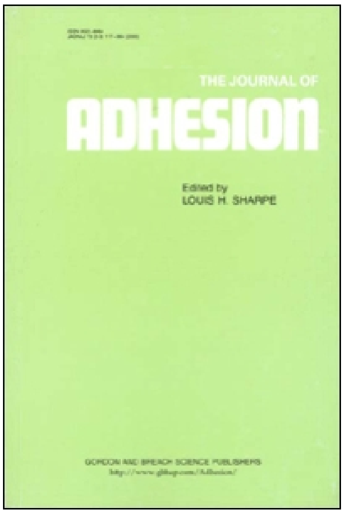

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# Correlation Between the Total Morphology of an Epoxy System and Some of its Properties

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# Correlation Between the Total Morphology of an Epoxy System and Some of its Properties†

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Due to the ever growing use of epoxy resins for structural applications, more information is required about their structure-properties relationship. Much work was done on this subject by us and by others, but many questions still remain unanswered. Some problems which require more detailed studies are the influence of factors like compositional changes in the resin (ratio of prepolymer-curing agent), postcuring and cooling of the polymerized resin from temperatures above $T_g$ to room temperature, on physical properties of the product.

KEY WORDS Amine cure; epoxy resin; mechanical properties; morphology; structure/property correlation; thermal effects.

In order to learn more on these subjects we continued to investigate a model system used by us in some previous studies, namely Epon Resin 826 crosslinked with various amounts of metaphenylene diamine. The experimental work included preparation of suitable specimens, measurement of their glass transition temperatures, analysis of log $G_{(10)}$ *vs.* $T$ curves and of DSC thermograms, bending tests at different temperatures and rates of strain and use of scanning electron microscopy in order to study the failure surface structure of the samples fractured by bending. The influence of

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accelerated aging (annealing) and of the testing procedure on properties of the polymers was investigated. An attempt was made to correlate the total morphology (chemical and physical structure) of the investigated polymers with some of their properties and the assumption of occurrence of microheterogeneities in the form of supermolecular structures seems to contribute to understanding of this relationship.

## INTRODUCTION

The evergrowing use of epoxy resins in structural applications for adhesives and matrices in composites requires more information about the structure-properties relationship. Much work was done in this field, but many questions still remain unanswered. Some of the problems which require further and more detailed study are the influence of compositional changes in the resin (ratio of prepolymer-curing agent) and of the process of post-curing and cooling of the polymerized resin from temperatures above $T_g$ to room temperature, on physical properties of the product. In order to learn more about these subjects which have been recently studied quite extensively,[1–7] we continued to investigate a model resin system used by us in some previous studies[8–10] and tried to correlate the total morphology (chemical and physical structure of the polymers) with some of their properties.

## EXPERIMENTAL

### Materials

The materials used were EPON RESIN 826, mainly diglycidyl ether of bisphenol A (DGEBA), a product of Shell Chemicals Ltd. and metaphenylene diamine (MPDA) cat. 98% pure, made by Fluka A.G. For sample preparation casting molds were made from RTV 630, a product of General Electric. Determination of the thermal expansion and of the torsion moduli of the specimens was performed in silicone oil M 200/200 (produced by BDH) used as heating medium.

### Sample preparation

Proper weight ratios of Epon 826 and MPDA were heated to 50–60°C, mixed thoroughly, degassed by pressure lowering to about 10 mm Hg for 10 minutes and cast into preheated RTV molds. The molds contained specimens for torsion modulus *vs.* temperature measurements (2 × 3 × 50 mm) and for determination of linear expansion of the resins (4 × 4 × 50 mm). The samples were cured and postcured in the molds in predetermined conditions of temperature and time and then, after removal from the molds, they were cooled overnight to room temperature by switching off the heating. (The specimens were removed from molds at temperatures above their $T_g$ in order to avoid introduction of stresses because of the larger linear thermal expansion coefficient of the rubbery mold than of the glassy epoxy resin.) All the resin samples were cast in the same conditions, heated for 1 hr at 120°C and postcured for 3 hrs at 172°C. Several resin compositions were investigated but, since the behavior of all of them follows a similar general path, most of the results presented and discussed in this paper refer to these with molar ratios of Epon 826 to MPDA-1:0.69, 1:1, 1:1.44.

### Testing apparatus and procedure

The tests included: (A) measurement of linear thermal expansion of the polymers as a function of temperature by use of slightly modified standard equipment;[11] (B) differential scanning calorimetry (DSC) by use of a Mettler TA 3000 apparatus; (C) measure-

TABLE I
Composition of investigated specimens

| Composition | MPDA phr | Epon 826:MPDA Molar Ratio[a] |
|---|---|---|
| A | 7.14 | 1:0.49 |
| B | 10.00 | 1:0.69 |
| C | 14.49 | 1:1 |
| D | 20.83 | 1:1.44 |
| E | 25.00 | 1:1.72 |

[a] Since Epon 826 does not consist of pure DGEBA and its MW is 360–376, the weight ratio Epon 826:MPDA = 6.9:1 was assumed to be stoichiometric.

ment of the 10-sec torsion modulus *vs.* temperature by use of a modified Gehman apparatus;[12] (D) density determination of the polymers at room temperature from sample weight in air and in distilled water containing a small amount of a detergent; (E) three-point bending test of specimens 4 × 4 × 25 mm executed at room temperature, 100 and 150°C in an Instron testing machine at rates of strain: 50 mm/min, 5 mm/min, 0.005 mm/min; (F) scanning electron microscopy, by use of a JEOL apparatus Model JSM 840, of Au/Pd (90/10) vacuum-coated failure surfaces of samples fractured in bending experiments. All numerical data cited as experimental results represent an average of 3–5 experiments.

## EXPERIMENTAL RESULTS

### (A) Linear thermal expansion

From measurements of linear thermal expansion of the samples heated at a rate of 1°C/min over a large range of temperatures the glass transition temperatures, $T_g$ of the polymers were determined. In order to check the influence of the testing procedure (heating the sample over a wide temperature range for a relatively long time) a second test was performed on the same samples shortly after they cooled down to room temperature from the first experiment. A difference was found in $T_g$ values in the two consecutive determinations and a higher value was obtained in the second run.

### (B) Differential scanning calorimetry

DSC measurements were used in order to follow enthalpy changes in the investigated polymers and for determination of their glass transition temperatures. The scans were performed at a rate of heating of 10°C/min. Data obtained for $T_g$ from the first thermogram and from the second scan performed on the same sample after it cooled down to room temperature, are listed in Table II. As in the measurements of linear thermal expansion, the $T_g$ values obtained from the second scan were higher in all cases than the values of $T_g$ derived from the first DSC scan.

TABLE II
Glass transition temperatures of different Epon 826–MPDA resin compositions

| Composition (molar) | $T_g$[a] °C I[c] | $T_g$[a] °C II[d] | $T_g$[b] °C I | $T_g$[b] °C II |
|---|---|---|---|---|
| A | 64 | 84 | 45 | 46 |
| B | 121 | 122 | 104 | 112 |
| C | 169 | 171 | 154 | 163 |
| D | 129 | 127 | 133 | 137 |
| E | 91 | 109 | 121 | 121 |

[a] From linear thermal expansion; [b] From DSC thermograms; [c] First determination; [d] Second determination.

### (C) Torsion Modulus–Temperature Relationship

A typical curve obtained in experiments with the investigated resins is shown in Figure 1 and four characteristic values were marked on the curves: $T_g$, $T_i$ – inflection temperature at $G_{10} = 10^9$ dynes/cm², $T_R$—the temperature and $G_{10R}$ the torsion modulus of the beginning of the rubbery plateau region. From values obtained for $G_{10R}$, the molecular weight of an average network chain was calculated by use

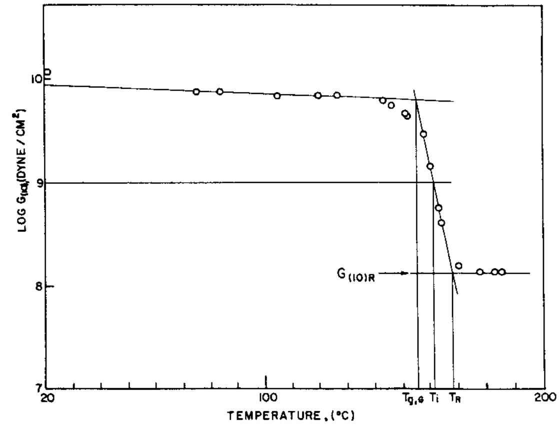

FIGURE 1 10 sec-Torsion modulus *vs.* temperature curve of an Epon 826-MPDA resin.

TABLE III
Data from strain modulus vs. temperature measurements of Epon 826-MPDA resins

| | Composition, (molar) | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| $T_g$, °C I[a] | 49 | 98 | 165 | 127 | 104 |
| II[b] | 50 | 106 | 166 | 130 | 109 |
| $T_i$, °C I | 63 | 114 | 171 | 138 | 141 |
| II | 63 | 121 | 173 | 114 | 118 |
| $T_R$, °C I | 84 | 135 | 178 | 156 | 128 |
| II | 86 | 138 | 182 | 156 | 132 |
| $G_{10R}$ I | 0.26 | 0.73 | 1.38 | 0.67 | 0.41 |
| dyne/cm$^2$ × $10^8$ II | 0.13[c] | 0.78 | 1.46 | 0.81 | 0.42 |
| $M_c$ I | 865 | 412 | 317 | 431 | 579 |
| II | 2933[c] | 398 | 306 | 394 | 570 |

[a] I—First determination, [b] II—Second determination on the same specimen. [c] The anomalous results are probably due to the extreme softness of the specimen.

of the equation $M_c = 293\ d/\log G\text{-}7$.[13] Once again, the influence of the experimental procedure was checked—by performing a second test on the same samples shortly after they cooled down to room temperature. The data for $T_g$, $T_i$, $G_{10R}$ and $T_R$ are listed in Table III.

### (D) Density determination

Data obtained from density measurements of the polymer are presented in Table IV:

TABLE IV
Density of different Epon 826 MPDE resin compositions at 25°C

| Composition (molar) | A | B | C | D | E |
|---|---|---|---|---|---|
| $d$, gr/cm$^3$ | 1.2164 | 1.2167 | 1.2155 | 1.2194 | 1.2211 |

The density of postcured samples decreases with the increasing amount of MPDA from MPDA-deficient molar ratios of the resin, reaches a minimum value for the stoichiometric composition and increases again with further increase in the amount of MPDA.

### Mechanical testing

The modulus of elasticity was calculated from results obtained in bending tests of the investigated specimens and the data are listed in Table V.

TABLE V
Modulus of elasticity (in bending) of different Epon 826-MPDA resins compositions, in GPa

| Composition (molar) | Rate of strain (mm/min) | Test Temperature °C RT | RT[a] | 100 | 150 |
|---|---|---|---|---|---|
| A | 0.05 | 3.39 | | | |
| | 5 | 4.01 | | | |
| | 50 | 7.61 | | | |
| B | 0.05 | 3.12 | 3.03 | 1.15 | 0.06 |
| | 5 | 3.45 | 3.50 | 2.56 | 0.04 |
| | 50 | 5.85 | 4.53 | 3.96 | 0.04 |
| C | 0.05 | 2.72 | 2.90 | 1.83 | 0.80 |
| | 5 | 2.78 | 2.96 | 2.04 | 1.03 |
| | 50 | 3.71 | 5.43 | 3.60 | 1.45 |
| D | 0.05 | 2.72 | 3.06 | 2.69 | 0.05 |
| | 5 | 2.85 | 3.25 | 2.88 | 0.04 |
| | 50 | 4.71 | 5.43 | 4.45 | 0.10 |
| E | 0.05 | 3.38 | | | |
| | 5 | 3.64 | | | |
| | 50 | 6.43 | | | |

[a] After annealing at 130°C for 336 hrs.

## AGING EXPERIMENTS

Postcured specimens with three resin compositions were annealed at 130°C for different lengths of time and some of their properties were measured. If the measurement involved heating of the specimen above 130°C, the experiment was repeated shortly after the specimen cooled down to room temperature. The experiments with annealed samples included measurements of their thermal expansion, DSC scans and three-point bending tests performed at room temperature.

## DISCUSSION

The highest $T_g$ in the investigated system was obtained for the resin with a stoichiometric Epon 826-MPDA ratio. This result agrees with data obtained in previous works on other epoxy-amine systems.[2,4,5,7] Since our determinations of $T_g$ were made by several methods, the numerical values are slightly different, but the general picture remains the same. Similarly, values of $T_i$, $T_R$ and $G_{10R}$, derived from torsion modulus *vs.* temperature measurements were the highest for the polymer with the stoichiometric ratio of the epoxy and amino compounds. In all cases, a second test performed on the same specimen, after it cooled down from the first experiment, showed an increase in the values of $T_g$, $T_i$, $T_R$ and $G_{10R}$. Such behavior of the investigated polymers can be explained by assuming that additional polymerization (crosslinking) took place in the samples during the heating procedure connected with the previous testing, resulting in nonreversible changes in the chemical network structure. The changes occur in all polymers and it seems that the crosslinking process in all heating conditions applied in this study was not complete. The effect of additional heating was most pronounced in the Epon-rich resins. This is probably due to the fact that the bifunctional prepolymer, when attached by only one end to the MPDA molecules, acquires relatively high mobility at higher temperature, which allows the active epoxy group to come close enough to residual nonreacted amine functions and continue the polymerization. It is also possible that some of the excess epoxy groups react with hydroxyl groups created during earlier opening of the epoxy rings in reaction with MPDA.

The low values of $M_c$ for the stoichiometric resin calculated from $G_{10R}$ (lower than $M_c$ of the prepolymer) is probably due to the presence of entanglements trapped during crosslinking.

Density measurements as well as determination of modulus values from bending experiments produced results which seem at first rather strange. The density, as well as the modulus, of the polymer with a stoichiometric ratio of components, both measured at room temperature, are the lowest when compared with data obtained for resins from the same series with a deficiency or with an excess of the crosslinking agent. Similar results were obtained by others who referred to them as "odd, unexpected, unusual, pecularities" *etc.*[4–7,14–16] Most authors explain this behavior of glassy polymers by assuming that they are in nonequilibrium state below $T_g$ and by consideration of changes occurring in the free volume of the resins. Upon regular cooling or quenching from above $T_g$ to room temperature, the polymers preserve conformations and inter- and intramolecular structure characteristic for their glass transition temperatures. The frozen-in structures, built and kept together to a large extent by secondary forces, are not equilibrium ones at room temperature. The free energy excess and lower entropy in the nonequilibrium state are driving forces in the polymer's tendency to reach equilibrium structures at room temperature, but this process is opposed by secondary forces acting below $T_g$. These forces are quite considerable in the investigated resin system due to its highly polar character; this approach and the nature of the structures was discussed earlier by one of the authors.[8–10,17] Polymers with compositions closer to the stoichiometric ratio of reactants have higher glass transition temperatures than those with an epoxy or MPDA excess and, consequently, their equilibrium structures at room temperature are further from those frozen in at $T_g$. Additional parameters that should be considered are the less-dense crosslinking in "non-stoichiometric" polymers and the plasticizing effect of the reagent in excess, which even if not free in the final product, reacted with only a part of its available functional groups. When a stoichiometric polymer with the highest $T_g$ in the series is cooled from above that temperature, large fluctuational holes are frozen-in at $T_g$. This leads to a low packing density at room temperature. In non-stoichiometric polymers, the free volume derived from fluctuational holes frozen-in at their $T_g$ is small and products with a larger room temperature density are obtained.[15] In search for additional arguments related to the reason why the modulus of the stoichiometic polymer is the lowest in room temperature, when compared with moduli of non-stoichiometric resins from the same series, some more facts have to be considered. One of them is the occurrence of residual thermal stresses in the resins, due to their contraction during the process of cooling. These stresses are much smaller in non-stoichiometric polymers (lower $T_g$, plastification, *etc.*); a method for calculation of those stresses, based upon a thermorheologically complex viscoelastic model with aspects of nonlinearity was suggested by Weitsman.[18] Another point for consideraton is the nodular structure of the polymer distinguished when SEM and TEM micrographs of the fractured specimens are studied. The resin with a stoichiometric composition in the series contains the smallest and probably also the most dense microheterogeneities chemically linked to the less dense interstitial polymer.[19–21] These considerations, together with the ones based on the free volume approach, may also contribute to explanation of the fact that, when the glassy polymers are heated, the difference between the modulus values of the nonstoichiometric polymers and the stoichiometric one decreases, see Table V and Ref. 7.

In earlier works reported by others and by us,[8–10,17,23–32] the presence of micron size heterogeneities, named by Lipatov "macroheterogeneities",[27] was observed. These heterogeneities, which are much larger (by up to three orders of magnitude) than the nodular microheterogeneities occurring because of local differences in cross-link density of the polymer, are built up by agglomeration of smaller structures held together mainly by intra- and intermolecular secondary forces and are formed during and after polymerization. The size and the shape of these structures are influenced by many factors and the subject was reviewed earlier.[17] Since it was assumed by some scientists that the fracture behavior of polymers may be associated with the nature of the large supermolecular structures,[28,30,31] we continued to investigate the subject by studying failure surfaces mainly of the two non-stoichiometric samples B and D (with a deficiency and excess of the crosslinking agent). The samples were fractured by bending at different rates of strain (0.05, 5, 50 mm/min) at room temperature and at 100°C. A few micrographs of failure surfaces of the fractured samples are shown in Figures 2 and 3 and in all cases regions with globular, deformed globular and/or elongated (fibrilar) structures can be seen. The structures are easy to detect in places where deeper crevices appear in the failure surfaces or where secondary cracks,

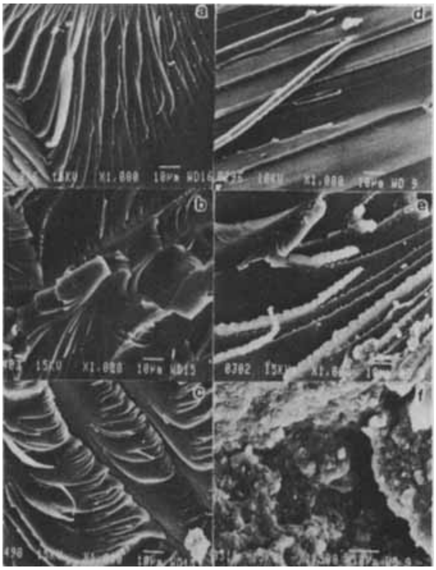

FIGURE 2 Micrographs of failure surfaces of Epon 826-MPDA samples with molar ratio 1:0.69 fractured by bending: a, b, c—at room temperature; d, e, f—at 100°C. Rates of strain: a, d—0.05; b, c—5 and c, f—50 mm/min.

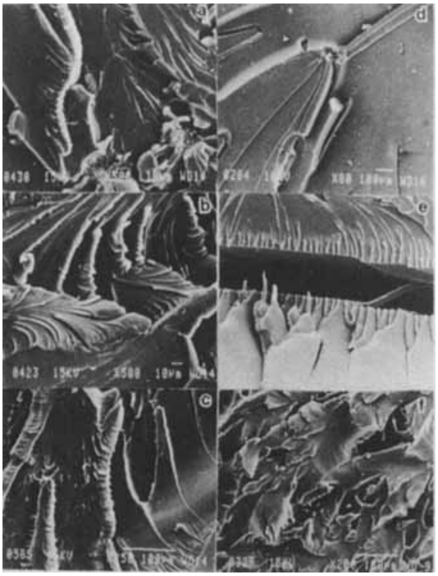

FIGURE 3 Micrographs of failure surfaces of Epon 826-MPDA samples with molar ratio 1:1.44 fractured by bending: a, b, c—at room temperature; d, e, f—at 100°C. Rates of strain: a, d—0.05; b, c—5 and c, f—50 mm/min.

perpendicular to the failure surfaces, occurred. As expected in both compositions, B and D, with the increase in rate of bending strain, an increase in the modulus can be noted. Again as expected, in both compositions with the decrease in rate of strain in samples fractured at 100°C, the failure surface became smoother and less structural details can be detected in SEM micrographs. Comparison of results obtained by investigation of both compositions is rather interesting. $T_g$ of the Epon-rich composition (B) is considerably lower than $T_g$ of the resin with an excess of MPDA and its modulus of elasticity in bending in room temperature is higher at all rates of strain than in samples of the resin D. In bending experiments, executed at different rates of strain at 100°C, the modulus of composition B drops quite considerably, while the drop of modulus values of resin D samples is moderate, similar to the behavior of the resin C with a component ratio of 1:1; this can be explained by the fact that the bending experiments were carried out at a temperature close to $T_g$ of the resin B. SEM micrographs show very clearly, especially in the case of composition B fractured at 100°C, Figure 2d, e, f, the ample presence of globular structures of different sizes built up from smaller globules in the failure surface of specimens bent at a rate of 50 mm/min, a decrease in the amount of globules and occurrence of many fibrilar structures formed by interconnected globules in samples fractured at a rate of 5 mm/min, and almost smooth fibrils present in specimens which failed at a rate of strain of 0.05 mm/min. Also, micrographs of fracture surfaces of samples D with an excess of crosslinking agent, which failed in bending at a rate of 5 mm/min in 100°C, show the presence of fibrils derived from larger globular structures, Figure 3e. In general, the SEM micrographs resemble those obtained and reported earlier, in investigation of the Epon 826-MPDA and Epon 826-DETA resins with the molar ratio of reactants 1:1.[8–10,17] Those, and previous observations, prove that there is a correlation between the rate of strain and the characteristics of supermolecular structures found in the failure surfaces of specimens fractured at a certain temperature. There is a distinct difference in structure of the fractured surfaces of the two resin compositions, the one with an excess and the other with a deficiency in the amount of crosslinking agent.

In spite of the fact that the whole study is in its initial stages only and it is very difficult to come up with conclusive statements, a few qualitative remarks supporting previous assumptions[17] can be made. By stressing the polymer specimens, a higher order of organization which depends on the rate of strain, is introduced into the material due to alignment of the existing globular structures, their deformation in the direction of straining and eventually creation of fibrils. Those new structures, which may or may not interact, persist mainly thanks to inter- and intramolecular physical forces acting inside the material. These forces are quite strong in the investigated epoxy system because of its highly polar character. Although the new supermolecular structures are of non-permanent character, (due to internal energy differences between the oriented and nonoriented state), their disintegration into non-oriented, randomly-dispersed globules is opposed by strong inter- and intramolecular secondary bonds and the relaxation times of the new structures may be very long, especially at temperatures far below the $T_g$ of the resin. The stress-oriented structures may change considerably such characteristics of the original material as $\sigma_b$, $\epsilon_b$, $E$, toughness, density, etc., but since the system contains nonequilibrium structures, those characteristics will tend to change with time and with temperature increase in order to reach the values they had before the stress application. This is one of the aspects of physical ageing of the polymer. Further investigation on the correlation between the total morphology of the epoxy system and its properties is taking place.

### Accelerated aging in sub-$T_g$ temperatures

Detailed description of experimental results, their analysis and discussion of problems regarding accelerated aging of the Epon 826-MPDA system in sub-$T_g$ temperatures for different lengths of time will be presented separately. In this paper only a part of the results, mainly those related to irreversible changes occurring during the annealing process, are mentioned. A typical picture of the influence of accelerated aging on the investigated polymers, annealed at $T_a = 130°C$ is shown in Figures 4 and 5. The effect, noticed also by others,[14,15,32] which is quite pronounced in resins with a deficiency or an excess of MPDA, is much weaker in the stoichiometric polymer, mainly due to the large difference between $T_a$ and the $T_g$ of the stoichiometric polymer. In all cases, in the first measurement of $\Delta l$ as a function of temperature after annealing, a

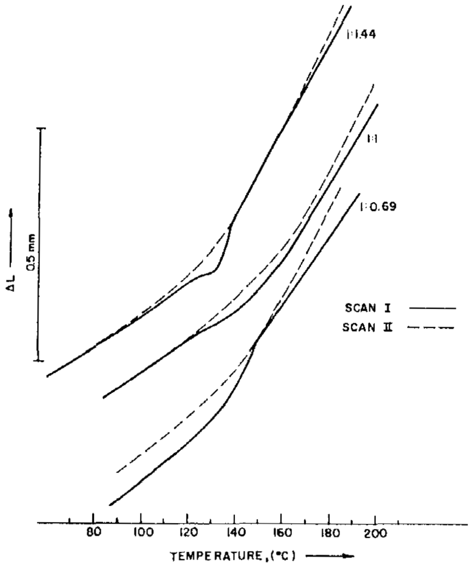

FIGURE 4 Linear thermal expansion *vs.* temperature of Epon 826-MPDA resins annealed for 336 hrs at 130°C.

volume relaxation can be noticed below the $T_g$ of the polymer. However, the second measurement, performed on the same sample, showed that, although the thermoreversible annealing effect disappeared, due to heating of the sample above its $T_g$ in the first experiment, a permanent small increase in the value of $T_g$ occurred,

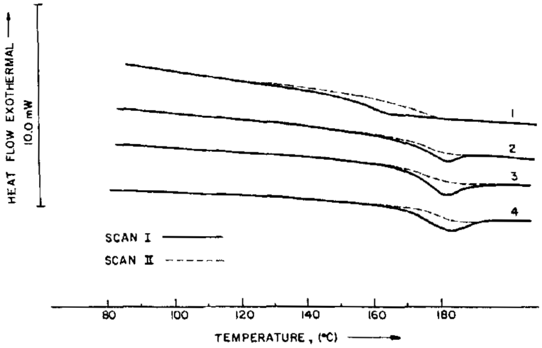

FIGURE 5 DSC thermograms of the stoichiometric Epon 826-MPDA resin: 1—as postcured; 2, 3, 4—annealed at 130°C for 99, 336 and 668 hrs, respectively.

Figure 4. Similar results can be seen in Figure 5, in which enthalpy changes occurring during the accelerated aging of the stoichiometric resin are recorded in the form of DSC scans. Again, heating above $T_g$ in the first measurement erases the thermoreversible physical aging effect, but a small change of permanent character takes place as a result of the experiment and of the length of the annealing period. That permanent change is far less pronounced under the same annealing conditions in the stoichiometric resin, than in those with an excess of one of the components.

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