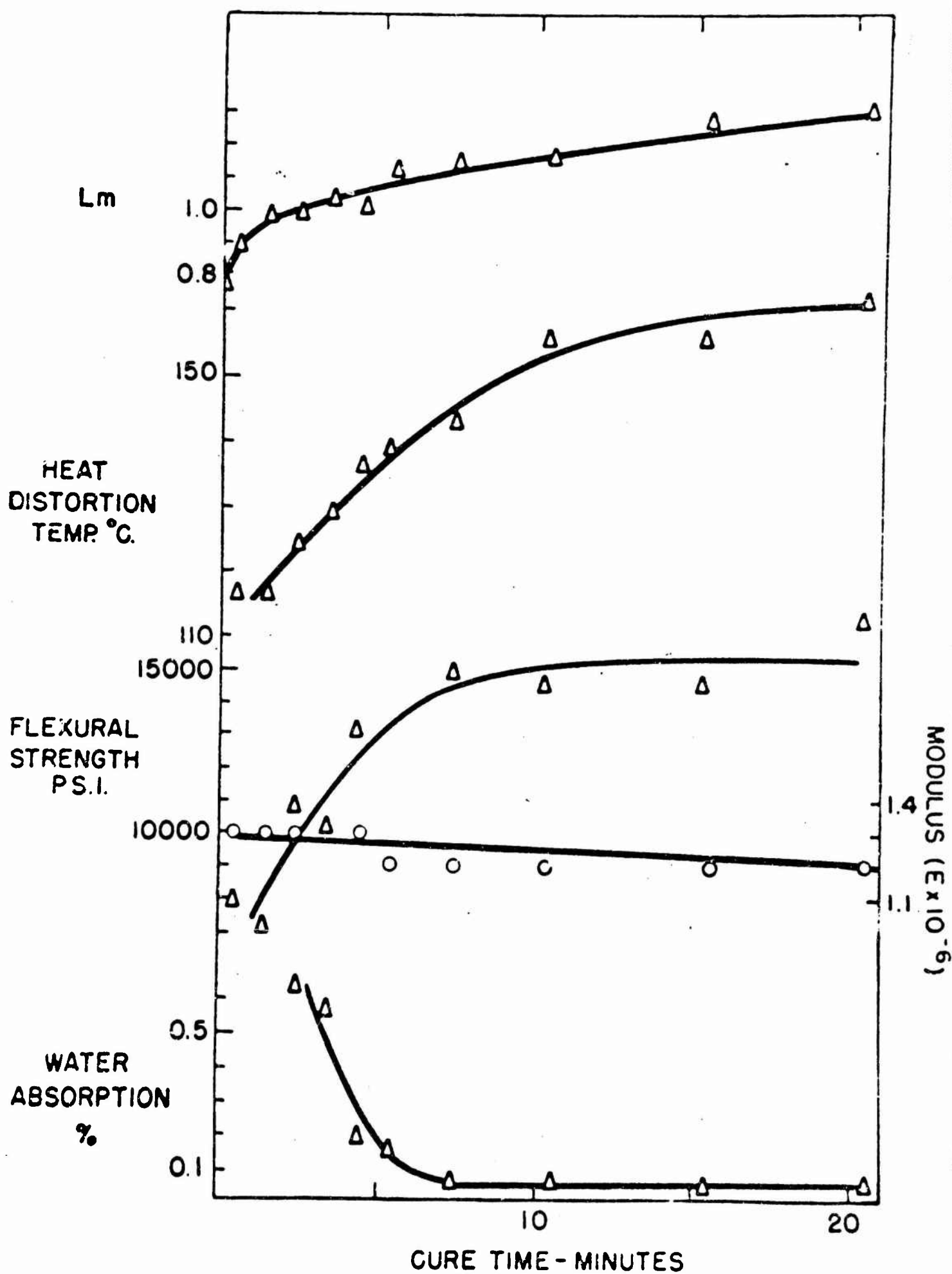


Figure 13



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13. ABSTRACT			
A review is made of the theoretical and experimental results of the effect of crosslinking on the physical properties of polymers. Both rubbers and rigid polymers are considered. Topics covered include: Types of network structures, methods of characterizing crosslinked polymers, swelling behavior, glass transitions, elastic moduli and dynamic mechanical properties, creep, stress-strain behavior, thermal properties, and anisotropic networks. The review is written from the practical viewpoint of the experimental scientist who is using crosslinked polymers but who is not an expert on the theory of crosslinking. Areas are pointed out where adequate scientific background information is lacking.			

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polymers crosslinking physical properties review						