

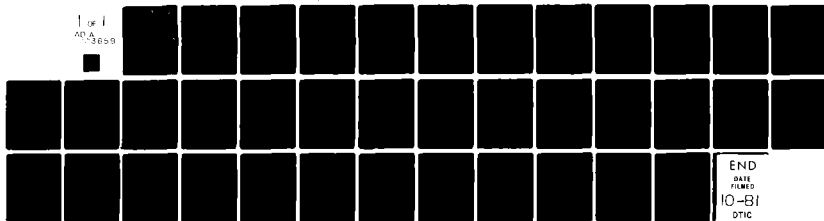
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NORTHWESTERN UNIV EVANSTON IL MATERIALS RESEARCH CENTER F/G 11/9
EFFECT OF SUB-T (G) AGING ON THE PHYSICAL PROPERTIES OF A FULLY--ETC(U)
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OFFICE OF NAVAL RESEARCH

Contract No. N00014-78-C-0276

Project No. NR 356 677

TECHNICAL REPORT NO. 4

"EFFECT OF SUB-T_g AGING ON THE PHYSICAL PROPERTIES
OF A FULLY CURED EPOXY RESIN"

by

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

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 4	2. GOVT ACCESSION NO. AD-A103 659	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EFFECT OF SUB-T AGING ON THE PHYSICAL PROPERTIES OF A FULLY CURED EPOXY RESIN		5. TYPE OF REPORT & PERIOD COVERED Annual, February 1980 to January, 1981
7. AUTHOR(s) T.-D./Chang, S. H./Carr, and J. O./Brittain		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Research Center and Department of Materials Science and Engineering Northwestern University, Evanston, IL 60201		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0276
11. CONTROLLING OFFICE NAME AND ADDRESS ONR Branch Office 536 S. Clark Street, Chicago, IL 60605		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-677
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 7, 1981
16. DISTRIBUTION STATEMENT (of this Report) See appended distribution list.		13. NUMBER OF PAGES 31
		15. SECURITY CLASS. (of this report) Unclassified
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Epoxy resins, molecular relaxations, thermally stimulated discharge currents, electrical polarization, mechanical loss processes, polymer network, cross-linking, sub-T aging.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The effect of sub-T aging on the properties of an epoxy resin system, diglycidyl ether of butanediol, DGEb, cured with 4-4' diaminodiphenyl sulfone, DDS, has been studied. Aging was found to increase the DSC endothermic peak, the density and the upper yield point. In contrast, the lower yield point was relatively unchanged. This result, together with the observation of the elimination of the DSC endothermic peak by deformation and the absence of a yield point after deformation suggested that the aging		

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effect was eliminated by deformation. The thermally stimulated depolarization, TSD, α -peak was found to decrease in strength with aging time. All of the observations were best rationalized on the basis of the free volume concept.

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"EFFECT OF SUB-T_g AGING ON THE PHYSICAL PROPERTIES
OF A FULLY CURED EPOXY RESIN"

INTRODUCTION

Epoxy resins are well known for their wide range of properties, processing ease, and high mechanical and adhesive strengths.¹ Earlier research focused attention on the chemical aspects of epoxy resins, i.e., curing kinetics and chemical modification. However, many investigations of the mechanical properties of epoxy resins have been reported in the recent past. In the last five years, a great many reports on the fracture of epoxy resins have been published owing to the increasing importance of epoxy resins in light weight composite materials applications. Studies of the ultimate strength, elongation to break, and modulus of epoxy resins by tensile test have been reported.²⁻⁸ Creep of epoxy resins has also been reported⁹⁻¹¹ and Morgan^{8,12,13} studied the microscopic failure processes of epoxy resin. Smith and co-workers¹⁴ reported on measurements of the bulk modulus by hydrostatic pressure. The yield/^{strength} of epoxy resins has been measured via tensile and compression tests.^{6,7,15,16} Whiting and Kline¹⁵ found that the yield strength increased with a decreasing amount of hardener (linear epoxy resin was used for this study). Ishai¹⁶ studied the strain rate and temperature effects on yielding and found good agreement with Eyring's theory. Yamini and Young⁶ reported good agreement with Bowden's theory. Pink and Campbell⁷ obtained activation parameters from rate theory consideration. However, the yield drop (or strain softening) accompanying the yielding process has not been explained.

Most investigators have selected chemical composition, curing process, and stoichiometric ratio as parameters for studying the mechanical and relaxation properties of epoxy resins. However, little work¹⁷⁻²⁰ was done on the effect

of aging on physical properties of epoxy resins. Buchman and Katz¹⁷ studied the effect of strain aging above T_g on the orientation of the epoxy resins. Morgan¹⁸ obtained a higher yield stress by aging an epoxy resin at 5°C below T_g . Ophir and coworkers¹⁹ studied the effect of sub- T_g aging on the strain to break and the rate of stress relaxation of an anhydride-cured epoxy resin. Recently, Kong and coworkers²⁰ reported linear relationship between the modulus and the logarithm of aging time for a DGEBA epoxy resin cured with DDM.

The correlation of mechanical strength and secondary relaxations has been made for a number of polymers²¹⁻²⁴. Bauwens^{21,22} found that the yield stress vs temperature curves for polyvinyl chloride and polycarbonate had transitions of the yield stress at the same temperature ranges as the peak temperatures of the secondary β -relaxations. Hartmann²³ found the impact strength of polycarbonate had a maximum at the peak temperature of secondary relaxation. Smith²⁵ showed that the fracture stress of a rubber at different temperatures and strain rate could be combined into a master curve which implies that a thermally activated process (relaxation) was associated with the fracture mechanism. A correlation between the relaxation transitions and the mechanical properties, as a function of the extent of curing, degree of crosslinking, has been reported for the epoxy resin DGEBA-DDS²⁶.

The purpose of the present study was to investigate the effect of sub- T_g aging on physical and mechanical properties of an epoxy resin system. A DSC endothermic peak was studied as an indicator of the extent of aging. Density, uniaxial compression and relaxation properties were systematically studied following the course of aging. Moreover, thermally stimulated depolarization, TSD, measurement²⁷, which is very sensitive to the structural changes in the polymers, was used to monitor the change of relaxation behavior during aging process. We also attempted to correlate the mechanical properties with the

relaxation behavior obtained by TSD. A better understanding of the mechanical deformation, relaxation behavior, and their interrelationships was made possible by this study.

CHOICE OF MATERIALS

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). The chemical structures of DGEb, DDS, and the resulted DGEb-DDS epoxy resin system after curing reaction are shown in Figure 1. The reason for choosing these materials was to obtain a cured epoxy resin with a glass transition temperature much lower than the temperature for curing reaction so that the extent of curing did not change during the aging and quenching processes. The aromatic amines in DDS have much lower reactivity than the aliphatic amines; therefore, the curing reaction occurs only at a high temperature (it actually takes 12 hours at 112°C to reach gelation point for this material). On the other hand, the flexible segment in the center portion of DGEb results in a lower glass transition temperature for the cured epoxy resins compared to the DGEBA epoxy resin frequently used by other researchers.

SPECIMEN PREPARATION PROCEDURES

1. **Mixing:** Stoichiometric amount of epoxy resins and curing agents were mixed by a magnetic stirrer at a temperature such that the curing agent can just be dissolved into the epoxy resin.
2. **Vacuum degassing:** It is difficult to prevent air bubbles from forming in the mixture during the mixing operation; therefore, vacuum degassing was required to obtain bubble-free specimens. Care must be taken not to apply so much vacuum that boiling of epoxy resins occurred. Normally, it takes less than five minutes to remove air bubbles.
3. **Casting:** Degassed mixtures were casted between two well-polished Teflon plates with spacers for controlling the thickness. The Teflon plates were preheated to 112°C before casting. For compression specimens, a mold made of silicone rubber with cavity of precise dimensions was used for casting. No release agents were used to avoid complications due to release agents which were used by previous workers.
4. **Curing:** Two step-curing processes were chosen in order to have better control on the curing extent of specimens and also prevent heat build-up. The first step was to cure the specimens at 112°C for 12 hours in a vacuum oven filled with 1 atm of dry nitrogen. At this point, the specimens had passed the gelation point. The second step was to postcure the specimens at 146°C for 27 hours. Specimens were then slowly cooled in the vacuum oven down to room temperature. Prior to aging treatments, all postcured specimens were heated to 15°C above T_g for 15 minutes and quenched by direct contact with aluminum blocks. This procedure was utilized in order to eliminate aging effects that may have occurred during the slow cooling in the vacuum oven from the 146°C postcuring temperature.

5. Aging: Aging treatments were done in a constant temperature oil bath. Samples were placed in a glass tube which was then immersed in the oil bath. The glass tube was flushed with dry nitrogen gas for about two minutes after the samples were introduced into the tube.

DETERMINATION OF EXTENT OF CURING

The extent of curing of epoxy resins was determined by Fourier Transform Infrared Spectroscopy following the absorption peak of epoxy group at 910 cm^{-1} . Detail procedures were described in the previous paper.²⁶

TSD MEASUREMENT

Disk specimens, 15 mil thick 3 cm in diameter with a center gold evaporated electrode area of about 2 cm in diameter, were used for TSD measurement. Poling time was fixed at 5 minutes for all cases in order to prevent structural change during poling. Poling temperature was 62°C for studying the α peak (we did not pole at higher temperature to preserve the aging effect). For β and γ peaks, specimens were poled at 26°C instead. Details of the experiment and apparatus were described elsewhere.²⁶

DIFFERENTIAL SCANNING CALORIMETRY

Perkin-Elmer Model DSC-2 differential scanning calorimeter was employed to monitor the aging process. The heating rate was $10^{\circ}\text{C}/\text{min}$ and specimen size was 10 mg. The same specimen was used repeatedly for different aging extent.

UNIAXIAL COMPRESSION

Rectangular specimens of size $1\times 1\times 2\text{ cm}$ were used for uniaxial compression test. The machine we used was the Instron Model 1125 universal testing machine. The crosshead speed was $1\text{ mm}/\text{min}$.

DENSITY MEASUREMENT

Density of epoxy resins was measured in a density column. The solution used was sodium bromide dissolved in water. The range was from 1.23 to 1.30 and the length of the column was 90 cm. This gave us the sensitivity of 0.0001 g/cm^3 per mm of column length. The preparation of the density column was described in ASTM standard D1505-68. To prevent errors due to water-sorbing, after the samples were dropped into the column, readings had to be taken as soon as possible. So, it is necessary to find out the amount of time required for samples to reach steady position. For this purpose, a sample which had been immersed in the solution for 1 day was dropped into the column. The position of the sample was recorded as a function of time and it was found that the positions of the sample did not change after 30 minutes. Therefore, for all of the samples tested, recording of the positions was taken at exactly 60 minutes after dropping the sample. By doing this, the possible density change due to water-sorbing was kept at a minimum amount.

RESULTS

All of the specimens studied were made of epoxy resin system DGEb-DDS. They were all precured at 112°C for 12 hrs. and then postcured at 146°C for 27 hrs. Fourier transform infrared spectroscopy study of these specimens showed that 99% of the epoxy groups were reacted. Because of the near completion of the reaction, one third of the molecular segments are amine segments and two thirds of the molecular segments are epoxy segments. The average molecular weight between crosslinking points can then be estimated to be $(M_A + 2 M_B)/3 \approx 208$.

The result of a compression test of a specimen quenched from 15°C above glass transition is presented in Figure 2. The true stress-true strain curve of epoxy resin system DGEb-DDS showed a yield point at a strain of 6.2%. After the yield point, the stress dropped about 19% and remained at a constant value as the deformation process continued. By using cross polarizers, we were able to investigate the deformation processes more closely. Shear bands were found to initiate from the ends of the rectangular specimens and then gradually extended through the whole specimen. The angle between the shear band and the compression axis was about 45 degrees.

After the compression test, the specimen which was originally compressed to half its length was heated to 15°C above its glass transition temperature (77°C) for 15 minutes. It was found that this specimen recovered to exactly the same shape and size as the original specimen. As this recovered specimen was compressed again, the true stress-true strain curve appeared to reproduce that of the fresh specimen within experimental error. This result is shown in Figure 2.

Figure 3 shows the effect of the sub- T_g aging treatment on the stress-strain behavior of DGEb-DDS compression specimens. The yield point was

dramatically enhanced by the sub- T_g aging treatment. A 23% increase of the upper yield stress was obtained for 54 hrs. of aging treatment at 62°C. The upper yield stress versus aging time was plotted in Figure 4. One can see that the yield stress increased steadily until 18 hrs. of aging. Beyond 18 hrs., the yield stress leveled off. In contrast, the lower yield stress level after yielding remained essentially unchanged. The elastic modulus and strain at yield point appeared to be unaffected by the aging treatment. In order to study the deformation process in greater detail, another specimen was aged at 62°C for 18 hrs. and then tested by compression with intermittent unloading and reloading. This loading and unloading curve was illustrated in Figure 5. The most important feature of this curve is that the high yield stress and yield drop disappeared when the specimen was compressed past the yield point. This yield point phenomena is observed in many glassy polymers but some deform homogeneously.²⁸ It is also noted that both the unloading and reloading curves were not straight lines. This is probably due to stress relaxation occurring during unloading and reloading. When the strained specimen was aged for 1 hr. at 62°C after the third unloading cycle, the yield point reappeared upon reloading, dashed curve. The stress-strain curve for the strain-aged specimen has been displaced because of the retraction that occurred during the aging treatment.

In order to understand what is going on during the sub- T_g aging process, several other physical properties of this epoxy resin system were measured. In Figure 6, results of differential scanning calorimetry measurements are illustrated. One can see that the quenched specimen shows a distinct step function, which is characteristic of the glass transition. The glass transition temperature, defined as the inflection point within the step, was 77°C. As the aging process proceeded, an endothermic peak appeared on the high tempera-

ture side of the transition and gradually increased its peak area. The endothermic peak area versus aging time was also plotted in Figure 4. The endothermic peak area increased rapidly as the specimen was aged. After 54 hrs. of aging at 62°C , the peak still was increasing, in comparison the upper yield stress leveled off after only 18 hrs. of aging at 62°C .

The density of this epoxy resin system was also monitored in the course of aging, Figure 4. A small monotonic increase in density was observed. The density of the postcured, 27 hrs. at 145°C , and quenched specimen 1.2863 was increased to about 0.12% to 1.2878 after 54 hrs. of aging at 62°C .

The samples which were compressed at room temperature were observed to retract when held at 62°C . As shown in Figure 6, where the percentage of recovery was plotted as a function of the aging time, the curve became linear after 4 hrs. of aging at 62°C .

Since TSD measurements are known to be very sensitive to changes in molecular structure of polymers, it was also employed in this study to investigate the aging process. A quenched specimen and a specimen aged for 18 hrs. at 62°C were tested for low temperature TSD, Figure 8. Almost no difference in the TSD β peak and γ peak was observed, but the high temperature end of the β peak was lowered by aging. Figure 9 shows the high temperature part of TSD thermogram for the same material. Note that all samples were poled at 62°C , i.e., the aging temperature for 5 minutes. The reason for poling at such a low temperature was to prevent the aging effect from being erased during poling at a higher temperature. Two peaks appeared in this TSD thermogram for either quenched or aged specimens. The peak at about 45°C did not seem to change with the aging treatment. However, the peak at 68°C was greatly reduced by aging. The strength of the relaxation of the quenched specimen was reduced by a factor of 4 by aging for 18 hrs. at 62°C . After aging and testing for

TSD for 5 cycles (from 0 hr. to 18 hrs. aging), the specimen was heated to 15°C above T_g (77°C) for 15 min. to erase the aging effect and then requenched. The TSD thermogram for this specimen reproduced the freshly quenched specimen. In other words, the aging effect on the TSD thermogram was also reversible. In Figure 10, the TSD α peak height was plotted against the density. A very good linear relationship between the TSD α peak height and the density was found.

DISCUSSION

The fact that, upon heating, samples of DGEb-DDS epoxy resin system retracted completely to its original length after being compressed to half its length indicated that the deformation process is entirely anelastic, at least up to 50% of strain. This behavior is quite different from the metallic materials but it seems reasonable because this material has a three-dimensional network structure. The retraction results suggest that the crosslinking points were not broken during the deformation process and the deformed molecular structure reverts back to the undeformed structure when the epoxy resin was heated above T_g . Additional evidence that crosslinking points were not broken is the reproducible compression curve. As far as compression property is concerned, no crosslinking seemed to be broken during the deformation process. It is surprising to note that linear polymers²⁹ also showed similar recoverability. In this case, the entanglements probably served as crosslinking points during the retraction.

The systematic increase of yield stress with sub- T_g aging time for these thermosetting materials, as shown in Figure 3, is similar to the results of many thermoplastics.^{30,31} An increase of a DSC endothermic peak and modulus and also a decrease of the creep and dynamic mechanical relaxation has been observed in aged thermoplastics. It was suggested³¹ that the increase of yield stress was due to the excess thermodynamic properties of polymeric glasses. Since we also observed an increase of the DSC endothermic peak, Figure 5, a decrease of the TSD α peak, Figure 8, and the increase of density, Figure 4, we may conclude that the effects of aging on physical properties of thermosets are similar to the observations made on aged thermoplastics. In other words, crosslinking does not change the intrinsic behavior of aging effects on physical properties of polymers.

There were several molecular theories proposed in the literature³² to

explain the yielding phenomena of polymers. Ishai,¹⁶ in his study on epoxy resins, found that the strain rate dependence of yield stress was in good agreement with the Eyring's theory.³³ However, Eyring's theory is not able to explain the strain softening after yielding. Another theory³⁴ explained the yielding phenomena by proposing that T_g is reduced by the applied stress, but again this theory does not predict the strain softening. Some authors^{35,36} envisaged the yielding as the progressive breakdown of entanglements. Strain softening could be explained by this theory as a breakdown of entanglements reduced the stress for deformation.

For epoxy resins which were highly crosslinked as the materials used in this study, the molecular segments were tied up at both ends by crosslinking points. It is unlikely that disentanglements could happen without breaking the chemical bonds in the molecular segments or at the crosslinking points. Since our specimens were seen to recover to the original dimension and reproduce the compression properties, no significant amount of chemical bonds were likely to be broken during the deformation process. This makes the explanation by disentanglements unlikely.

Careful investigation of the compression curves shown in Figure 3 revealed that the change in the stress at the lower yield point was relatively small compared to the change of yield point by the effect of aging. In other words, all of the specimens aged to different extent showed little difference after deformation. This may imply that the aging effect could be erased by mechanical deformation. The unloading-reloading curves, Figure 5, also supported this notion. Here the yield point, which is an indication of the extent of aging, was seen to be depressed if the unloading-reloading was done after yielding occurred.

The typical method of monitoring the extent of aging is to investigate

the DSC endothermic peak. If the mechanical deformation could erase the aging effect, it must also erase the endothermic peak altogether. This led us to investigate the DSC endothermic peak of an aged specimen after being rolled. As shown in Figure 11, this was proven to be the case.

Our results so far indicated that the yielding phenomena and the effect of aging could be best explained by the free volume concept. Any processing parameters, i.e., aging and crosslinking, which reduce the free volume of epoxy resins, would enhance the yield point. The decrease of density, Figure 4, and the decrease of enthalpy (as a result of endothermic peak in DSC) both indicated a decrease of free volume during the aging process. This decrease in free volume, in turn, enhanced the yield point. Mechanical deformation probably recreated the free volume in the aged specimen, thereby reducing the stress level after the yield point (strain softening). Indeed, quenched specimen, which preserved most of the free volume in the material above the glass transition temperature, showed the smallest amount of strain softening after yielding. We, therefore, conclude that free volume concept not only rationalizes the enhancement of the yield point by aging, but also explains the existence of strain softening.

The result of TSD low temperature region showed that the β and γ relaxation peaks were unaffected by the aging treatment. As discussed in our previous paper,²⁶ this fact implied that both the β and γ peaks are most likely due to very localized motion of molecular segments. A few workers also reported similar results on PVC,³⁷ PET³⁸, and polycarbonate³⁰ for their secondary dynamic mechanical relaxation peaks. The only difference in the thermogram was the decrease of the high temperature end of the β peaks by aging treatment. This is more likely due to the decrease of the tail of the α peak. In contrast to the insensitivity of β and γ peaks to sub- T_g aging, the α peak, the peak at 68°C, was very dramatically decreased in size by the aging treatment, Figure 9.

The difference was more than four times that between the quenched specimen and the specimen aged for 18 hrs. Note that the density changed only 0.12% and the yield stress changed only 23%. This result shows that the TSD α peak is much more sensitive to the changes in the structure of polymers than other physical properties. This suggests that TSD might be a useful technique for monitoring the structures and properties of polymers during processing, at least in epoxy resins. The fact that the α peak height was reduced indicates the population of mobile molecular segments was decreased. Since the peak temperature remained constant, the activation energy probably was not affected significantly. Again, the free volume concept successfully explains this result. The decrease of free volume reduced the number of molecular segments which have enough space to move, therefore α peak decreased. The peak at 45°C was not changed by the aging treatment, the baseline was lowered by the change of the α peak. The origin of this peak was not determined, but just like the β and γ peaks, it may be also due to localized motion because of its insensitivity to the aging treatments. Consider next the correlation between the relaxation behavior and the mechanical properties, from the results mentioned above, it is apparent that when the peak height of the relaxation was decreased, the yield stress was enhanced. The decrease of relaxation peak implied that the movement of molecular segments was more difficult and the stress required to deform the material should be higher. Thus, the correlation between the TSD α peak and the yield stress.

CONCLUSIONS

1. The compression true stress-true strain curve of DGEB-DDS epoxy resins showed an upper yield point, strain softening and a lower yield point.
2. The deformation of DGEB-DDS epoxy resins which were cured 99% was anelastic up to at least 50% of strain. The deformed specimens recovered to their original dimensions after heating above the glass transition temperature. Below T_g , the recovery also occurred, but the speed of recovery was much slower.
3. Aging treatment enhanced the yield point and strain softening of DGEB-DDS epoxy resins. The amount of change was about 23% at aging temperature of 62°C. The flow stress was relatively unchanged compared to yield stress.
4. For compression test, unloading after yield point reduced the yield point, but aging after deformation resulted in a return of the yield point phenomenon.
5. Aging treatment introduced a DSC endothermic peak which increased in strength as the time of aging increased.
6. The density of epoxy resins was increased by aging treatment.
7. The TSD α peak was reduced dramatically by aging treatment while the β and γ peaks were almost not affected at all.
8. The TSD α peak was found to be much more sensitive to the change of epoxy resins compared to other physical properties.
9. The variation in the TSD α peak without T_g -aging correlated well with the yield point to epoxy resins.
10. The increase of density, the increase of DSC endothermic peak, the enhancement of yield point and strain softening and the decrease of TSD α peak were successfully explained by the free volume concept.
11. Mechanical deformation erased the aging effect.

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FIGURE CAPTIONS

- Figure 1. Network formation of DGEb-DDS epoxy resin system.
- Figure 2. Typical stress-strain curve obtained by uniaxial compression for DGEb-DDS epoxy resin samples. The dashed curve shows the result for specimen retested after compressing and heated to 15°C above T_g to recover its original dimension.
- Figure 3. Stress-strain curves for a series of DGEb-DDS epoxy resin which were aged for different lengths of time, tested in compression.
- Figure 4. Yield point, DSC endothermic peak area, and density of DGEb-DDS epoxy resin system as a function of aging time. The yield point data were obtained from Figure 3 and the DSC endothermic peak data are from Figure 6.
- Figure 5. Unloading-reloading curve for a DGEb-DDS epoxy resin postcured for 27 hrs. at 146°C and aged at 62°C for 18 hrs. The dashed curve was the compression curve for a sample aged at 62°C for 1 hr. after the third loading-unloading sequence.
- Figure 6. DSC result for DGEb-DDS epoxy resin for samples aged at 62°C for different lengths of time.
- Figure 7. Percent recovery of the DGEb-DDS epoxy resin sample which had been compressed to half of its original length and then aged at 62°C .
- Figure 8. Low temperature part of the TSD thermogram for DGEb-DDS epoxy resin samples which were quenched (solid line) and aged (dashed line).
- Figure 9. High temperature part of the TSD thermogram for DGEb-DDS epoxy resin, showing the effect of aging at 62°C .
- Figure 10. Relationship between the TSD α -peak height and the density of DGEb-DDS epoxy resin samples which were aged at 62°C for different lengths of time.

Figure 11. Effect of rolling on the DSC of aged DGEB-DDS epoxy resin. The solid line represents DSC for sample that was not rolled.

Formation of DGEBA-DDS epoxy resin system

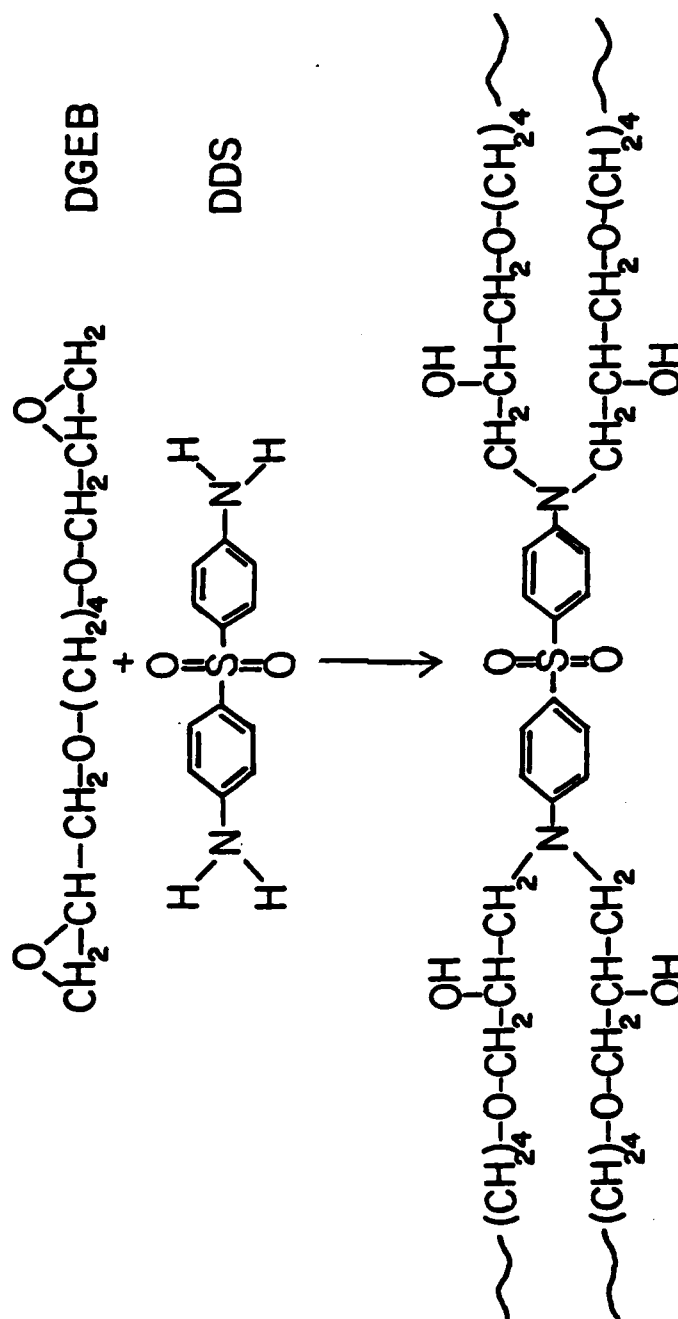


Figure 1.

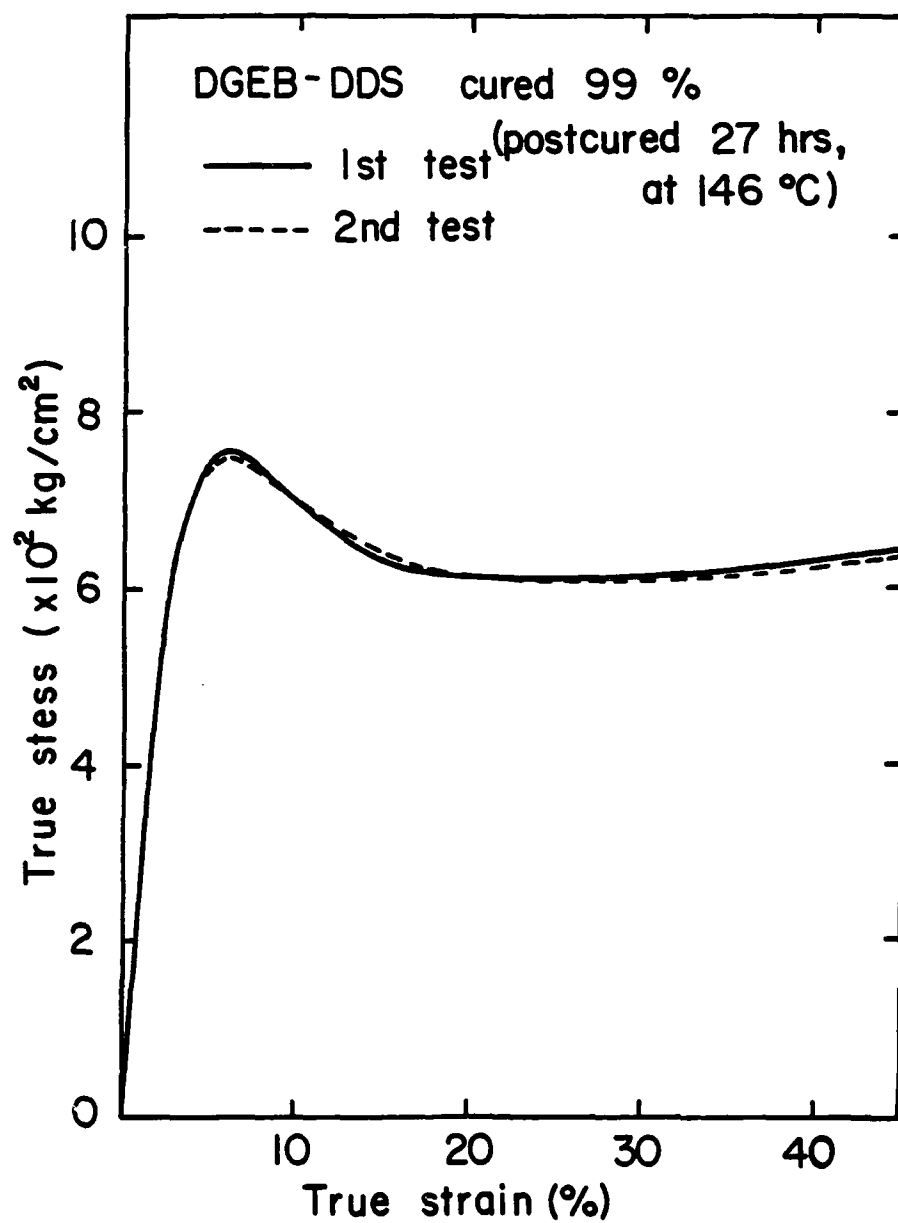


Figure 2.

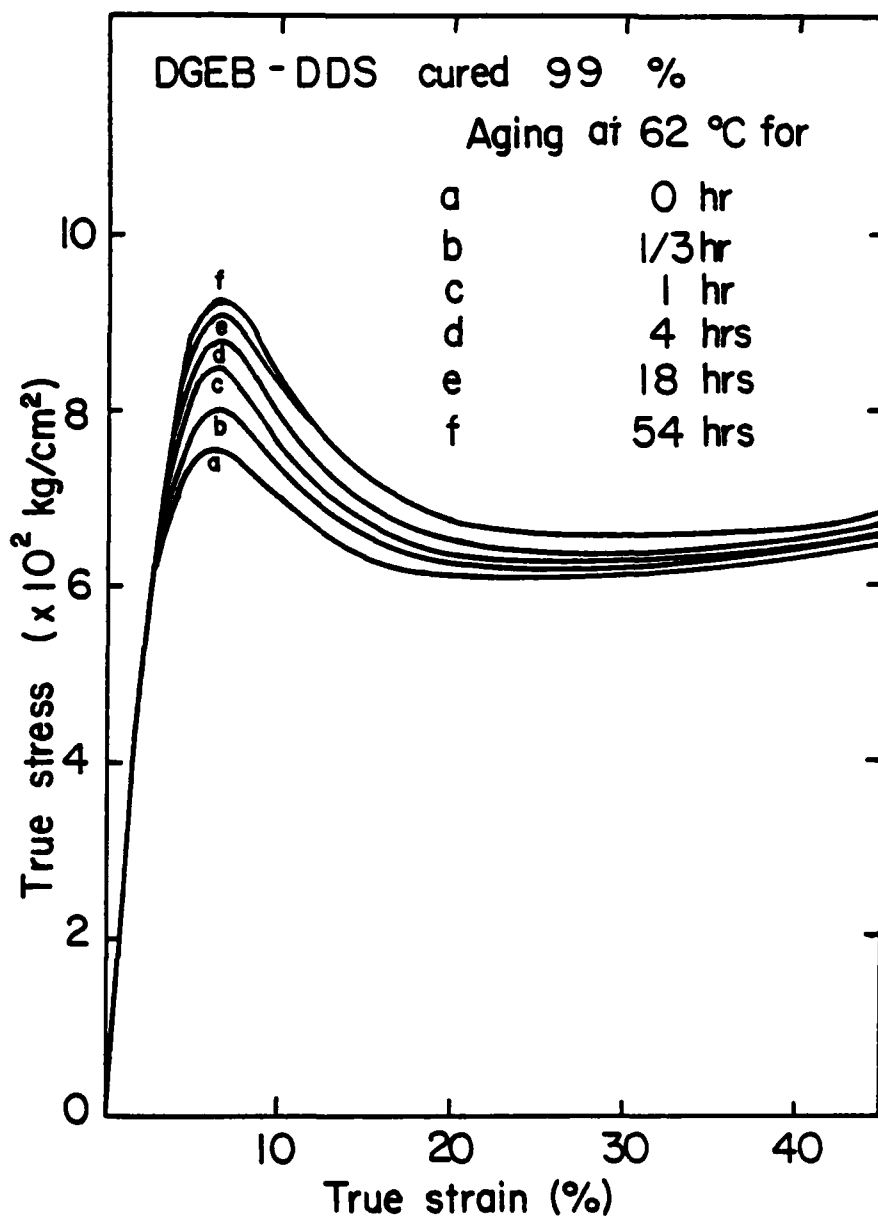


Figure 3.

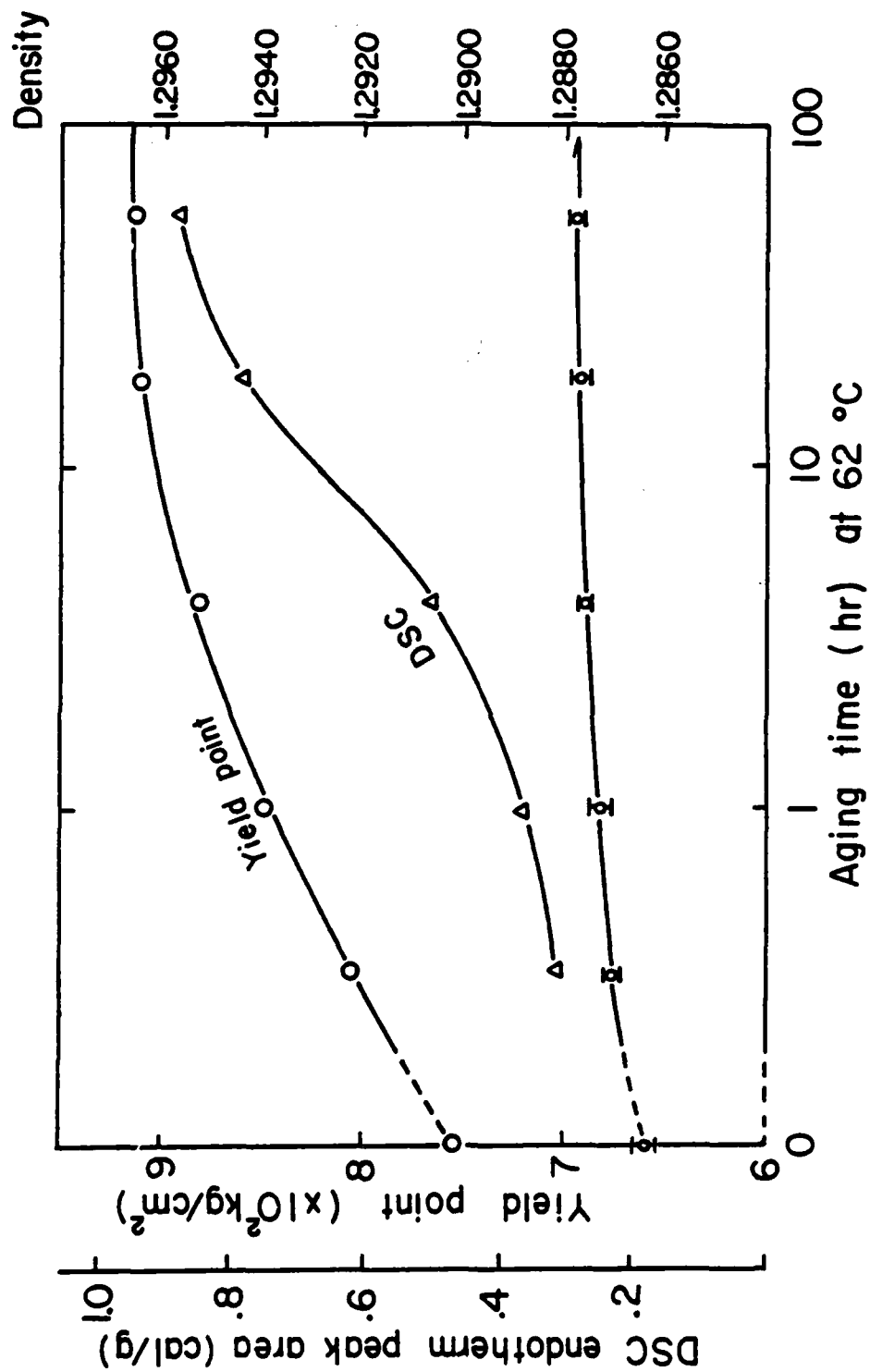


Figure 4.

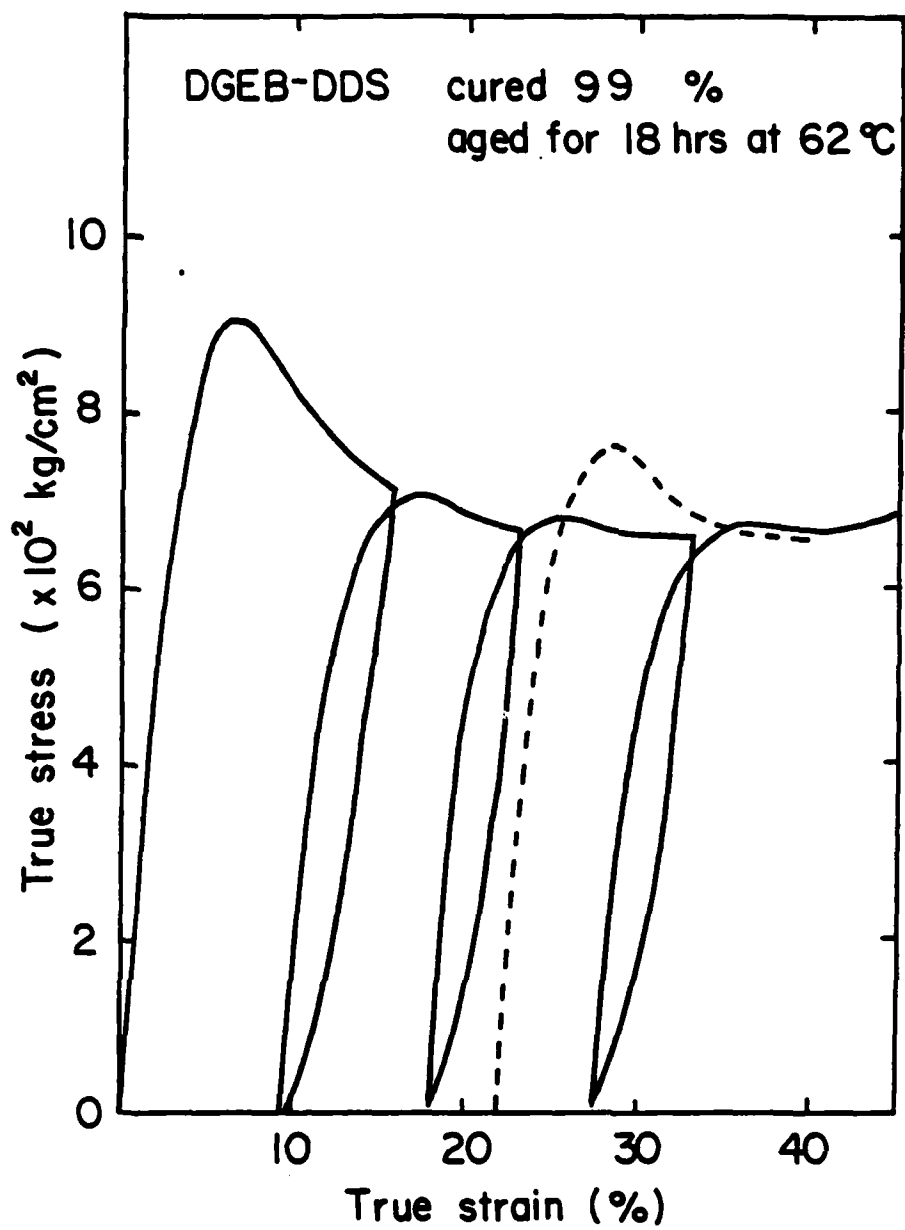


Figure 5.

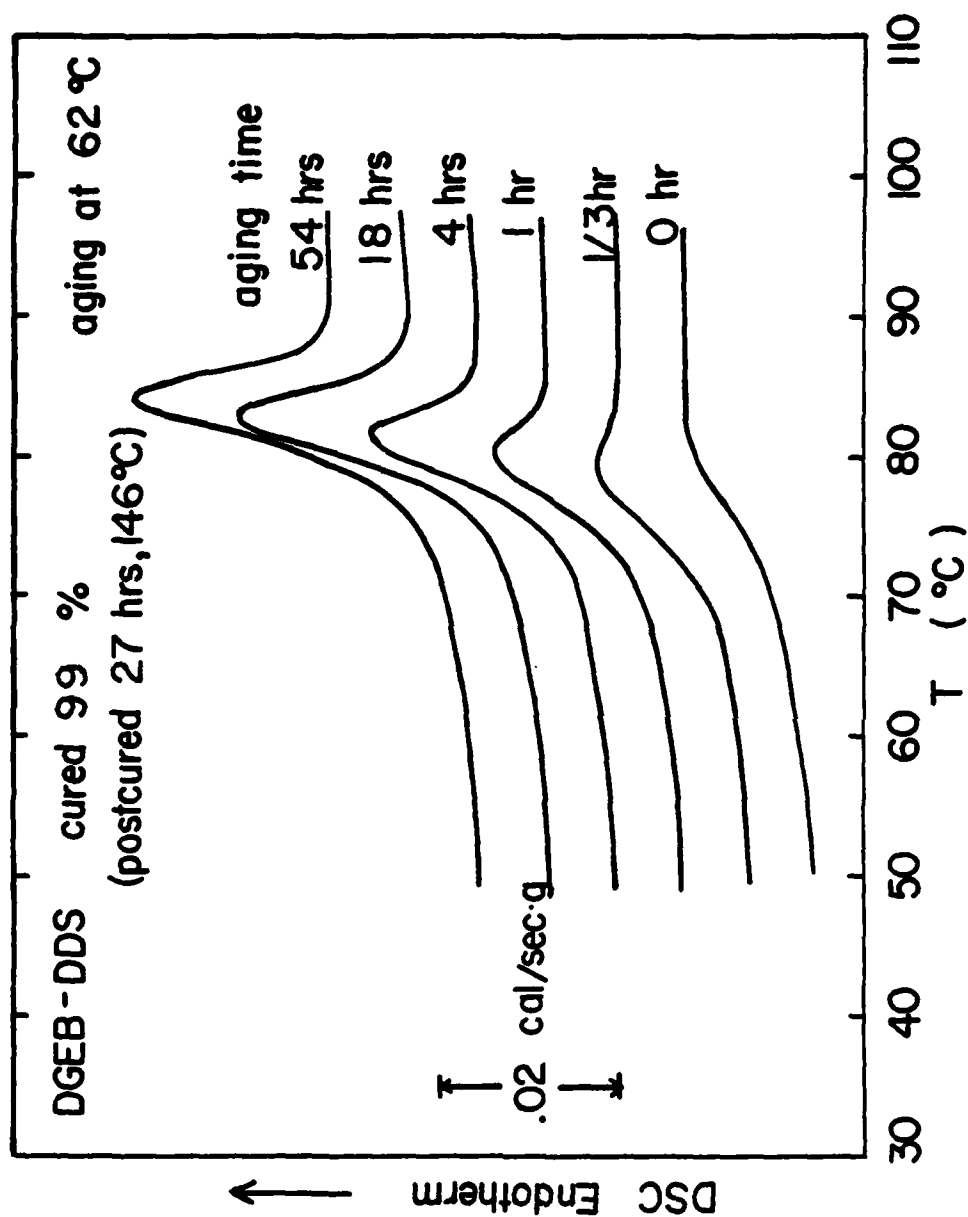


Figure 6.

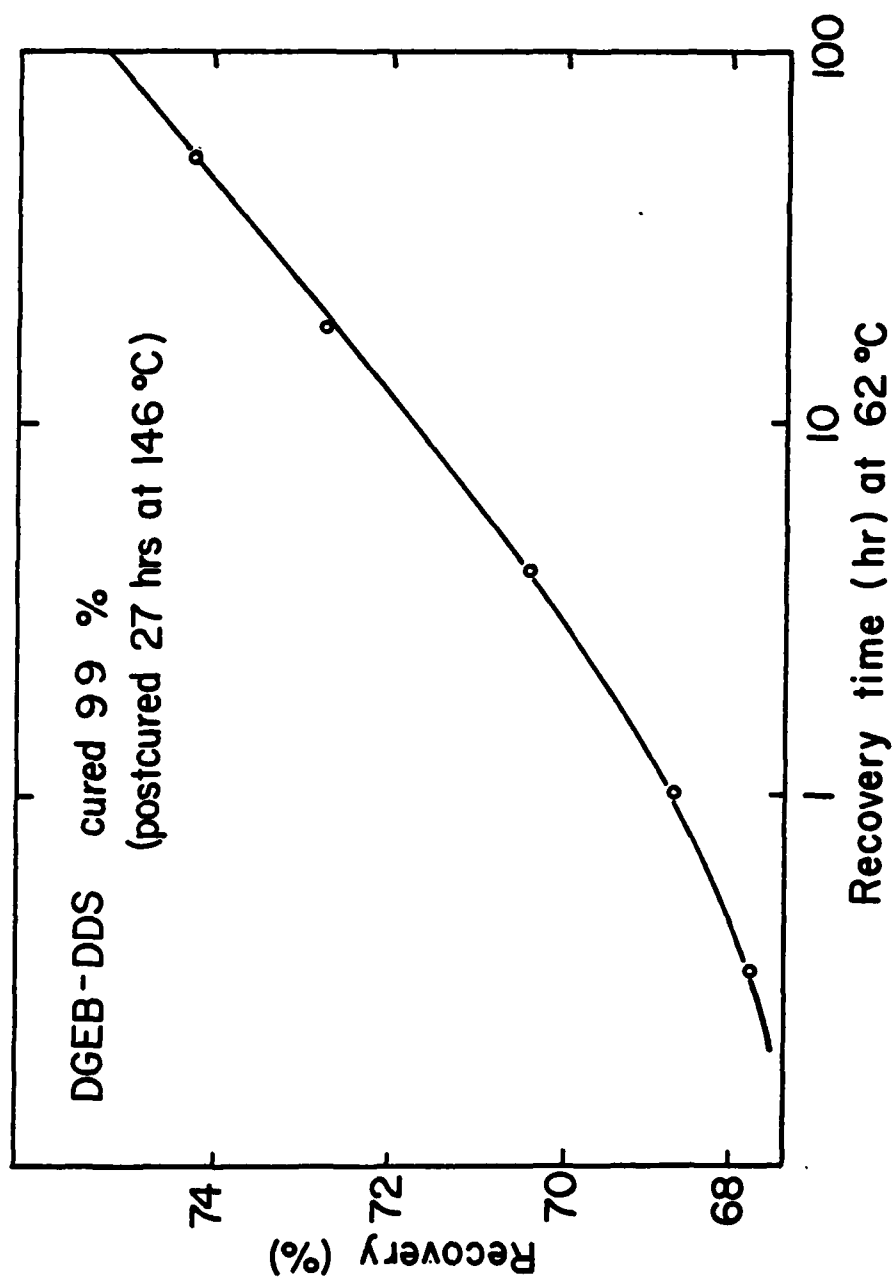


Figure 7.

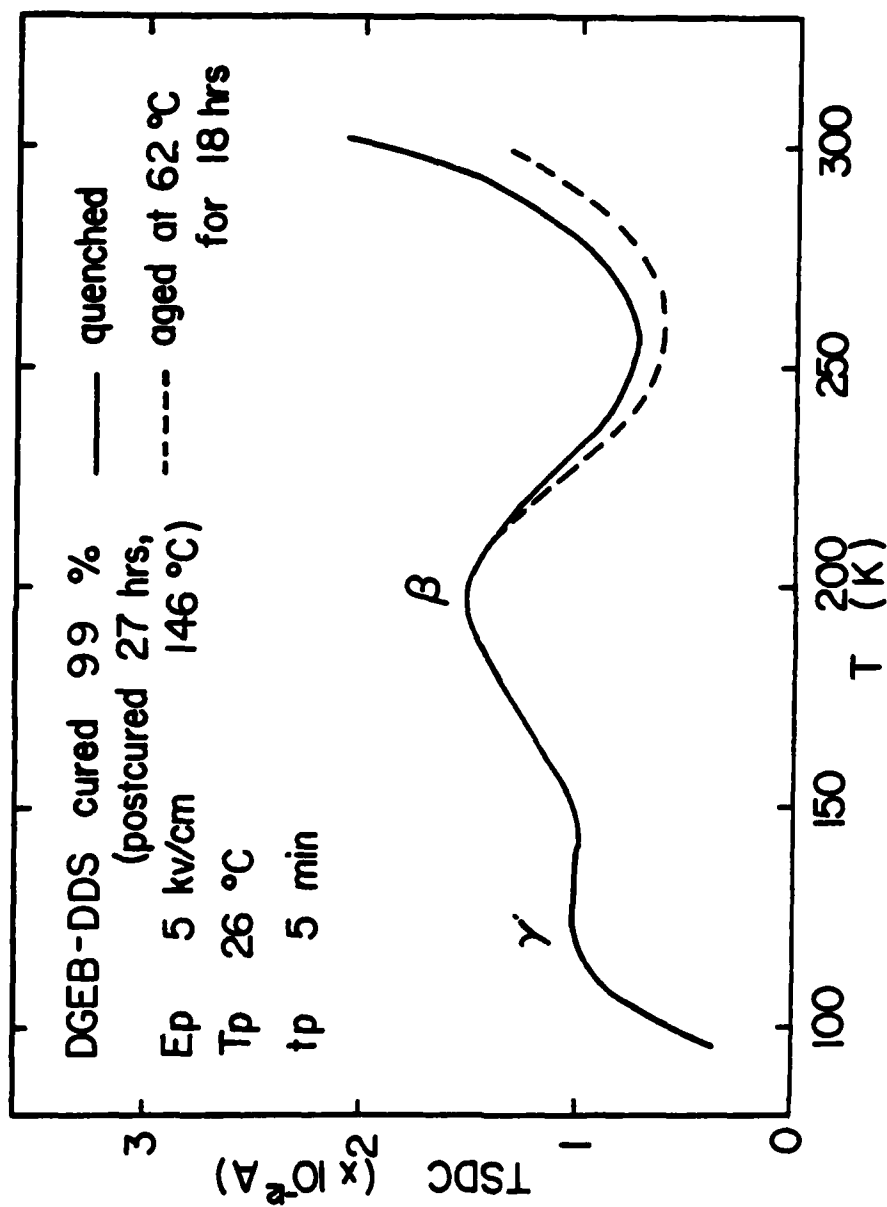


Figure 8.

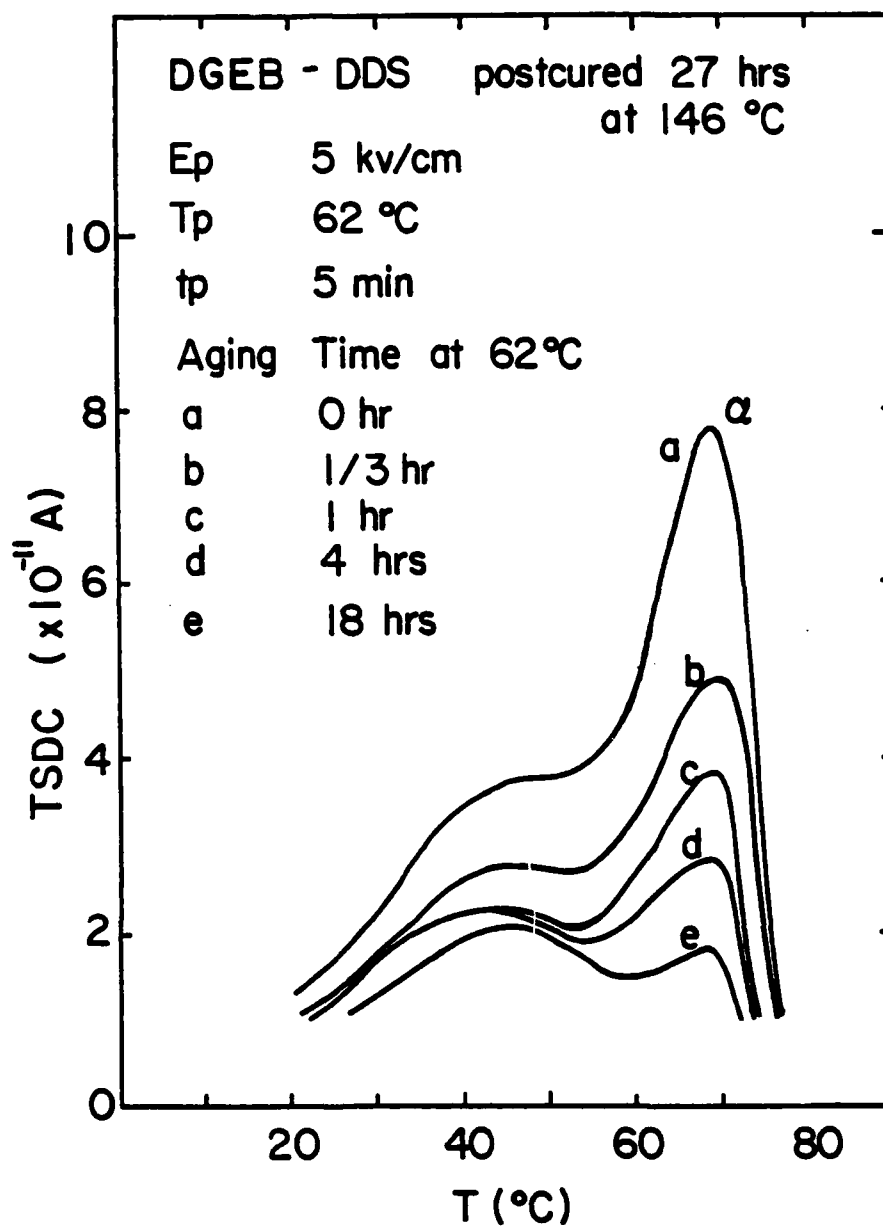


Figure 9.

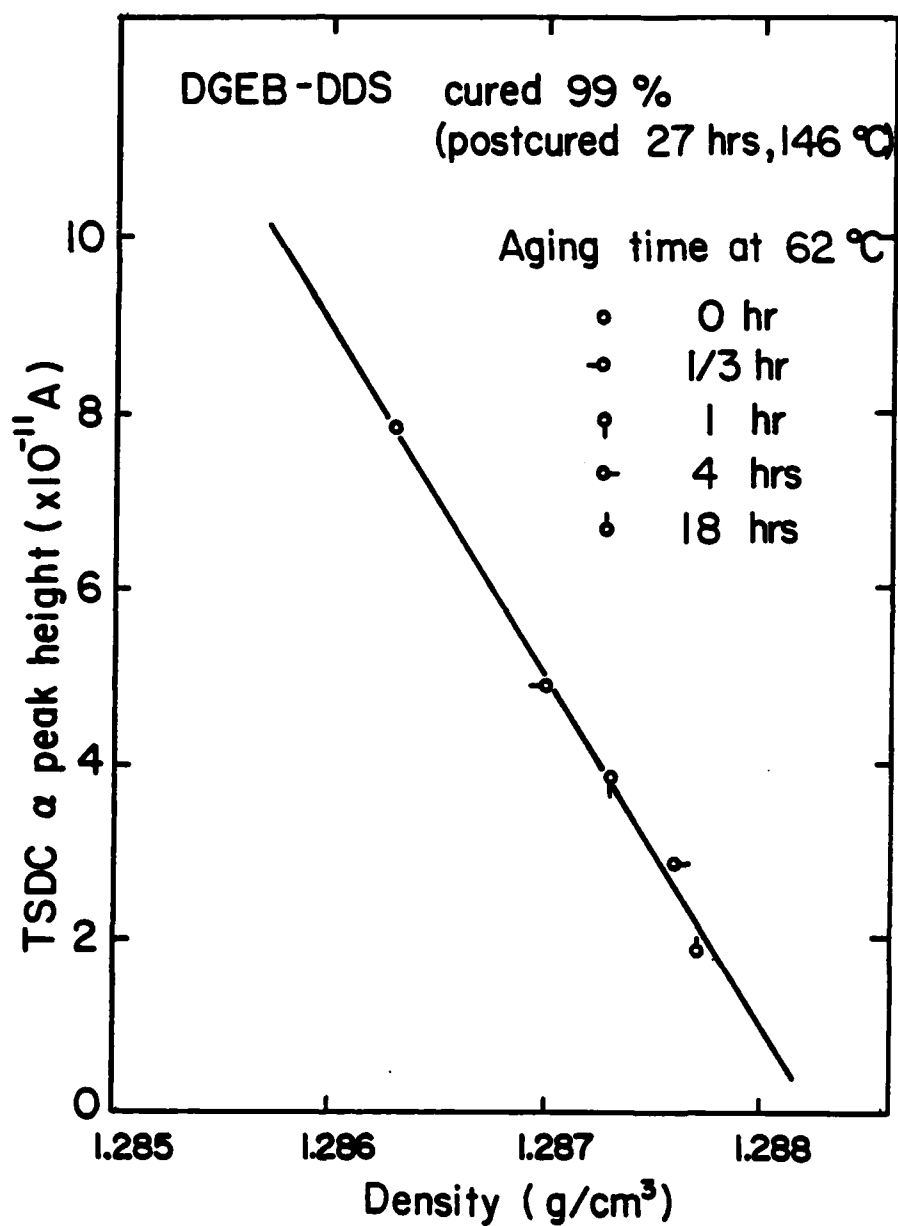


Figure 10.

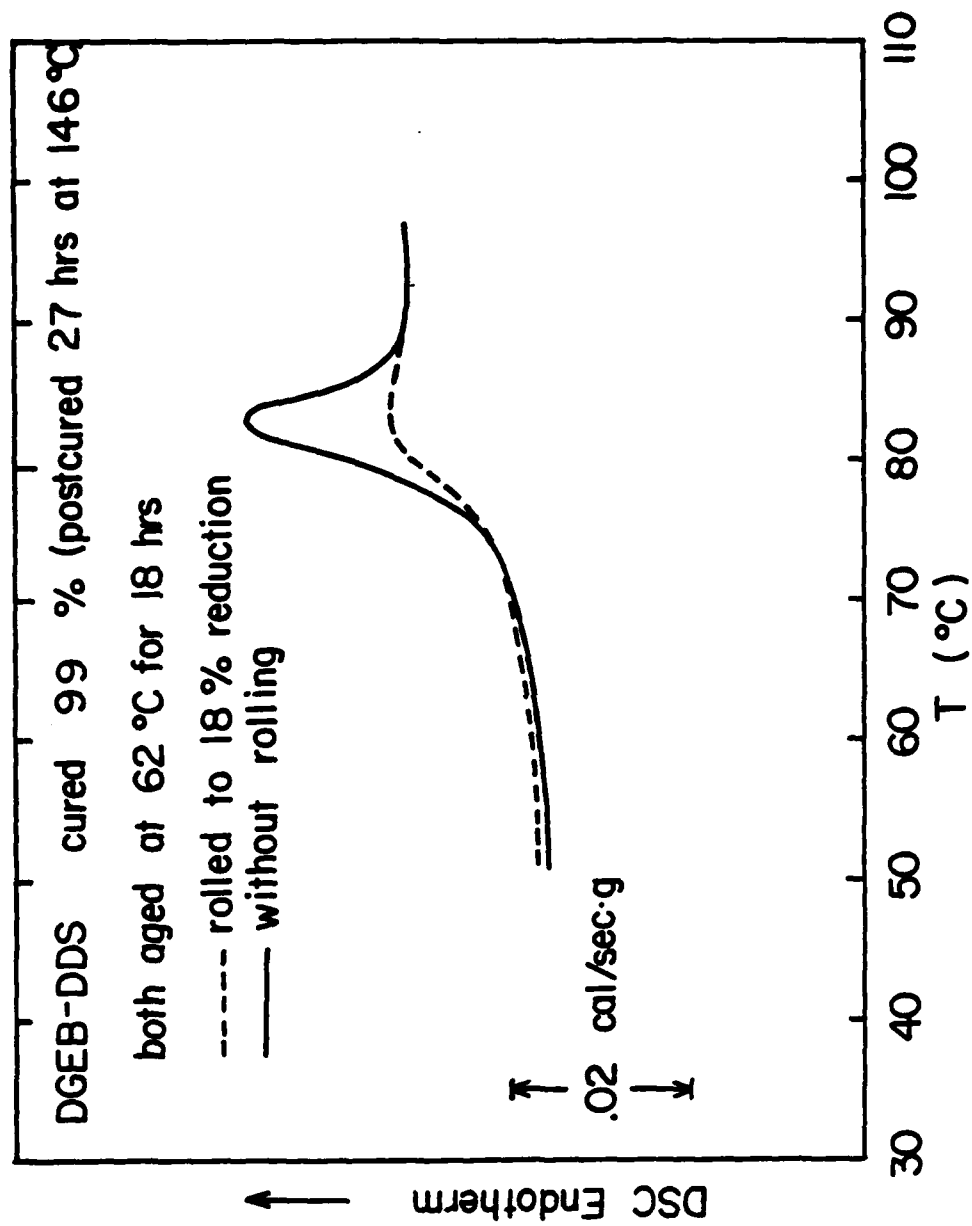


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