

Sub-T_g annealing studies of rubber-modified and unmodified epoxy systems

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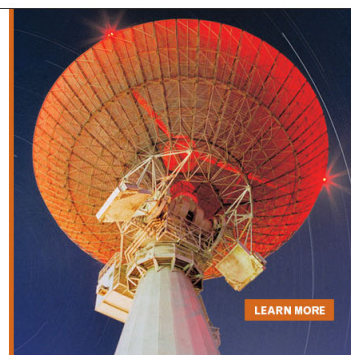
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Sub- T_g annealing studies of rubber-modified and unmodified epoxy systems

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Epoxy network systems based on DGEBA (bisphenol-A-diglycidyl ether) and NMA (nadac methyl anhydride) systems modified with the low molecular weight CTBN (carboxyl-terminated butadiene-acrylonitrile copolymer) rubbers were prepared and studied. It was found that below the glass transition of the epoxy matrix these materials displayed time-dependent changes in their mechanical properties; specifically, the strain to break as well as the rate of stress relaxation were observed to decrease in a near-linear behavior with the logarithm of time at sub- T_g annealing. Calorimetric methods clearly showed a simultaneous decrease in enthalpy with time that behaved in a similar fashion as the time-dependent mechanical properties. All the calorimetric and mechanical data are qualitatively related. The importance of this phenomena is considered in view of the widespread use of epoxies. Similar behavior is expected for other network glasses thermally quenched into a nonequilibrium state.

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INTRODUCTION

For the last several years there has been a growing interest in the nonequilibrium behavior of linear glassy polymers.¹⁻⁴ Much of this interest stems from the work of Kovacs,⁵ which indicated that when polyvinyl acetate is rapidly thermally quenched from above its glass transition temperature, T_g , the volume of the system slowly decreases (densifies) with time. The rate of this process depends on both the temperature below T_g and on how long the material has been annealed, commonly called sub- T_g annealing at a given temperature. Associated with this time dependence of volume is a decrease in enthalpy. Although it has been shown that enthalpy is a better characterization parameter than the volume,⁶ the two parameters are nearly identical in their time-dependent behavior.¹ Because of this, and due to the facility of monitoring enthalpic changes by differential scanning calorimetry, DSC, the enthalpy is one of the most common parameters used to follow the degree of nonequilibrium character of a thermally quenched polymeric glass. Associated with this "relaxing" of the system to its equilibrium state has been the common term "enthalpy relaxation." The molecular basis for this nonequilibrium behavior has been discussed elsewhere^{1,7} and, in brief, arises from the quenching of free volume into polymer system due to the inability of the polymer chains to achieve their equilibrium conformation and configuration as the temperature of the system is lowered through T_g . That is, due to the rapidly increasing viscosity as T_g is approached, the molecules essentially undergo a "log-jam" effect and excess free volume is quenched within the system. Some degree of molecular motion occurs below T_g , and with time the molecular system does ap-

proach the true equilibrium state, i.e., the equilibrium values of volume, enthalpy, or other state function variables.

Associated with the approach to equilibrium are noticeable effects on the mechanical and dielectric behavior.⁸ As a common example, it has been noted for amorphous polyethylene terephthalate, PET, that the degree of ductile behavior is enhanced immediately after quenching below T_g , whereas the system may display more brittlelike behavior at a later time for the same strain rate conditions.¹ More recently, Johnson *et al.*⁸ showed that the dielectric relaxation rate also decreases with sub- T_g annealing time. Matsuoka has similarly shown that stress relaxation rates and creep to failure are also strongly coupled to the enthalpy relaxation process and to the loss of free volume.⁷ Other researchers also have demonstrated the correlation of time-dependent mechanical properties of polymeric glasses with enthalpic relaxation.⁹⁻¹² This physical aging phenomena has also been observed in network glasses but only a limited study has been done.^{9,13,14}

In this paper we report results of investigation on the enthalpy relaxation process and its effect on mechanical properties for a selected group of network glasses. Specifically, we have prepared epoxy networks from liquid resins based on Epon 828. As discussed shortly, related rubber modified epoxy systems have also been prepared for similar investigation. We believe this study represents the first such systematic study on network glasses and their degree of enthalpic relaxation behavior.

MATERIALS

The epoxy network was formed by polymerization of DGEBA (bisphenol-A-diglycidyl ether, Epon 828, Shell Chemical Co., epoxy equiv. weight = 186) with NMA (nadac methyl anhydride) as a curing agent and the use of BDMA (benzyl dimethylamine) as a catalyst. Modification of the

^{a)}Work done at Western Electric Engineering Research Center, Princeton, N.J. 08540.

TABLE I. Formulation (wt%).

Material	Epon 828	CTBN 1300×13	Rubber ^a	CTBN 1300×15	NMA	BDMA
828-0-0	53.4	45.6	1.0
828-13-27	60.0	13.1	39.0	1.0
828-13-10	60.0	13.1	39.0	1.0

Cured at 170 °C for 1 h

^aEpon 828 and rubber were prereacted with ϕ, P catalysis

glassy network was achieved by the addition of CTBN (carboxyl-terminated butadiene-acrylonitrile copolymer) epoxy adducts. The two CTBN rubbers [CTBN (1300×13) and CTBN (1300×15), B.F. Goodrich Chemical Co., $M_w = 3500$] are capped with DGEBA in order to reduce the variables during curing. These adducts of CTBN and DGEBA are prepared by heating an excess of the epoxide with the rubber at 150 °C for 1 h with 0.1% triphenylphosphine by weight. The completion of the carboxyl epoxide reaction was followed by titration of the carboxyl groups and by gel permeation chromatography. The solubility of the CTBN rubber within the epoxy network is governed by the acrylonitrile content, i.e., the higher the acrylonitrile component, the more soluble the rubber.¹⁵ In order to facilitate the discussion, a material description follows: the first number is the basic resin, the second number is percent rubber, and the third number is percent acrylonitrile content, i.e., 828-13-10 (Epon 828, 13% rubber, and 10% acrylonitrile). Different compositions used in the study were prepared according to Table I.

EXPERIMENTAL

An Instron model TMS was used for the stress-strain and stress-relaxation experiments. Dog-bone-shaped samples were prepared in accordance to ASTM D 1708-66. The sample's length was 22.25 mm, width 4.75 mm, and typical thickness 1.5 mm. The stress-strain experiments were performed at strain rate of 5% min⁻¹. The resin components were mixed as described above and poured into a Dow Corning silicon RTV 3110 mold, preheated to 170 °C. The samples were cured 1 h at 170 °C. After curing, the samples were separated from the mold, heated to 150 °C for 5 min, and quenched in ice water. The quenching time was taken as time zero. The annealing temperature as well as the temperature of the stress-strain and stress-relaxation tests was 23 °C. In the stress-relaxation experiments the samples were stretched within a 3-sec interval to an elongation of 1.12%. The stress was recorded as a function of time, and the results are given as the percent of stress relaxation in the first 10 min. Three to six samples were tested in the stress-strain and stress-relaxation modes for each annealing time. Typical scattering range of the results was 20%, but it reached up to 50% error for the ϵ_b data. Similar spread in fracture energy data has been observed for DGEBA systems cured with amines.¹⁶

A Perkin Elmer DSC-2 instrument was used for the differential scanning calorimetry studies. The samples for this experiment were disks 5 mm in diameter, cut from 0.3-mm-thick film that was cured in a Teflon^R mold for 1 h at

170 °C. These samples were fit into sample pans; their weight was about 8 mg. Next, the samples were heated to 150 °C for 5 min and quenched to 23 °C; this time was taken as time zero with respect to sub- T_g annealing. Sub- T_g annealing was performed at three different temperatures: 23, 40, and 60 °C.

DSC scans were made with a 10 °C min⁻¹ heating rate. Each sample was scanned through its glass transition, cooled rapidly, and scanned again. The second scan served as a reference DSC trace of a quenched sample. The integration of the specific heat with respect to the temperature yields the enthalpy difference between the initial and final temperatures. Both the quenched and annealed samples have the same enthalpy above T_g (because they are at equilibrium); therefore, any difference in the area under the C_p curve represents an enthalpy difference between the annealed and quenched samples at their sub- T_g state. After matching the two scans in their flat regions below and above the glass transition, the "relaxation" enthalpy was obtained by subtracting the areas under the two curves and dividing by the sample weight.

RESULTS AND DISCUSSION

Stress-strain experiments

The stress-strain curves of the three different formulations taken 10 min after quenching are shown in Fig. 1. The following effects are observed:

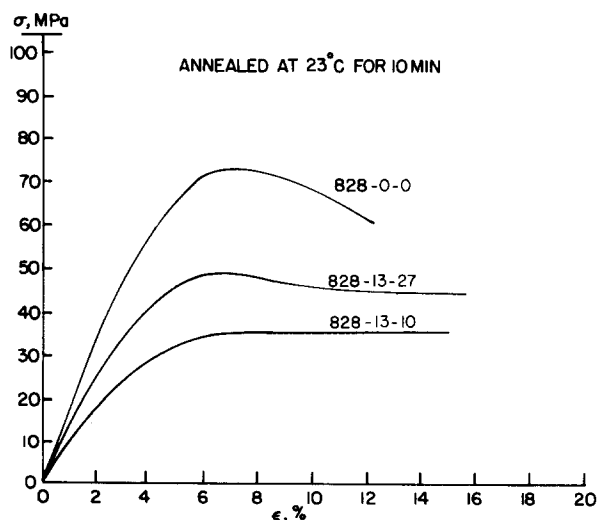


FIG. 1. Stress-strain curves of the epoxy series, measured at 23 °C, 10 min after quenching from above T_g .

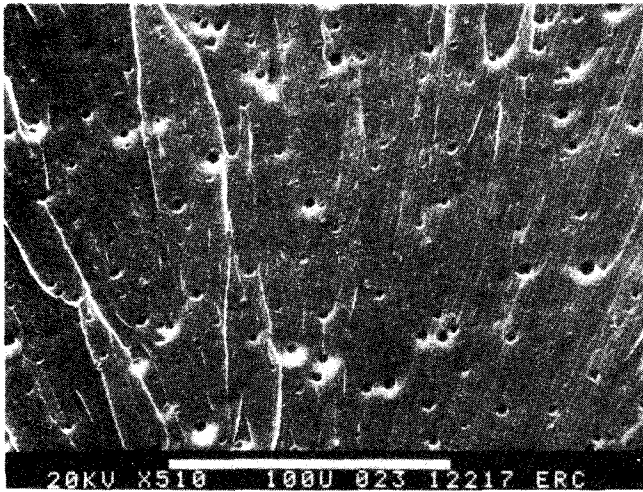


FIG. 2. SEM micrograph taken from the fracture surface of a 828-13-27 tensile specimen (marker = 100 μm).

(1) The rubber modified epoxies have lower Young's modulus, E , and higher strain to break, ϵ_b , in contrast to the nonmodified epoxy.

(2) The 828-13-27 material has a higher modulus than the 828-13-10 material.

The lowering of the modulus by the presence of the rubber is obvious. The separated rubber particles reduce the effective cross section that bears the load. The difference in the modulus between the two materials is explained by their different CTBN rubber composition. The 1300 \times 13 rubber contains 28% acrylonitrile, while the 1300 \times 15 rubber contains only 10% acrylonitrile. The solubility of the 1300 \times 13 rubber in the epoxy is higher, and as all the other parameters that define the extent of phase separation, like temperature, catalyst, and chemical reactivity^{15,17} remained unchanged for the two rubbers, the 1300 \times 15 rubber shows a higher degree of phase separation than the 1300 \times 13 rubber (Figs. 2 and 3). The increase in ϵ_b due to the presence of rubber is well known in effect though the rubber's role is somewhat controversial.¹⁸⁻²³

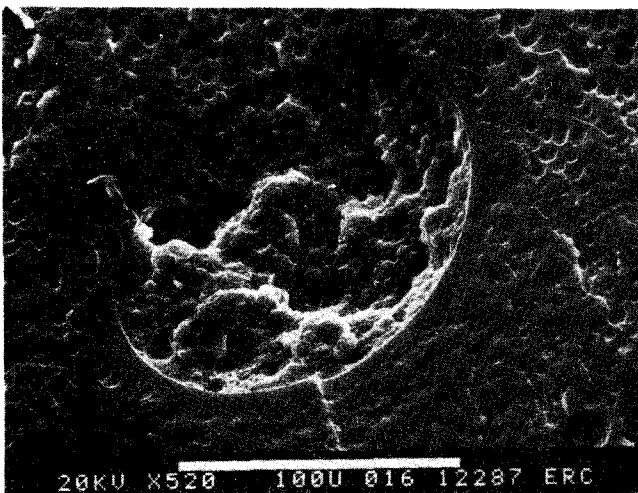


FIG. 3. SEM micrograph taken from the fracture surface of a 828-13-10 tensile specimen (marker = 100 μm).

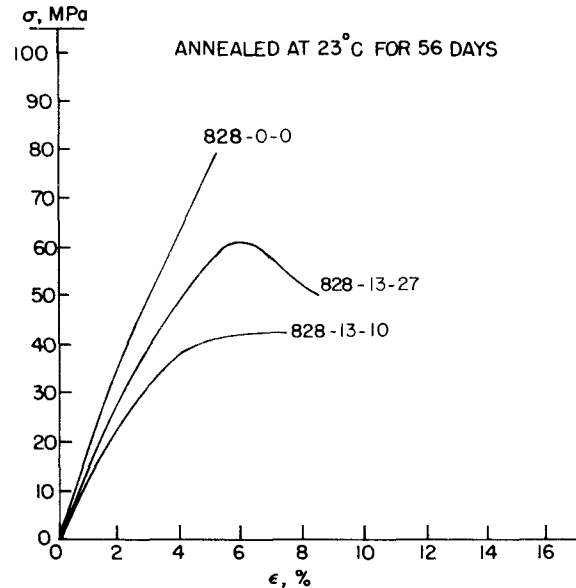


FIG. 4. Stress-strain curves of the epoxy series, measured at 23 $^{\circ}\text{C}$, 56 days after quenching from above T_g .

The stress-strain curves for the three materials after 56 days annealing at 23 $^{\circ}\text{C}$ are given in Fig. 4. The 828-0-0 material shows quite brittle behavior, while the rubber modified samples still show a yield point; however, their strain to break is now about half of that obtained 10 min after quenching. Upon heating the sub- T_g -annealed samples above the glass transition and quenching, the samples "forget" their annealing history, and the whole process repeats itself. These time-dependent effects have been reported for many linear thermoplastic systems and the process is often called physical aging of glassy polymers.¹

The values of the strain to break at 23 $^{\circ}\text{C}$ are plotted as a function of the sub- T_g annealing time for the three materials as shown in Figs. 5-7. Since the time-dependent phenomena appear for both the 828-0-0 and the rubber modified samples, it is indicated and expected that the aging process is taking place in the glassy epoxy matrix. As mentioned earlier, the rubber modification increases the magnitude of the strain to break, but it is difficult to draw conclusions regarding the type of rubber with respect to the difference in the aging rate of the matrix due to the high degree of scattering of the data.

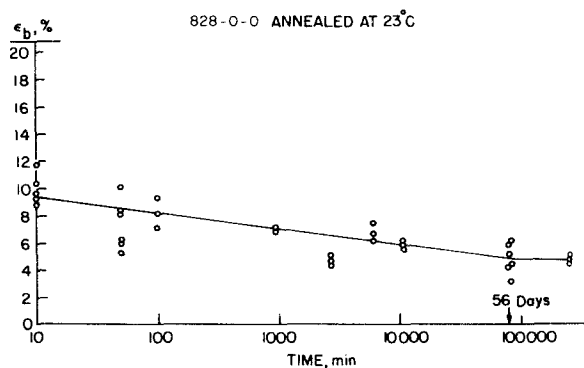


FIG. 5. Strain to break (ϵ_b) of 828-0-0 as a function of sub- T_g annealing time.

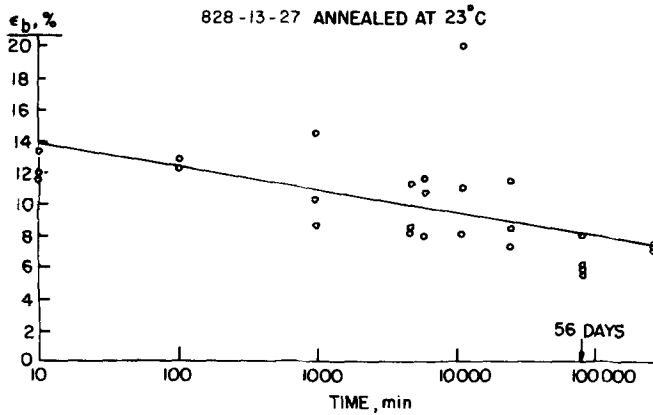


FIG. 6. Strain to break (ϵ_b) of 828-13-27 as a function of sub- T_g annealing time.

Stress-relaxation experiments

The stress-relaxation curves of 828-13-27 with 3- and 20 000-min annealing at 23 °C are given in Fig. 8. The observed effects upon annealing display an increase in the initial stress level as well as decrease in the relaxation rate. The higher initial stress is caused partially by the higher modulus of the aged sample and partially due to the smaller extent of relaxation during the stretching period. For each sample the relaxation rate was measured as a percent of stress relaxation during the first 10 min. Figures 9–11 show this percent of stress relaxation as a function of sub- T_g annealing time for the three samples. The data in Figs. 9–11 suggest that the aging process stops at about 10^5 min. However, due to the scattering of the experimental points, only data taken at longer times will confirm the equilibrium state. The similarity between Figs. 9–11 and those of strain to break (Figs. 5–7) clearly indicate that these two time-dependent processes are affected by the same aging mechanism. This behavior is expected, for we speculate that as the network chains lose mobility during the aging process (due to the decrease in the free volume), the ability to dissipate stress is reduced. This results in a more rapid build up of stress concentration which will initiate cracks in the material; thereby leading to failure at lower strain.

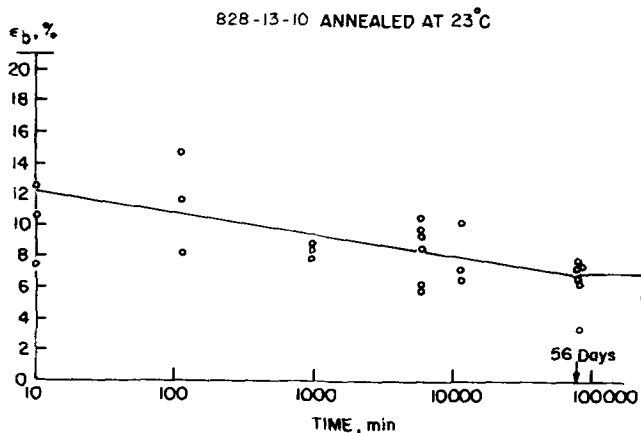


FIG. 7. Strain to break (ϵ_b) of 828-13-10 as a function of sub- T_g annealing time.

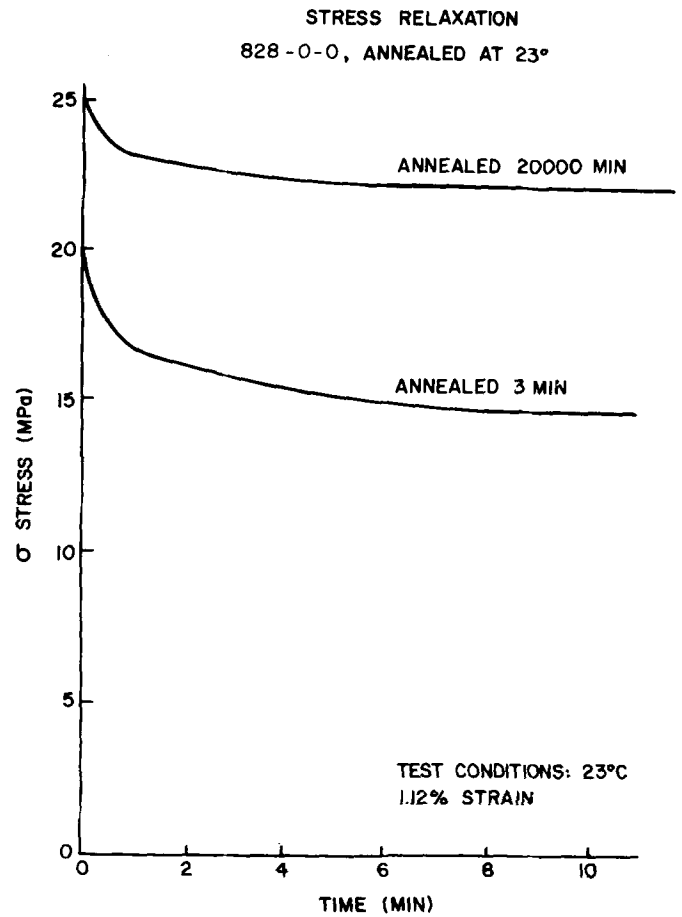


FIG. 8. Stress-relaxation curves of 828-0-0 measured at 23 °C, 3 and 20 000 min after quenching from above T_g .

Differential scanning calorimetry

Figure 12 shows the DSC scan of the 828-0-0 sample after 52 000 min (36 days) at 23 °C. The full line is the first scan, and the dotted line represents the second scan taken right after cooling from the initial one. [The glass transition temperature for this sample is defined as the midpoint in the

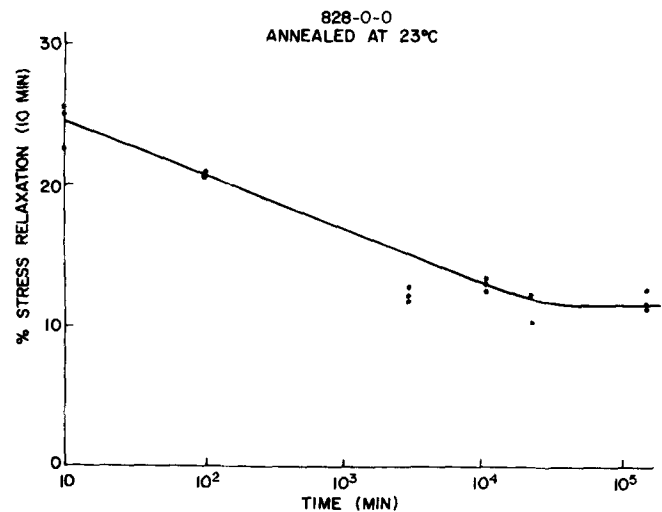


FIG. 9. Percent stress relaxation of 828-0-0 as a function of sub- T_g annealing time.

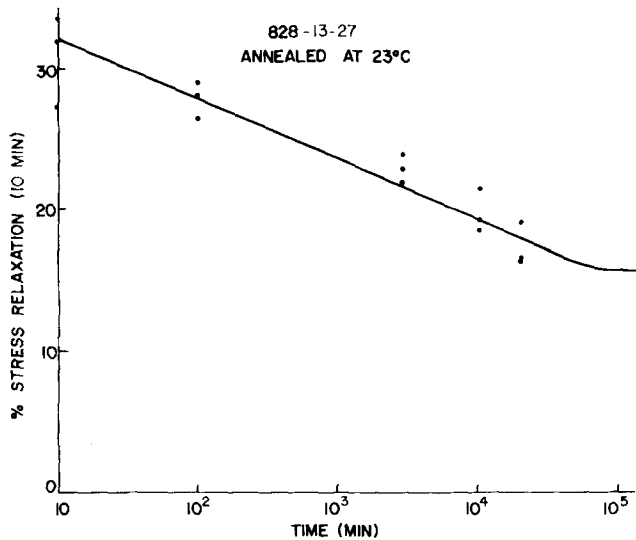


FIG. 10. Percent stress relaxation of 828-13-27 as a function of sub- T_g annealing time.

specific heat (C_p) transition.] The following observations were made:

- (1) The enthalpy relaxation peak (68 °C) appears well below the glass transition (87 °C).
- (2) This phenomenon is reversible, i.e., upon annealing the sample after cooling from above the glass transition, the relaxation peak will again be present and grow with time.
- (3) The glass transition of the annealed sample is somewhat higher than in the quenched state.
- (4) During the annealing, the relaxation peak is shifting to higher temperature while also growing in magnitude (Fig. 13). After 100 min annealing at 23 °C, the center of the relaxation peak is at 53 °C, while after 50 000 min at 23 °C, the peak's center moves to 68 °C.

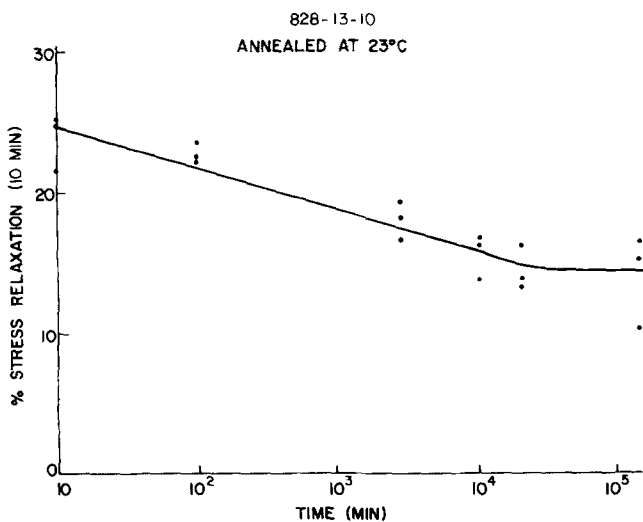


FIG. 11. Percent stress relaxation of 828-13-10 as a function of sub- T_g annealing time.

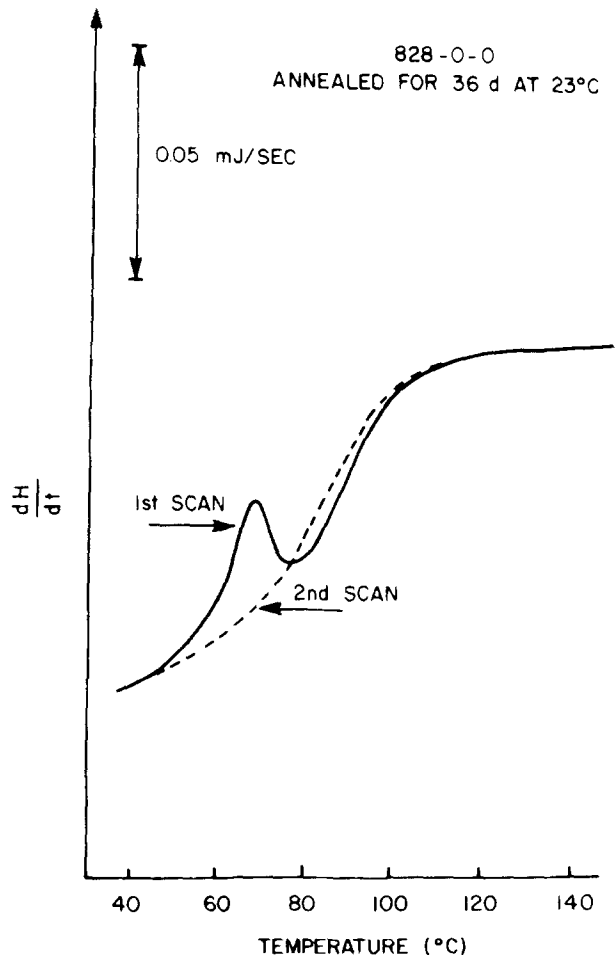


FIG. 12. typical DSC traces of the epoxy series.

Some additional observations were made at different annealing temperatures, these are as follows:

- (1) For a given annealing time, the position of the relaxation peak depends upon the sub- T_g annealing temperature; it shifts upward as the sub- T_g annealing temperature increases (Fig. 14).
- (2) The growth rate of the relaxation peak depends upon the annealing temperature in that an increase in the annealing temperature will accelerate the growth of the enthalpy relaxation peak (Fig. 14).

Effects of this nature have been reported by Kreibich and Schmid (14). They explain these phenomena as phase separation and orientation processes that take place upon annealing well below T_g . We have some strong reservations about the proposed explanation, although we do not question the existence of inhomogeneity in this material. It is unlikely that a phase separation will take place in the glassy network well below its glass transition. The DSC traces do not support this assumption either. If the growth of the sub- T_g relaxation peak represented the phase separation, it should have moved with time from the main glass transition (to lower temperature) rather than approaching it during the annealing. In the current study we have observed that if the annealing temperature is low enough (55 °C below T_g), the enthalpy relaxation peak starts to grow on the flat portion

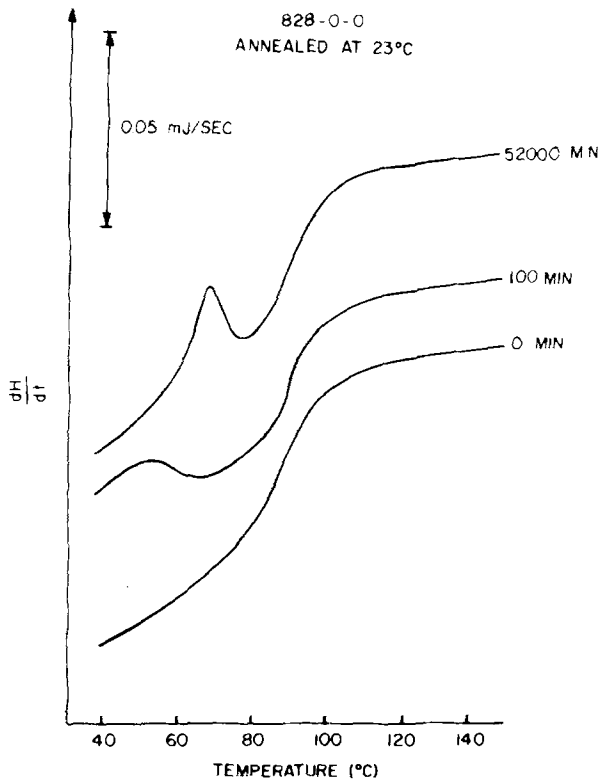


FIG. 13. Annealing time effects on the DSC traces of 828-0-0.

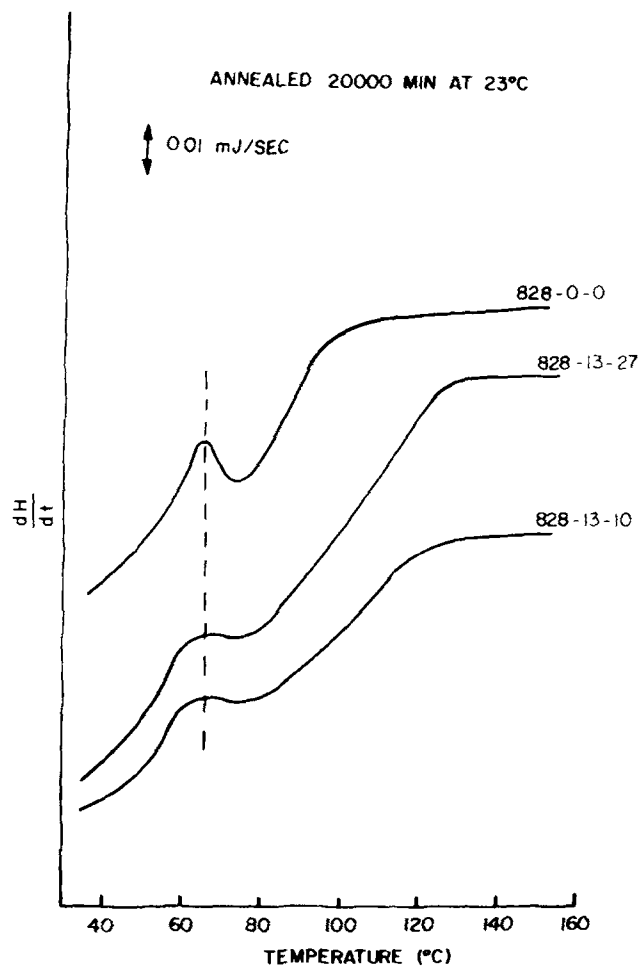


FIG. 15. Rubber modification effects on the DSC traces of the epoxy series.

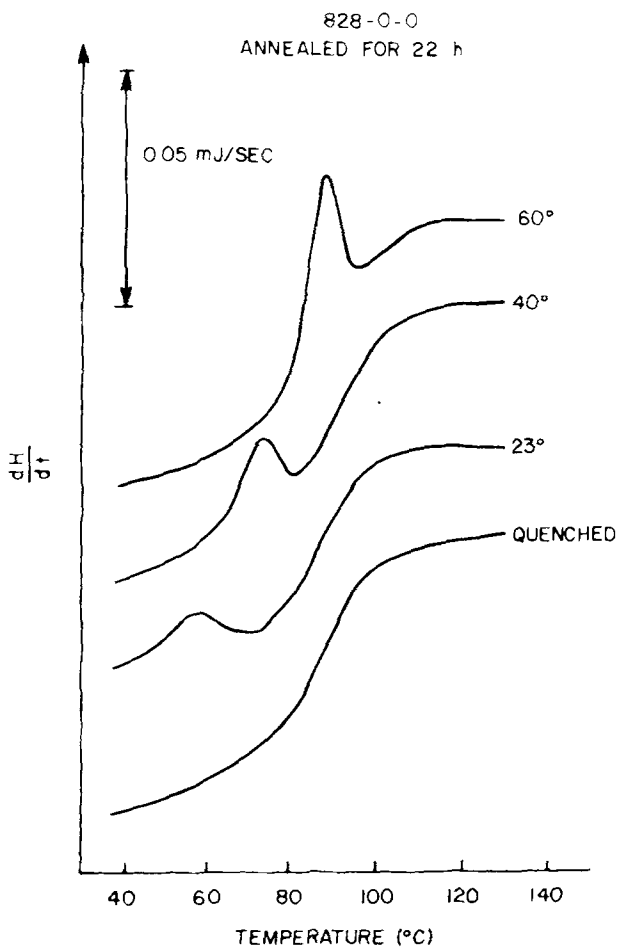


FIG. 14. Annealing temperature effects on the DSC traces of 828-0-0.

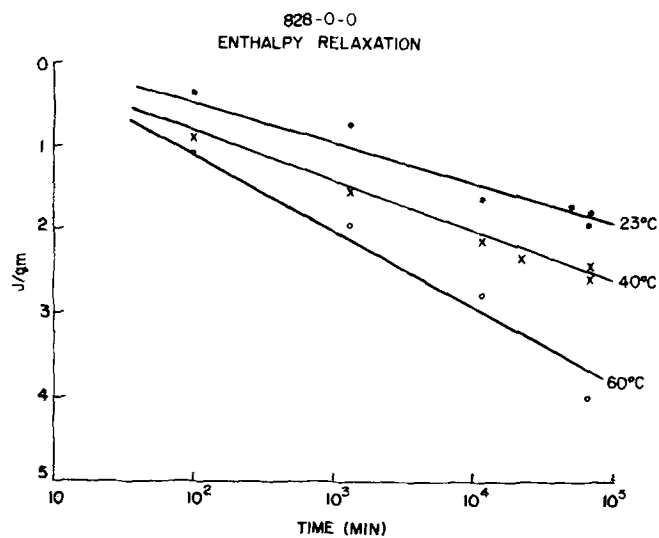


FIG. 16. Enthalpy relaxation as a function of annealing time and temperature of 828-0-0.

(below T_g) of the DSC trace rather than a step change indicating a second glass transition.

In Fig. 15, the temperature dependence for each of the two rubber modified systems is compared with that of the unmodified epoxy, for a sub- T_g annealing temperature of 23 °C and an annealing time of 20 000 min. The observed effects are as follows: (1) The glass transition of the modified epoxies is spread over a slightly wider range of temperatures than for the 828-0-0 sample, and the former's midpoint is also higher. (2) The enthalpy relaxation peaks are similar in position and behavior to those observed in the 828-0-0 sample; however, their growth rate is different due to the different glass transition temperature and the lower volume of glassy material.

As mentioned earlier, the relaxation enthalpy was found by superimposing the first and second DSC scans for each sample. The main problem with this procedure is the difficulty on matching the two scans below and above the glass transition (possibly due to the change in the contact area between the sample and the pan). Figure 16 shows the relaxation enthalpy versus logtime of 828-0-0 at three annealing temperatures. One can see the similarity between the 23 °C plot and the appropriate strain to break and stress-relaxation plots. At this point there is not enough data for accurate comparison of the rate constants obtained by the three techniques; however, their similarity indicates that one can strongly suspect that the changes in strain to break, stress relaxation, and enthalpy relaxation are caused by the physical aging process—enthalpy relaxation—an important phenomenon arising from the nonequilibrium state of quenched glassy polymers.

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