

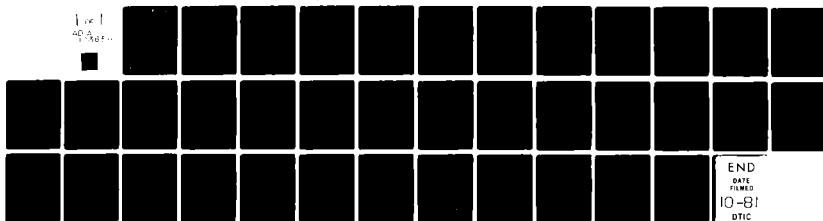
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EFFECT OF CROSSLINKING ON THE PHYSICAL PROPERTIES OF AN EPOXY R--ETC(U)
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EFFECT OF CROSSLINKING ON THE PHYSICAL PROPERTIES OF AN EPOXY RESIN"

by

T.-D. Chang, S. H. Carr, and J. O. Brittain

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found to increase linearly with the crosslinking density. The modulus, the upper yield point, the lower yield point, and the degree of retraction of a deformed sample all increased with the degree of crosslinking. The thermally stimulated depolarization, TSD, β -peak was found to vary with crosslinking density, but the γ -peak was not changed. The TSD α -peak was found to decrease in strength, but increased in temperature as the crosslinking density increased. This observation suggests that TSD measurements are a good monitor of crosslinking density of epoxy resins, particularly near the final stage of the crosslinking reaction.

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"EFFECT OF CROSSLINKING ON THE PHYSICAL PROPERTIES OF AN EPOXY RESIN"

Introduction

The effect of crosslinking on polymers has been the subject of a relatively small amount of research.¹⁻⁷ The glass transition temperature has been found to increase with the degree of crosslinking.¹⁻⁴ In fact, this observation has provided a means to estimate the crosslinking density by measuring the glass transition temperature.^{1,3,4} The dynamic mechanical α -relaxation peak was found to be broadened and shifted to higher temperature with higher crosslinking density.² Crosslinking also greatly reduces the creep of a rubbery material⁵ and decreases the specific volume^{1,6,7} and the coefficient of thermal expansion.^{6,7}

The effect of crosslinking density on the properties of epoxy resins has been studied by varying the stoichiometric ratio of epoxy resins and curing agents in order to control the degree of crosslinking. Kenyon and Nielsen⁸ found that the dynamic mechanical α -relaxation peak temperature reached a maximum at stoichiometry. The ultimate tensile strength was also found to reach a maximum at stoichiometry by some researchers,⁹ while others¹⁰ reported that the ultimate strength was insensitive to the stoichiometric ratio. Kim and coworkers¹¹ did observe a small minimum of ultimate strength at stoichiometry. The elastic modulus has been reported to be independent of the stoichiometric ratio.⁹⁻¹¹ But Shelby¹² found that elastic modulus was minimum at stoichiometry and more recently Yamini¹³ observed a decrease of elastic modulus with an increase in the amount of curing agent. The elongation at break in a tensile test was found to be independent of the stoichiometric ratio in some cases,^{9,10} though the data were rather scattered. However, Kim and coworkers¹¹ reported a maximum of elongation at break at stoichiometry. To sum up, no clear conclusion can be drawn from the reports in the literature on the effect of crosslinking upon the characterization on properties of epoxy resins.

We believe that changing stoichiometric ratio would inevitably alter the chemical composition of the materials. Therefore, the effect of crosslinking, as studied by changing stoichiometric ratio, would depend very much on the kind of curing agent employed. To avoid this complication, in this study the stoichiometric ratio was fixed, and the crosslinking density was changed by controlling the extent of curing.

While some of the previous investigations did study the effect of crosslinking for a fixed stoichiometric ratio, most of these researchers did not monitor the crosslinking density or the extent of curing of the epoxy resins. A careful search of the literature showed that most of the reported papers were studying the effect of crosslinking density at near completion of the curing reaction. This small variation resulted in an insensitivity of crosslinking effect or inconclusive trend in the measurements. Other workers saw an effect on the relaxation behavior of epoxy resins by postcuring though the range of crosslinking density variation was small. Generally speaking, the β -relaxation, as measured via dynamic mechanical technique, increased in peak height and shifted to higher temperature with an increase in postcuring time or temperature.¹⁵⁻¹⁷ Although postcuring resulted in a decrease in the strength of the α -relaxation, it also caused the peak temperature to rise.¹⁵ However, Shito¹⁸ reported that no systematic change of α -peak was found. In view of the previous works, we believe that the effect of crosslinking density on the epoxy resins can be clarified if the crosslinking density is monitored and controlled over a wider range.

The purpose of the present study was to clarify the effect of crosslinking on the physical properties of epoxy resins by fixing the stoichiometric ratio and varying the crosslinking density over a fairly large range. The physical properties investigated included density, compression properties, relaxation

processes via thermally stimulated depolarization, TSD, and thermal property, DSC. The density was monitored for its direct indication of free volume change. The compression test was chosen for studying the deformation behavior because epoxy resins have quite limited ductility in tension. TSD was used to investigate relaxation processes because of its high sensitivity to the change of structures in polymers. The relationships of these properties are discussed in detail. Finally, a correlation between mechanical properties and relaxation behavior was made and found to be influenced by crosslinking density.

EXPERIMENTAL

Since the detailed experimental procedures were described in our previous paper,¹⁹ only the most relevant information is listed in the following.

1. Materials and specimen preparation

The epoxy resin selected for this study was diglycidyl ether of butanediol (DGEb) and the curing agent chosen was the 4-4' diaminodiphenyl sulfone (DDS) (Figure 1). The reasons for choosing this combination were: (1) DDS has a low reactivity with the epoxy group and requires a high curing temperature. Thus, the extent of curing does not change appreciably at room temperature and the control of the extent of curing was readily achieved. (2) DGEb has a relatively flexible carbon chain backbone so that the T_g of the resulted epoxy resin is low compared to the curing temperature. Therefore, the extent of curing was held unchanged even for measurements performed close to the glass transition temperature. This material selection made our study of TSD α -transition as a function of the extent of curing quite attainable.

DDS was dissolved into DGEb and the mixture was vacuum degassed and then casted onto well-polished preheated Teflon plates or silicone rubber molds for making DSC and compression specimens respectively. In the case of TSD specimens, the epoxy resin-curing agent mixture was poured into a liquid cell (details are described in our previous paper¹⁹) with electrodes made of pure copper. Curing was carried out by two steps; first, the resin system was heated to 112°C for 12 hours. At this point, the material had just passed its gelation point. Second, the partially cured resin was postcured at 146°C for various lengths of time in order to control the extent of curing. Both thermal treatments were carried out in a dry nitrogen atmosphere and the samples were furnace cooled from the elevated temperatures to room temperature.

2. Measurements

The extent of curing of the epoxy resins was determined by FTIR following the absorption peak of epoxy group at 910 cm^{-1} with the absorbance of the phenyl group at 1610 cm^{-1} as an internal standard. The differential scanning calorimetry (DSC) measurements were made on a Perkin-Elmer model DSC-2 calorimeter. The heating rate was $10^{\circ}\text{C}/\text{min}$. The uniaxial compression tests were made via an Instron, model 1125, testing machine. The crosshead speed was $1\text{ mm}/\text{min}$ and the specimen dimension was $1 \times 1 \times 2\text{ cm}$. The density was measured in a density column which had a sensitivity of $.0001\text{ g. cm}^{-3}/\text{mm}$. The temperature of the column was maintained at 23°C . The TSD measurements were made in a system previously described.²⁰ The poling field was $5\text{ KV}/\text{cm}$ and the poling time was 5 minutes. The poling temperature was 77°C for high temperature TSD measurements and was 26°C for measurements at lower temperatures and the rate of heating was $3^{\circ}\text{C}/\text{min}$. One important thing to note is that the specimens were quenched (heated to 15°C above T_g for 15 minutes and then quenched by direct contact with aluminum blocks) before performing the density, compression, DSC and TSD measurements. This procedure was utilized in order to eliminate any effect of sub- T_g aging upon the properties of interest. Our unreported results²¹ showed that most of the properties of epoxy resins were affected appreciably by sub- T_g aging. Part of the reason why some workers^{9-11,14} may have obtained scattered data or peculiar trends is probably associated with their failure to control the "state of aging" which is affected by the cooling rate after curing process. Our specimens were heated and quenched from above T_g in order to eliminate the contributions of the "aging process".

RESULTS

The curing extent (determined by FTIR) of DGEb-DDS epoxy resins which were postcured for different periods of time was shown in Figure 2. It is seen that without postcuring (i.e., specimen which was cured at 112°C for 12 hrs.), the extent of curing was about 80% as determined by the percentage of epoxy groups reacted. As the postcuring time was increased, the extent of curing also increased steadily. After 9 hrs. of postcuring, the extent of curing reached 99% and stayed at this level for longer postcuring time. The change of density as a function of postcuring time is also shown in Figure 2. The density increased from 1.2830 for samples without postcuring to 1.2868 after 9 hrs. of postcuring, a change of about 0.3%. Further postcuring seemed to decrease the density a little, this may be due to thermodegradation or vaporization of small molecules, because the curing extent did not decrease. When density data are plotted against the extent of curing, a linear relationship was found, Figure 3. This result strongly suggested that the extent of curing directly influenced the physical properties of epoxy resins and is a better parameter than curing temperature or curing time.

The differential scanning calorimetry data for epoxy resins with different extent of curing are presented in Figure 4. These DSC curves all showed steps which are typical of the glass transition in polymers. The shape of the curves was similar, but the height of steps seemed to decrease with an increase in the extent of curing. The temperature where the steps occurred shifted to higher temperature. The temperature at the inflection point was taken as the glass transition temperature of this epoxy resin system. Figure 5 shows the plot of the glass transition temperature as a function of postcuring time. The glass transition temperature increased from 45°C for specimen which was not postcured to 77°C for specimens postcured for more than 9 hrs.

There was no drop off for 27 hrs. of postcuring as happened in the case of density.

The results of the uniaxial compression tests are illustrated in Figure 6. The specimen without postcuring had an upper yield point at about 5.5% strain. The stress decreased by about 38% after yielding, then followed with a constant lower yield stress region. The other specimens showed very similar features. The modulus was increased and both upper and lower yield points were drastically increased by postcuring. However, the magnitude of the yield drop remained essentially constant except for the specimen which had been postcured for 1 hour. In Figure 7, the modulus and the upper and lower yield stress are plotted as a function of postcuring time. The modulus increased about 60% and leveled off after 9 hrs. postcuring and the upper and lower yield stress were doubled by 9 hrs. of postcuring and leveled off after 27 hrs. of postcuring. Another interesting effect of the postcuring was the increase in the ability of a deformed specimen to retract upon subsequent heating, Figure 8. Samples which were compressed to half of their original lengths were heated to 15°C above their glass transition temperatures for 15 minutes and then cooled down to room temperature to measure the percent recoverability. It was found that the sample without postcuring could only recover to 99.2% of its original length (note that the accuracy to measure the length of our samples was better than 0.1%). As the samples were postcured longer, e.g., 9 hrs., the recoverability reached 100%.

Figure 9 shows the results of the low temperature TSD measurements. As previously reported,¹⁹ two TSD peaks were found below room temperature. The γ peak, which occurred at $\sim 120\text{K}$, did not seem to change systematically with postcuring time. In contrast, the magnitude of the β peak located at $\sim 185\text{K}$ was enhanced by the postcuring, the maximum change was about 18%. The peak

temperature also shifted to higher temperature with an increase in the post-curing. Figure 10 shows the high temperature part of the TSD thermogram. The poling time was kept short, 5 minutes, to reduce the possible curing reaction occurring during the poling process. Fortunately, with our selection of materials, the reaction temperature (146°C) was much higher than the poling temperature. Therefore, the effect of crosslinking on the TSD α -peak was not influenced by the poling process. Only one TSD peak, (the α -peak), appeared between 0°C and 80°C . The α -peak temperature was 57°C for the specimen without postcuring. With increasing postcuring time, the α -peak temperature was seen to increase up to about 70°C after 9 hrs. of postcuring. Further postcuring did not seem to increase the α -peak temperature. However, the α -peak height was reduced by a factor of more than 14 by the postcuring. The TSD α -peak height was plotted against the density of the material (Figure 11). There is a fairly good linear relationship, though the correlation was not as good as with the aging effect.²¹ Note the slope for crosslinking effect was much larger than that for the aging effect.

DISCUSSION

It is important to note that we had obtained a range of the extent of curing of about 20% (Figure 2). This is as much as can be obtained for this material because the gelation point was about 58% curing and 80% of curing was about the minimum requirement for the material to have some strength for handling. The gelation point mentioned here was calculated from equations derived by Flory:²² $\alpha_c = 1/f-1$ and $\alpha_c = p_c^2$, where α_c is the critical branching coefficient, f is the functionality of the curing agent (for DDS, $f = 4$) and p_c is the extent of curing at gelation. This extent of curing ensured us of a substantial range of properties as previously shown.

The crosslinking density can be calculated if the extent of curing and the relative reactivity of primary amine and secondary amine are known.²³ Unfortunately, the relative reactivity of primary amine and secondary amine were not analyzed in our study. We thus employed an empirical method to obtain the crosslinking density from the molecular weight between the crosslinking points, M_c , which was estimated from the shift of glass transition temperature by the following equation:²⁴

$$M_c = 39,000 / (T_g - T_{g_0})$$

where T_{g_0} is the glass transition temperature of the uncrosslinked polymers. In our study T_{g_0} was 216 K (the glass transition temperature of the epoxy-curing agent mixture without curing as determined via DSC). The calculated M_c is listed in Table I. The crosslinking density was obtained from the M_c data by the relation: crosslinking density = $(3/2 M_c)^{-1}$ (for the epoxy resin system studied here, the crosslinking point is at the nitrogen atom and three segments were joined at each crosslinking point, but each segment is shared by two crosslinking points, thus $3/2 \times M_c$ is the molecular weight correspond-

ing to one crosslinking point). The result of the crosslinking density estimation is also shown in Table I. The crosslinking density changed by about 24%, which is close to the change of the extent of curing. This result indicated that the extent of curing is a fairly good indicator of the crosslinking density. This finding is not surprising because at the later stage of the curing reaction, each epoxy-amine reaction would generate two crosslinking points, hence the same proportional change for extent of curing and crosslinking density.

The increase of the density with the curing extent suggested that the free volume in the epoxy resins was reduced by the crosslinking. The free volume was decreased probably because the molecular segments were tied up by crosslinking points. The amount of density change was .3%, which is much larger than that obtainable by sub- T_g aging (for sub- T_g aging, the change only was about .12%).²¹ In other words, it is more effective to increase the density of epoxy resins via crosslinking compared to sub- T_g aging. The linear relation between density and the extent of curing suggests that the incremental increase in crosslinking corresponds to the decrement in free volume for the same degree of crosslinking. This result is in agreement with the effect of crosslinking on other polymers.^{1,6} However, Shibayama and Suzuki⁷ reported linear relationship of specific volume with logarithm crosslinking density for unsaturated polyesters.

The increase of the modulus with curing extent is rationalized on the basis of the increase in density due to the increase in the crosslinking. The crosslinking might also contribute to an increase of modulus by adding stronger chemical bonds. The systematic variation of the modulus with crosslinking differs from that of previous workers⁹⁻¹⁴ who reported inconsistent trends as described in the introduction. For people who studied the effect of crosslinking by changing the stoichiometric ratio,^{9,10,12,13} the change in chemical

composition may cloud the effect of crosslinking per se on the modulus. The small change in modulus observed by Morgan¹⁴ may have been due to the small change in crosslinking density in his epoxy resins (he did not monitor the amount of crosslinking density).

The increase in the stress at both the upper and lower yield points by crosslinking can also be explained by the density change and the decrease in the ability to relax under an externally applied force. The yield point is a measure of a material's resistance to plastic deformation. The yield point also depends on the relaxation of the material (an evidence is the strain rate dependence of the yield point). The decrease in the magnitude of the α -relaxation, as shown by TSD measurements, correlates with the increase of the yield point. The only workers¹³ who did study the crosslinking effect on the yield point varied the stoichiometric ratio and found that increasing the curing agent lowered the yield point. No conclusion about the effect of crosslinking on the yield point was drawn, presumably because of the change in chemical composition (their result showed that yield point is a function of the percentage of curing agent rather than crosslinking density).

It is important to note that the 24% difference in the crosslinking density leads to a more than 2-fold change in the stress of both the upper and lower yield points and a 60% change of modulus. The mechanical strength of the epoxy resins seemed to be greatly enhanced by the last 20% of curing reaction. Therefore, this last 20% change of curing extent is practically of most importance and should be monitored accurately. Unfortunately, the conventional method to monitor curing process is infrared spectroscopy, which is insensitive to the last few percents of the extent of curing.

The fact that crosslinking increased the recoverability of epoxy resins tells us that crosslinking introduced "memory" to the polymers. Just like

chemical bonds in linear polymers, crosslinking points in the thermoset are not broken during the deformation process. Therefore, the cured specimens recover their original shape when there is enough mobility among the molecular segments. In contrast, other molecular solids with small molecular weight cannot recover. This, of course, also clearly demonstrates that deformation in epoxy resins, at least to strains of about 50%, are anelastic in nature and not plastic.

The origins of the two low-temperature relaxation peaks appearing in most epoxy resin systems were found to be due to localized molecular motions in our previous paper.¹⁹ If we assume that the β peak is due to large scale cooperative motion of molecular segments, the systematic increase of the β peak height cannot be explained. Since large scale cooperative motion would be expected to be restricted by the crosslinking, increased crosslinking should lead to a reduction in peak height rather than the observed increased peak height. In the previous paper, we suggested that the β peak was due to the newly-created segments during curing reaction. Note that the β peak height was found to increase 18%, which is about the same as the increase in the extent of curing. This fact seems to support our previous suggestion.

TSD α peak height decreased dramatically compared to the small change in β and γ peaks. The decrease in peak area implied that the number of molecular segments, which were able to move, was reduced. The increase of α peak temperature indicated that the activation energy for motion of the molecular segments had increased. The crosslinking seemed to tighten the structure of the epoxy resins, thus the increase of activation energy and the decrease in mobility of molecular segments. The strength of the TSD α -transition was found to have a linear relation with the density of the DGEb-DDS epoxy resin, when we studied the effect of sub- T_g aging, and this linear relation has been rationalized as a free volume effect.²¹ In order to analyze the change in free volume with

the degree of crosslinking, the strength of the TSD α -peak has been plotted against the density for the postcured epoxy in Figure 11, the data for the effect of sub- T_g aging on the same parameters is also shown in Figure 11. While a roughly linear relationship is also observed in the study of the crosslinking effect, the free volume effect cannot be the only cause for the change in the strength of TSD α peak in this latter case. Since the slope of the density dependence of TSD α peak heights was much larger than that for the effect of sub- T_g aging, there must be some reasons other than the decrease in free volume that caused the major portion of the decrease in TSD peak height. This additional factor must be due to the molecular segments being crosslinked and immobilized relative to their uncrosslinked mobility. In other words, the crosslinking not only influenced the relaxation behavior by joining or linking of the molecular segments, but also restricts the movement of many of the molecular segments.

The dependence of the strength of TSD α peak on the crosslinking density demonstrated that TSD technique is a very promising technique for monitoring the crosslinking density, especially at the region close to completely cured, where infrared spectroscopy is insensitive. Compared to 0.3% change of density, 10% change of T_g , 60% change of modulus, 2-fold change of the stress at both the upper and lower yield point, it is surprising to see a 14-fold change of TSD α peak height. Note also that the two specimens postcured for 9 hours and 27 hours respectively showed the same glass transition temperature elastic modulus, extent of curing, small difference in the stress level at the yield point, but about a 30% difference in the TSD α -peak height was observed.

The correlation between the TSD α -peak and the mechanical properties was apparent in this study, e.g., the decrease in peak height and the increase in

the modulus and stress at the yield point. If we compare this result with the correlation observed for aging effect, we note that while sub- T_g aging increased the stress at the upper yield point, the lower yield point was much less affected. The difference for the TSD α -peak in these two cases is that the sub- T_g aging does not change the activation energy, but crosslinking does, Figure 10. This observation suggests that the stress at the lower yield point can be associated with the activation energy of α relaxation and the stress at the upper yield point was determined by the population of molecular segments, which were able to relax.

Finally, a point must be made concerning the origin of the TSD α -transition. First, we note that the α -transition, as measured by DSC and TSD, differs by about 7°C for the fully-cured epoxy resin. The TSD α -transition occurs at a lower temperature and the reason for the lower transition in the electrical measurement resides in both a frequency effect and in the source of the current in the TSD measurements. The current density in TSD measurements is the sum of the polarization current dPs/dt and the conduction current $\sigma(T)E$:

$$J(t) = \frac{dPs(t)}{dt} + \sigma(T)E.$$

The source of the depolarization current is the movement of dipoles as the glass transition is traversed and for the conduction current, the source of the current is the charge carriers, both ionic and/or electronic, and the direction is opposite to the polarization current. At low temperature $\sigma(T)$ is small but increases exponentially with temperature, i.e., $\sigma = \sigma_0 e^{-H/kT}$, and above T_g , the conduction current could cancel out a large portion of the depolarization current.²⁵ Therefore, as the TSD measurements are made at an increasing temperature, the component of the current through the shunt resistance decreases and the ohmic conduction current through the specimen increases.

Ideally, the TSD measurement is supposed to be done under short-circuited condition, then E would be zero and no conduction current would occur. In practice, a finite value of resistance is shunted on the electrometer in order to produce a detectable voltage signal. The higher the resistance is, the larger E would be. At the same time, when the signal level is increased, the conduction current also increased and part of the depolarization current will be cancelled. If the TSD measurements were made in the temperature range where the conduction current is large, then high temperature side of the TSD peak would be reduced by the opposite conduction current. Since all of our TSD measurements were done by an electrometer shunted with $10^{10} \Omega$ resistance, it is likely that the high temperature portion of the TSD α peak might be effected by the conduction current.

Conclusion:

1. By controlling a wide range of crosslinking density, we were able to obtain clear conclusions for the effect of crosslinking density.
2. The density of epoxy resins was found to increase linearly with the crosslinking density.
3. The compressive modulus, the yield point and the flow stress were increased with increasing crosslinking density.
4. The recoverability of epoxy resins increased with crosslinking density.
5. The TSD β peak was found to increase systematically with the crosslinking density and the amount of change was about proportional to the change in curing extent. This supports our previous suggestion¹⁹, that the β peak is caused by the newly-created molecular segments during curing reaction.
6. The TSD α peak height decreased dramatically by crosslinking and the peak temperature was increased by crosslinking.

7. TSD is a more sensitive technique to monitor the curing process of epoxy resins, especially the last few percent of curing reaction could be monitored by following the TSD α peak.
8. A clear correlation between the TSD α peak and the mechanical properties was found.

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Table I

<u>Postcuring time</u> <u>at 146°C, hrs.</u>	<u>Extent of curing,</u> <u>(%)</u>	<u>Mc</u>	<u>Crosslinking density</u> <u>($\times 10^{21}$/g)</u>
0	30	382	1.05
1	87	368	1.09
3	93	315	1.27
9	99	291	1.38
27	99	291	1.38

FIGURE CAPTIONS

- Figure 1. Network formation of the DGEb-DDS epoxy resin system.
- Figure 2. Change of the extent of curing and the density as a function of the postcuring time for the DGEb-DDS epoxy resin system. The extent of curing was determined by FTIR and the density was measured in a density gradient column.
- Figure 3. Linear relationship between the density and the extent of curing for the DGEb-DDS epoxy resin system.
- Figure 4. DSC scan of DGEb-DDS epoxy resin samples which were postcured for different lengths of time.
- Figure 5. Glass transition temperature of DGEb-DDS epoxy resin samples as a function of postcuring time. T_g values were taken as the inflection point in Figure 4.
- Figure 6. Stress-strain curves for DGEb-DDS epoxy resin samples tested by uniaxial compression. Samples were postcured for different lengths of time and quenched to room temperature prior to testing.
- Figure 7. Upper yield point, lower yield point, and modulus of DGEb-DDS epoxy resin system plotted as a function of postcuring time. Data from Figure 6.
- Figure 8. Recovery of DGEb-DDS epoxy resin as a function of postcuring time. Samples were compressed to half of the original length and then heated to 15°C above T_g for 15 minutes. The percent recovery was taken as the ratio of the length after heating and before compression.

Figure 9. Low temperature part of the TSD thermograms for DGEb-DDS epoxy resin system samples postcured for different lengths of time.

Figure 10. High temperature part of the TSD thermograms for a series of DGEb-DDS epoxy resin samples postcured for different lengths of time.

Figure 11. TSD α peak height vs density for DGEb-DDS epoxy resin. The circles are data obtained by changing the aging time. The triangles were obtained by varying the postcuring time.

Formation of DGEB-DDS epoxy resin system

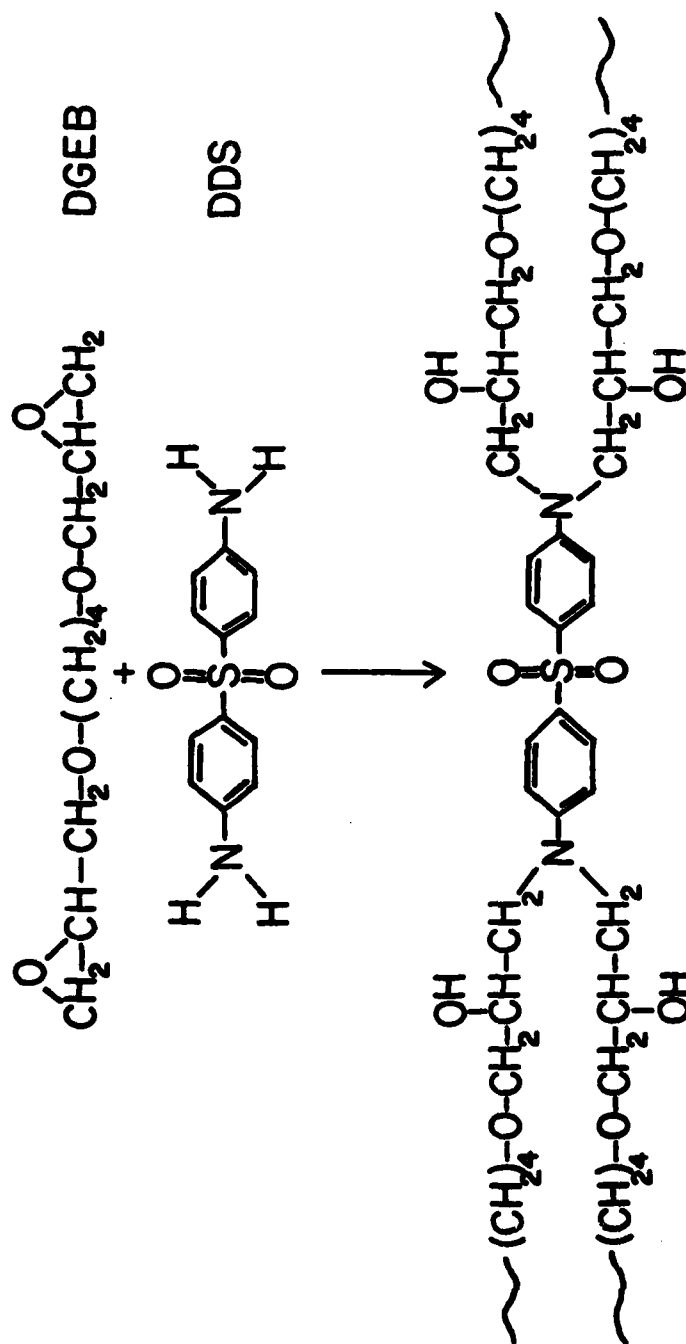


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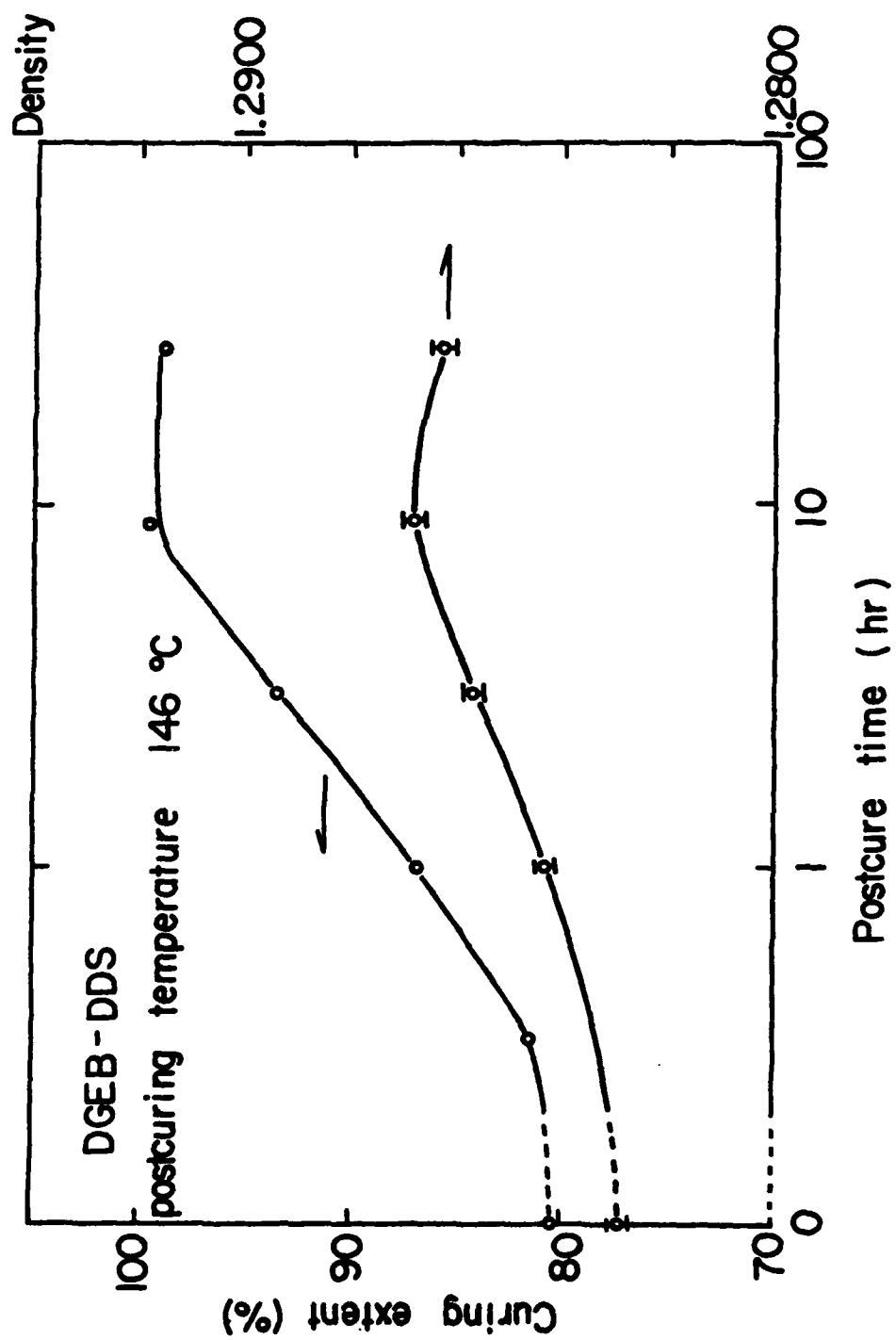


Figure 2.

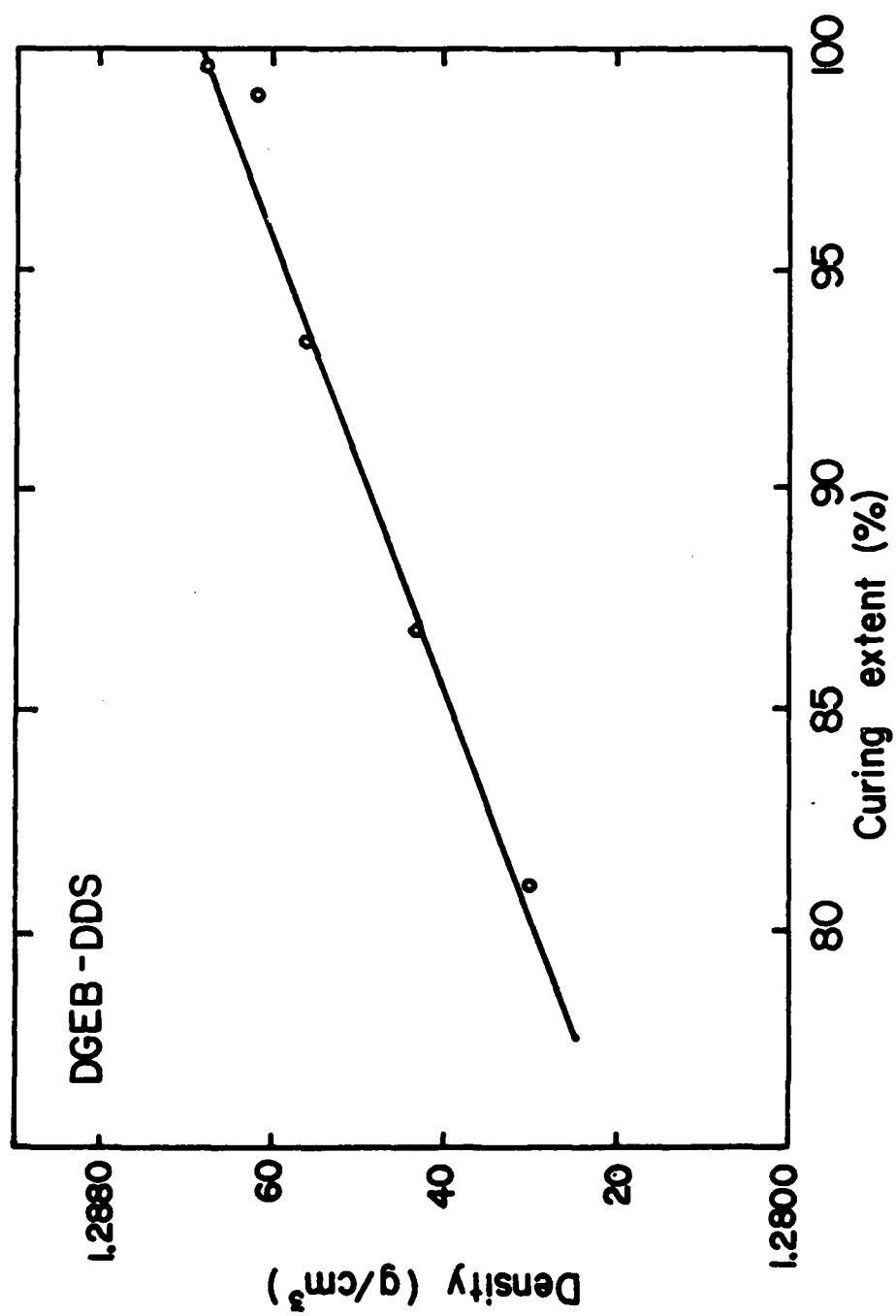


Figure 3.

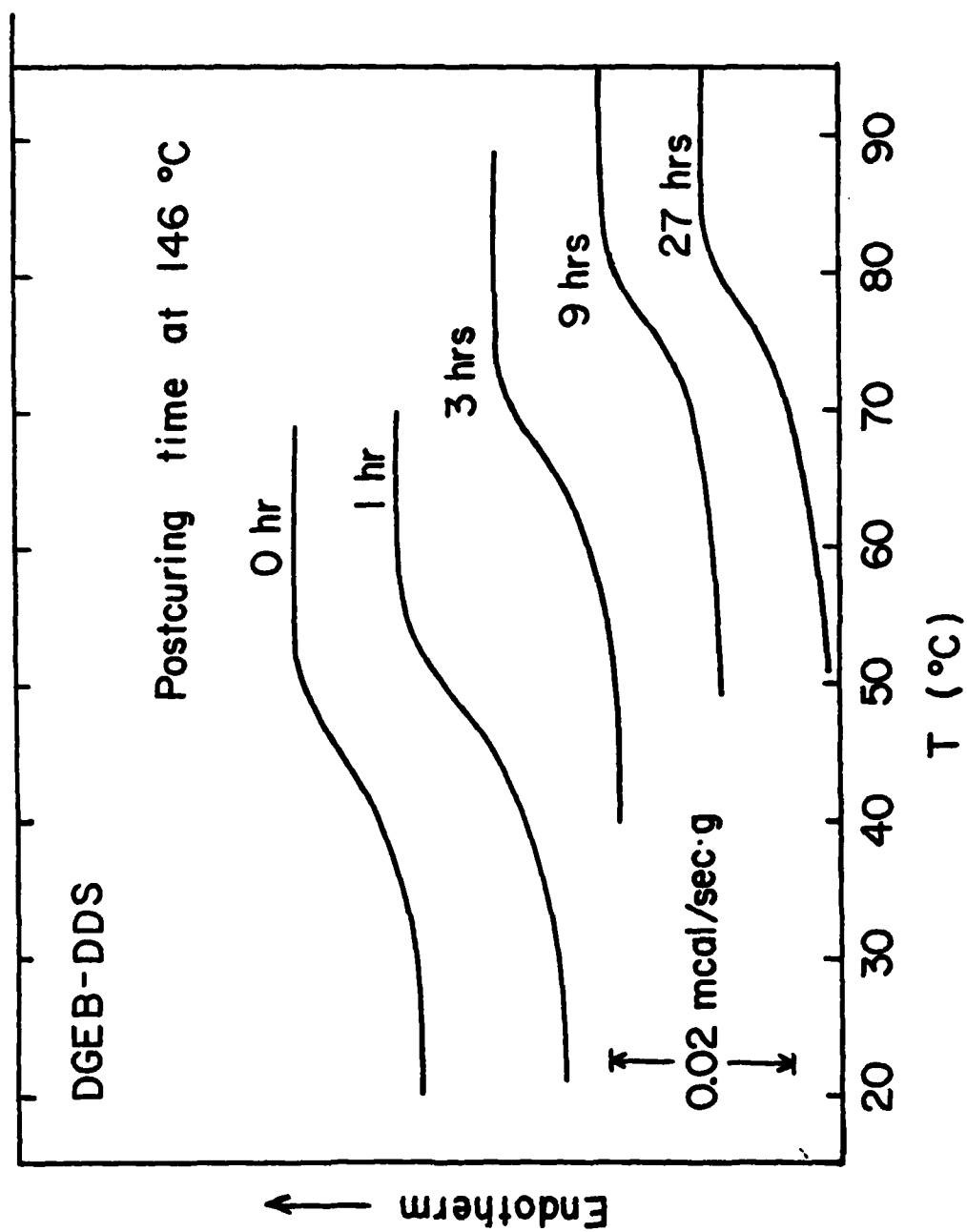


Figure 4.

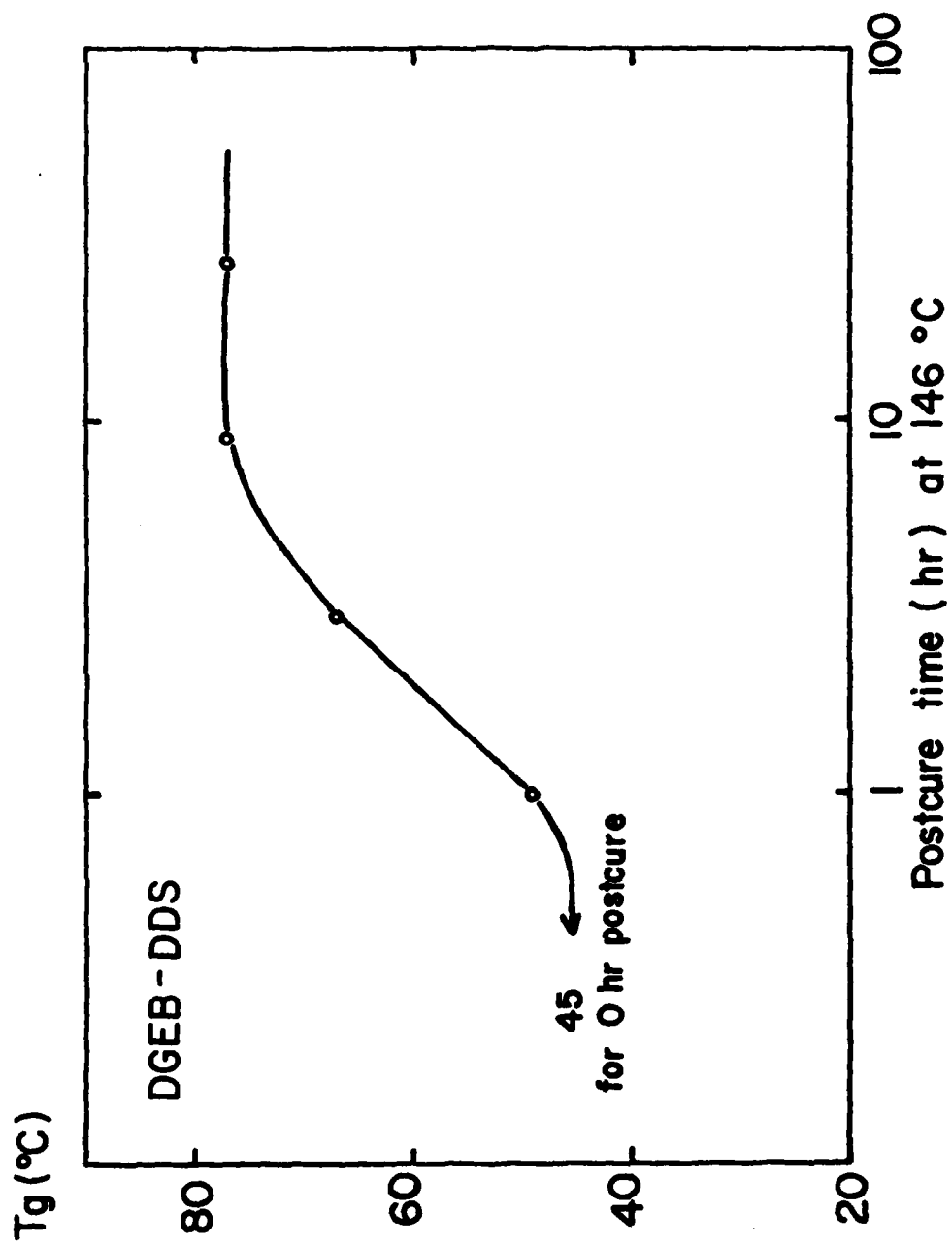


Figure 5.

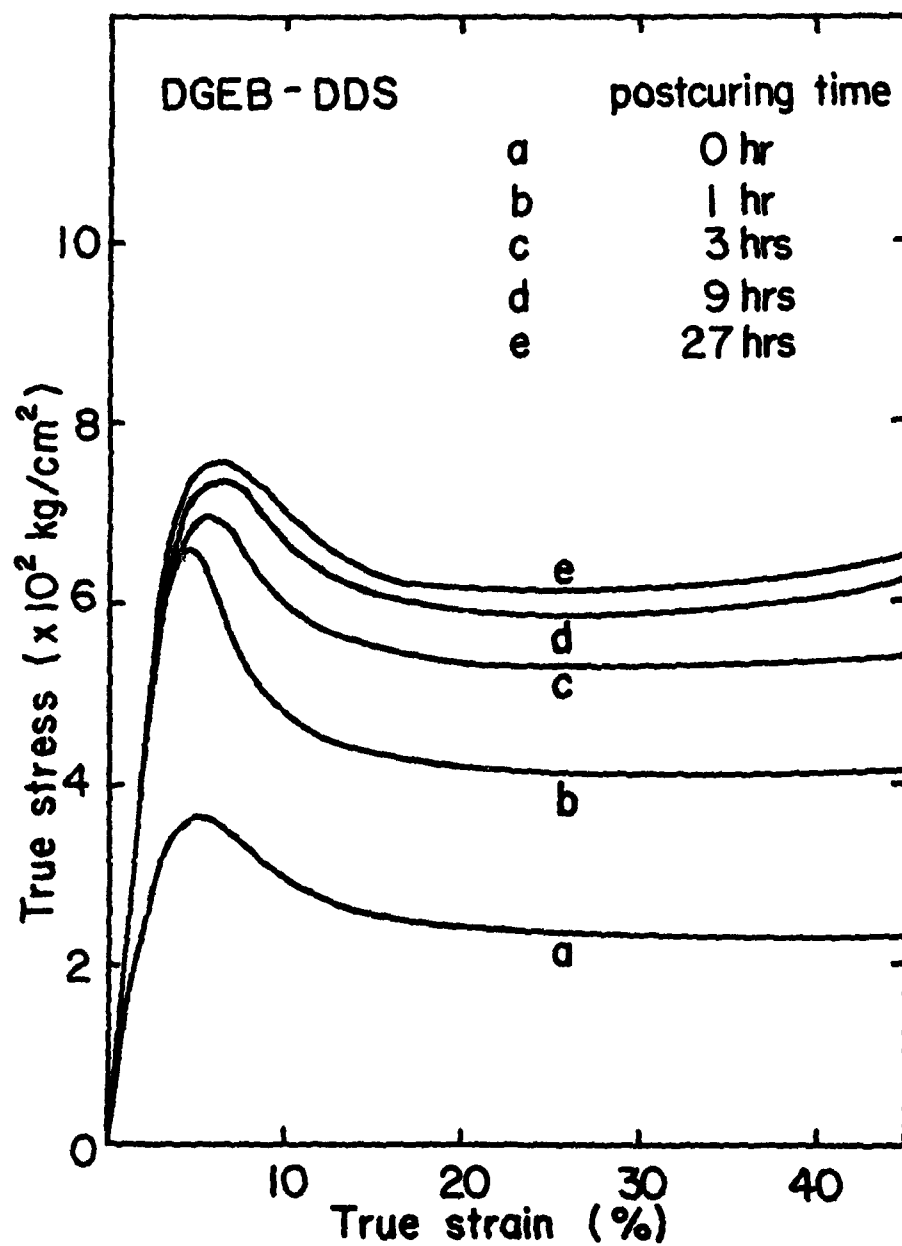


Figure 6.

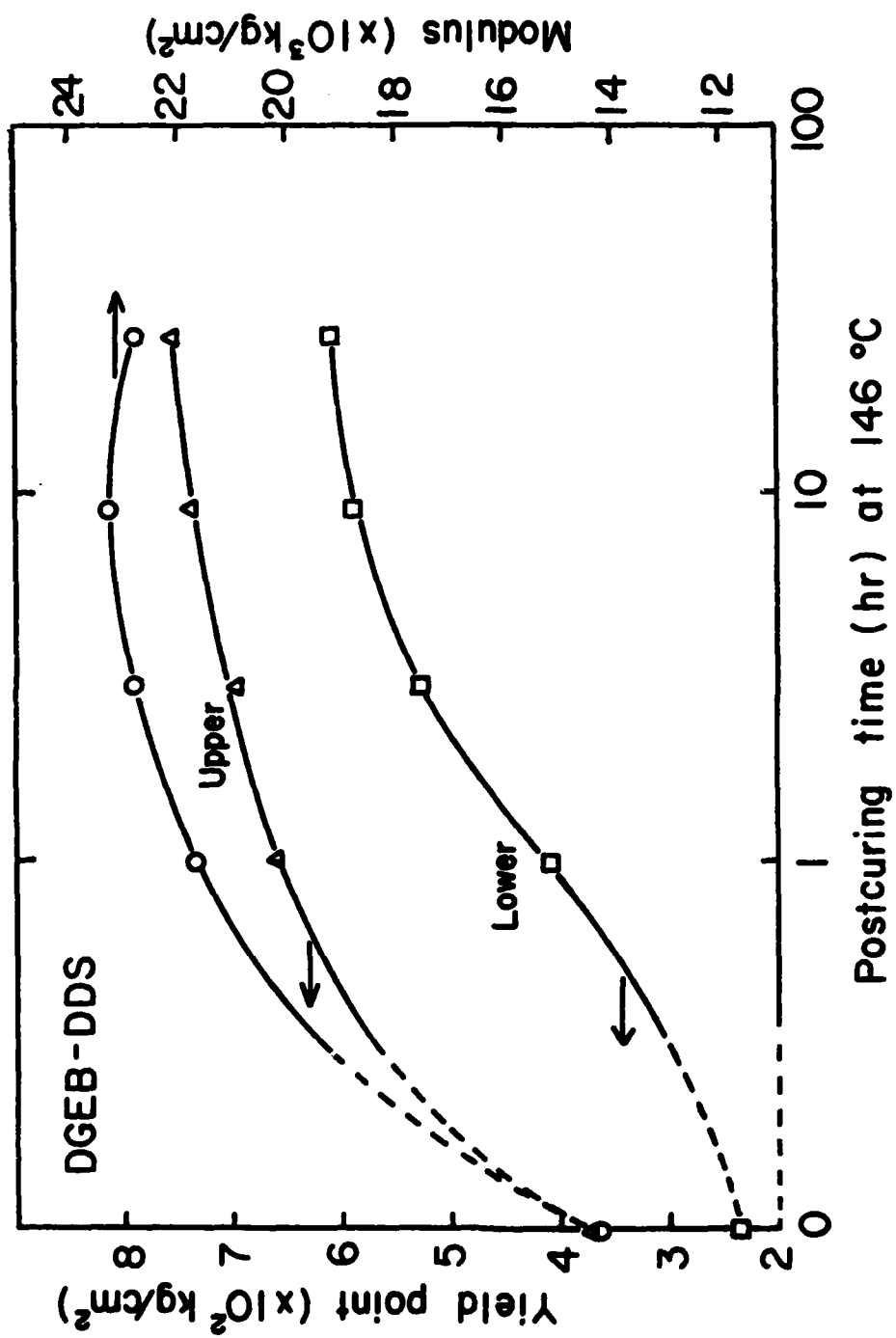


Figure 7.

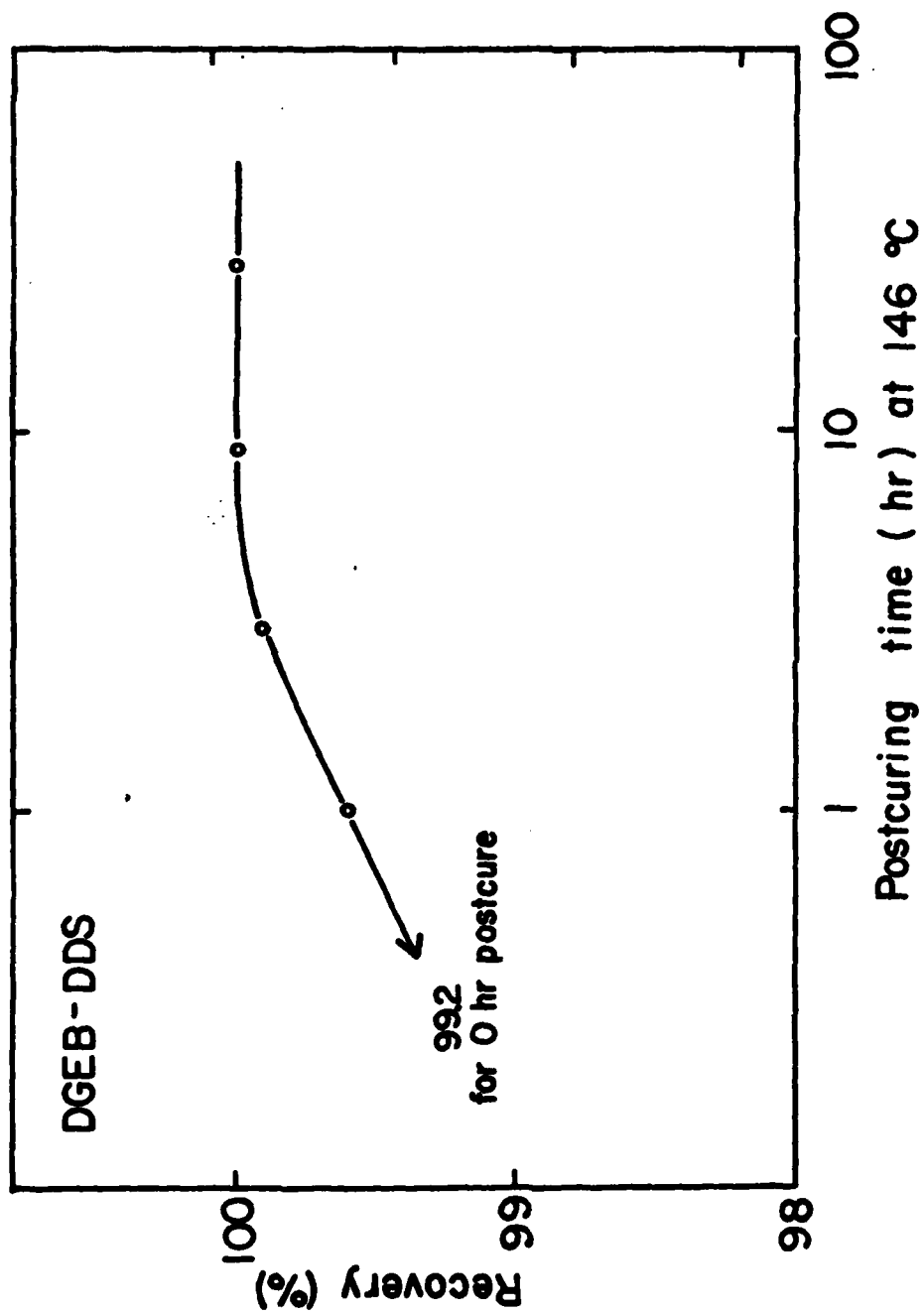


Figure 8.

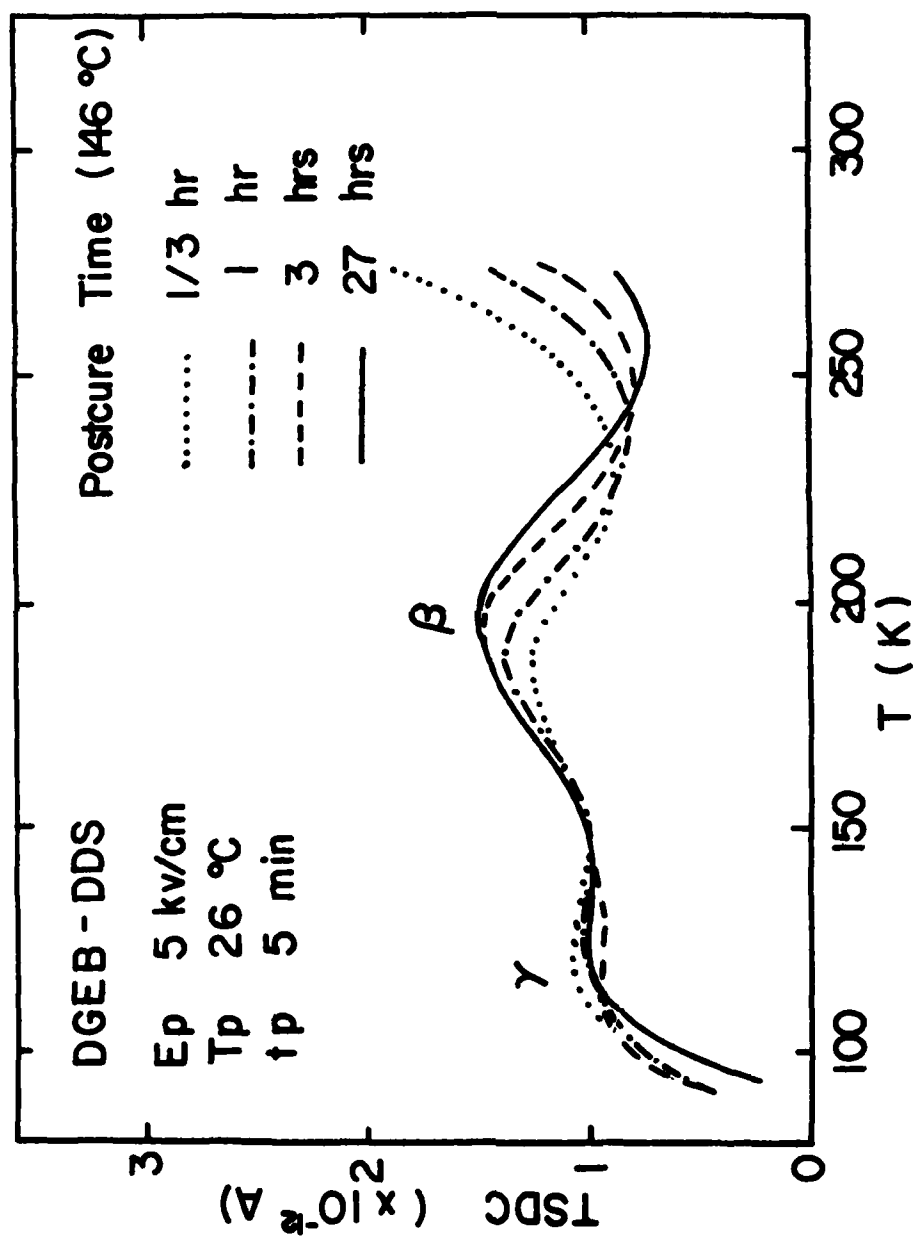


Figure 9.

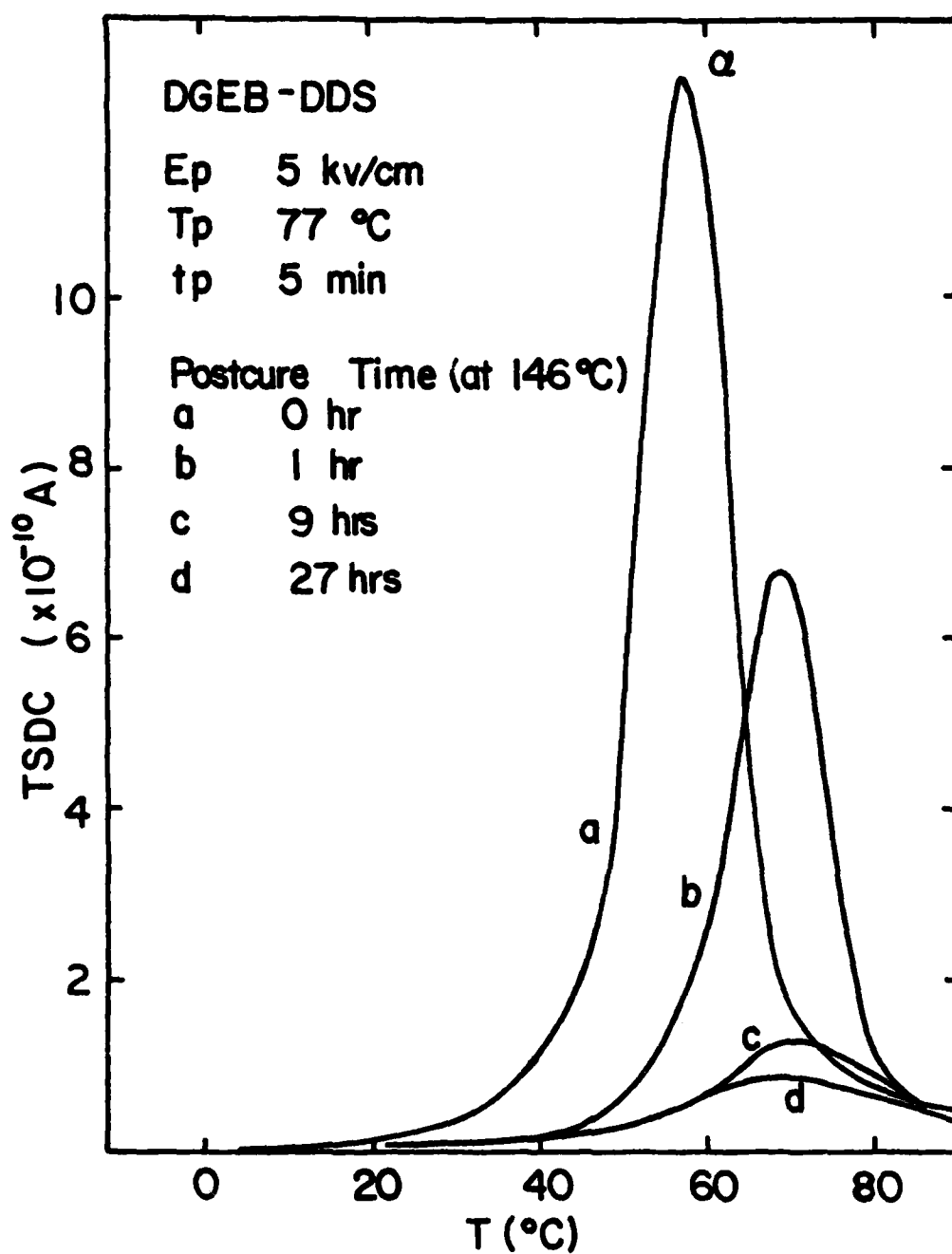


Figure 10.

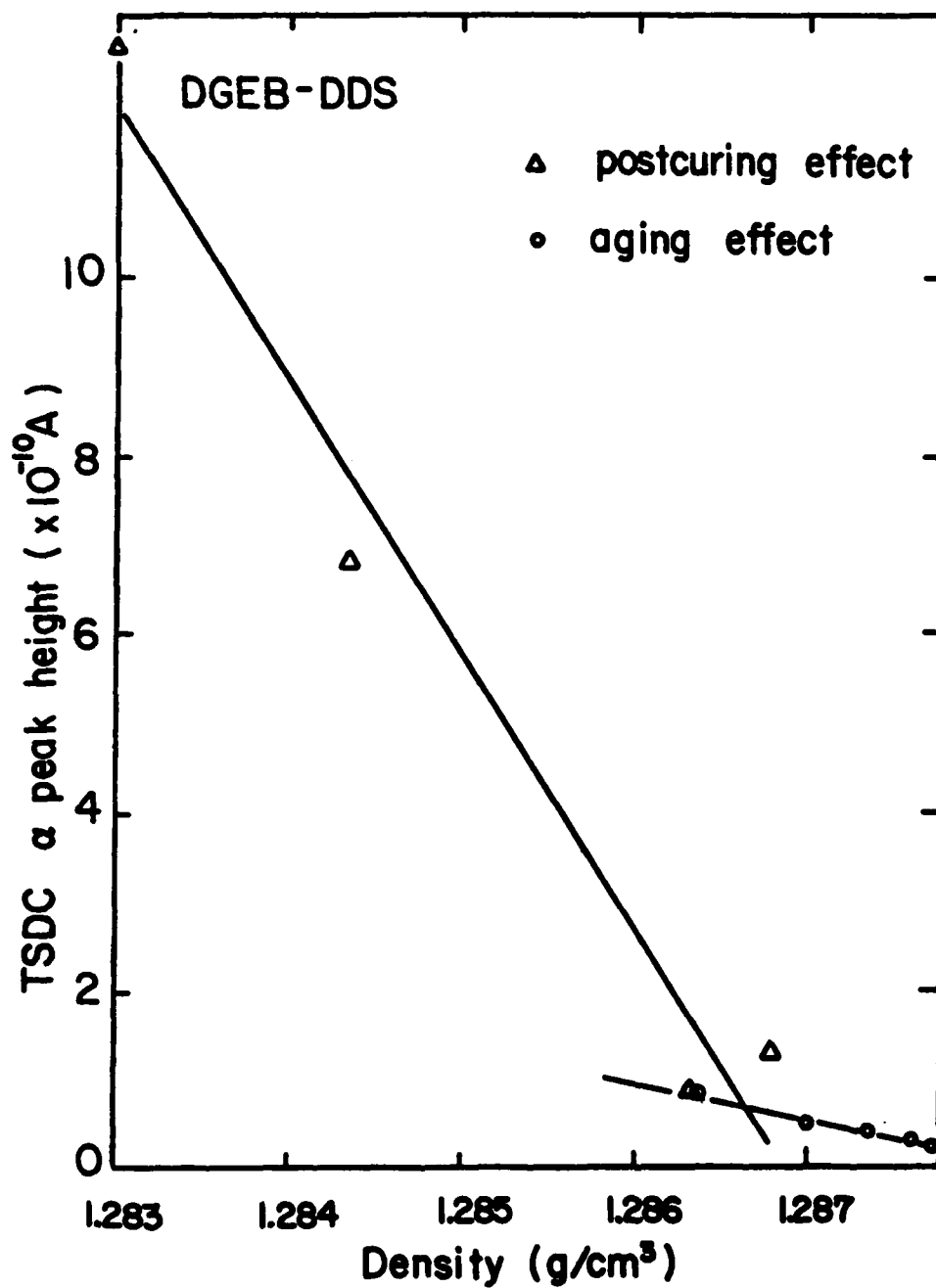


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