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Physical Aging of Linear and Network Epoxy Resins

by

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Network and linear epoxy resins principally based on the diglycidyl either of bisphenol-A and its oligomers have been prepared and studied. Both diamine and anhydride crosslinking agents were utilized. In addition some rubber modified epoxies and a carbon fiber reinforced composite was investigated. All of these materials display time-dependent changes in many of their properties when they are stored (following quenching) at temperatures below their glass transition temperature (sub-T_g annealing). For example, the degree of stress relaxation for a given time period is observed to decrease in a linear fashion

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with the logarithm of time during sub-T_g annealing. Young's modulus and yield stress were also found to increase in physical aging Solvent sorption experiments initiated after different sub-T_g annealing times have demonstrated that the rate of solvent uptake can be indirectly related to the free volume of the epoxy resins. Water affecting the physical aging of these epoxy resins was not found to be a significant variable. Residual thermal stresses were also found to have little effect on the physical aging process. although this variable was not studied in detail. Finally. the physical aging process also affected the sub-T_g properties of uniaxial carbon fiber reinforced epoxy material and the effects were as expected. The importance of the recovery or physical aging phenomenon. which affects the durability of epoxy glasses is considered in view of the widespread applications for these resins as structural materials.

A

ABSTRACT

Network and linear epoxy resins principally based on the diglycidyl ether of bisphenol-A and its oligomers have been prepared and studied. Both diamine and anhydride crosslinking agents were utilized. In addition, some rubber modified epoxies and a carbon fiber reinforced composite was investigated. All of these materials display time-dependent changes in many of their properties when they are stored (following quenching) at temperatures below their glass transition temperature (sub-T_g annealing). For example, the degree of stress relaxation for a given time period is observed to decrease in a linear fashion with the logarithm of time during sub-T_g annealing. Young's modulus and yield stress were also found to increase in physical aging. Solvent sorption experiments initiated after different sub-T_g annealing times have demonstrated that the rate of solvent uptake can be indirectly related to the free volume of the epoxy resins. Water affecting the physical aging of these epoxy resins was not found to be a significant variable. Residual thermal stresses were also found to have little effect on the physical aging process, although this variable was not studied in detail. Finally, the physical aging process also affected the sub-T_g properties of uniaxial carbon fiber reinforced epoxy material and the effects were as expected. The importance of the recovery or physical aging phenomenon, which affects the durability of epoxy glasses, is considered in view of the widespread applications for these resins as structural materials.

INTRODUCTION

A polymer does not in general achieve thermodynamic equilibrium when quenched through its glass transition temperature, T_g, to some lower temperature. This is because the motion of the polymer chains is impaired by the significant increase in viscosity as the glass transition temperature is approached from above and thus the polymer is unable to reach its equilibrium conformation or its equilibrium degree of packing. One of the characteristics of the quenched glassy state is an excess of trapped free volume. One consequence of the excess free volume is a lowering of the bulk polymer density. As might be expected this change in free volume alters the molecular mobility and hence influences the segmental relaxation or retardation times.

Thermodynamic state functions such as enthalpy and volume of a newly quenched glass are in excess of their equilibrium value. As a result, there exists a driving force towards the equilibrium glassy state as sub-T_g annealing progresses. This time-dependent sub-T_g annealing process is referred to as physical aging and it is generally viewed as a recovery phenomenon. Basically, there are two aspects to physical aging--volume recovery and enthalpy recovery. This paper will principally report on findings indirectly relevant to the volume recovery aspects of physical aging. One of the authors has presented earlier results on the time dependent enthalpy changes in epoxy networks (1).

Physical aging is distinguished from other aging processes such as chemical aging in that the former is "thermoreversible." That is, the thermal history can be erased and physical aging can be reinitiated again by annealing above T_g, followed by another quenching through the glass transition. In contrast, chemical aging processes, such as photo-oxidation and thermal degradation of polymers in general and additional crosslinking in thermosets in particular are not characterized by such thermoreversibility. In this regard, the studies discussed here are associated with the former subject.

Physical aging is typically observed when the sub-T_g annealing temperature (T_A) is between T_g and T_β, where T_β (as determined at low frequency) is the highest secondary transition temperature below T_g. The physical aging process has been suggested to be too slow to be of significance at temperatures below T_β as has been reported (2-3). (Various values for T_β of various epoxies have also been reported in the literature (4-6).

The physical aging of linear polymers (thermoplastics) has been widely studied (2,3,7-10). However, little attention has been paid to physical aging in network polymers (thermosets). Only recently has there been any systematic reports of the physical aging process in network epoxy glasses (1, 11). The initiation of this newer work on networks is hardly surprising in view of their widespread applications - particularly with the growing importance of long term durability to design considerations.

Of particular importance is the fact that physical aging has a significant influence on the mechanical properties of quenched glasses or partially glassy polymers. Mechanical property variations during physical aging include: an increase in the tensile yeild stress, flexural yield stress, and elastic modulus; decreases in impact strength, fracture energy, ultimate elongation, and creep rate; and often a transition from ductile behavior to brittle fracture (1-3, 7, 8, 10, 11). Electrical properties such as dielectric constant and dielectric loss have also been reported to change during physical aging (2, 12). Most of these findings, however, have been based on experiments performed on linear glassy systems. This paper represents one of the few studies of physical aging of epoxy network glasses.

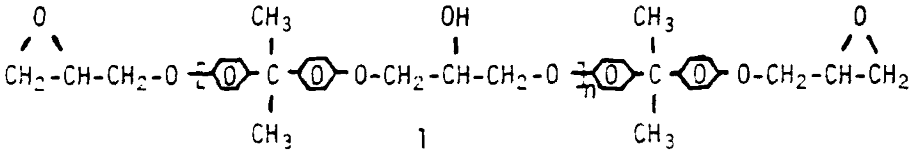
EXPERIMENTAL

1. Materials

The physical aging behavior of several epoxy systems have been investigated within this broad study. Specifically, we have either varied the chemistry by using different crosslinkers, modifiers, etc., or have altered a given system somewhat by using different cure procedures. Some of the syntheses and preparation procedures that were utilized are given below.

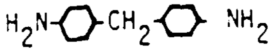
Network Epoxies

A) One network epoxy was prepared by reacting the diglycidyl ether of bisphenol-A (EPON-828, Shell)[1], with the diamine, bis(p-aminocyclohexyl) methane (PACM-20, DuPont)[2]. The structures of these two components are shown below.



1

The diglycidyl ether of bis-phenol-A (EPON 828 when 0.2 < n < 1.0



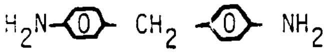
2

PACM-20

The curing reaction was performed by first degassing the two separate components in a vacuum oven for 15 minutes at a temperature of 60°C. The two components were then cast within a period of 2 minutes in a Dow Corning RTV 3110 silicone rubber mold which had been preheated to 60°C.

The curing of the network epoxy was carried out as either a one-stage or a two-stage reaction. For the one-stage reaction, the mold was left in an oven at 190°C for 1-1/2 hours (Resin 1A). For the two-stage reaction, the mold was left in an oven at 85°C for 1/2 hour and then the temperature of the oven was raised to 150°C for 2-1/2 hours (Resin 1B). Both resulted in a resin with a T_g of about 150°C. The T_g was determined from the inflection point in a differential scanning calorimetry (DSC) measurement.

B) A second network epoxy (designated as WE_0) that was studied was prepared by reacting the crosslinking agent, 4,4'-methylene dianiline, 3, with a resin containing bisphenol-A, the diglycidyl ether of bisphenol-A, and the polyglycidyl ether of a phenol-formaldehyde Novalac, 4. The structures of the latter component and the crosslinker are shown below.



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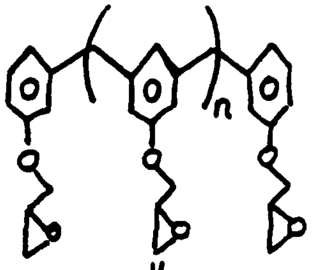
4,4' - methylene dianiline (MDA) (Tm=89°C)



4

Polyglycidyl ether of phenol-formaldehyde Novolac (n = 1.6)

The resin components 3 and 4 were supplied by Western Electric, Engineering Research Center, Princeton, New Jersey.

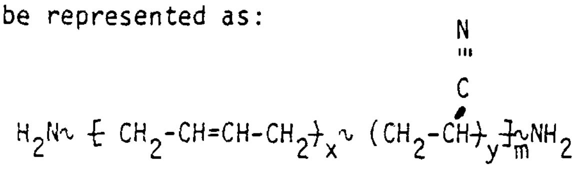
The curing reaction for the WE_0 resin was performed by first degassing the resin mixture at atmospheric pressure for 15 minutes at a temperature of 60°C. The crosslinking agent was added, dissolved and mixed homogeneously with the resin. Casting was also carried out in a Dow Corning RTV 3110 silicone rubber mold, which was preheated to 160°C. The WE_0 epoxy was cured for 3 hours at 160°C. The T_g was found to be 106°C by DSC measurement. Following the curing reaction, the epoxy samples were easily separated from the mold and stored in vacuum dessicators at room temperature.

C) A third crosslinked epoxy network was prepared by reacting EPON 828 (Shell) the diglycidyl ether of bisphenol-A with nadic methyl anhydride (NMA) in stoichiometric proportions and in the presence of the catalyst benzyldimethyl-amine (BDMA). In this reaction, the components were mixed at 170°C for one minute and poured into a preheated RTV mold as discussed above. The T_g of this network was found to be 85°C.

Rubber Modified Epoxy Networks - The epoxy components for resin 1A (or 1B), were modified by the addition of reactive short chain elastomers during curing. Specifically three different elastomeric modifiers were used and are described below:

a) Amine terminated butadiene acrylonitrile copolymers (ATBN).

These systems are identical in nature to the well known carboxyl terminated butadiene acrylonitrile copolymers (CTBN) used for improving impact strength of epoxy systems. In brief the copolymer additive may be represented as:



$$H_2N\sim\left[CH_2-CH=CH-CH_2\right]_x\sim\left(CH_2-\overset{\overset{N}{\equiv}\atop C}{CH}\right)_y\Big]_m\sim NH_2$$

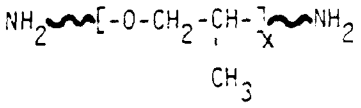
5

Structure of ATBN copolymer

It should be understood, however, that this copolymer is of a random nature, i.e., the values of x and y are small. The number average molecular weight of the copolymers studied was either 3,600 or 5,200 g/mol. The rubber represented up to 8 percent by weight of the balanced stoichiometric composition. This modifier is believed to react with the epoxy during the curing process and compete with the diamine crosslinker (PACM-20), 2, used in our resin composition. However, as the reaction proceeds, the rubber containing chains become incompatable with the epoxy network thereby promoting phase separation of a discrete rubbery phase that may serve in the bulk as an "energy absorber and craze initiator.

b) Amine terminated polypropylene oxide, 6, "Jeff amine",

This modifier is represented as:



$$NH_2\sim\left[-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-\right]_x\sim NH_2$$

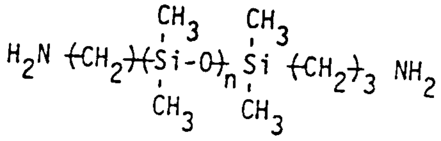
6

Structure of "Jeff Amine"

Two different molecular weight additives, either 400 or 2000 g/mol were used. The weight percentage added was 6.7 in both systems. As in the case of the ATBN, the amine end groups in the structure above are the reaction sites.

c) Diaminotetrafunctional poly(dimethylsiloxane) (PSX)

This modifier is represented below where the value of n can be varied from 1 to 100 or higher. This rubber was prepared by equilibrating the disiloxane (n=1) with the cyclic tetramer. Details of the synthesis will be reported separately (13).



$H_2N(CH_2)_2(\overset{CH_3}{\underset{CH_3}{Si}}-O)_n\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3\,NH_2$

2

Structure of diaminotetrafunctional dimethylsiloxane

Again this is tetrafunctional crosslinking agent and will compete with PACM-20 in the curing reaction.

Linear epoxies were prepared by reacting equilmolar mixtures of bisphenol-A. The linear epoxy labelled AEP-6 was catalyzed by benzyltrimethylammonium hydroxide, whereas the linear epoxy labelled as AEP-7 was catalyzed by tetramethylammonium hydroxide. AEP-6 and AEP-7 resins have identical T_g's of 95°C and also display similar behavior during mechanical tests. Further details on the preparation of AEP-6 and AEP-7 resins have been reported elsewhere (14).

A uniaxial carbon fiber reinforced epoxy composite was also investigated. The specific epoxy material utilized was the Hercules 3501 resin system often employed for composites. This material was used as received from NASA/Langley through the courtesy of Dr. H. Price. The plys had been constructed to give a uniaxial system. Curing was not totally complete, for the T_g of the cured system displayed a T_g of 85°C. Prior to testing, the material was raised to 100°C for a few minutes and then quenched into ice water followed by drying.

2. Measurements

Dog-bone-shaped crosslinked samples were prepared by direct casting within the RTV molds mentioned earlier. The dimensions of these samples were in accordance with ASTM specifications, however, the thickness sometimes varied as will be discussed later within the section on Results and Discussion. The linear epoxy systems were first compression molded at 160°C into films from which analogous dog-bone-shaped samples were stamped with an ASTM cutter. These samples were then stored within a dry environment until physical aging studies were initiated by heating to 10-15° above T_g and quenching into water followed by drying using a blotting procedure.

A Perkin Elmer DSC-2 was used for all T_g determinations. A scan rate of 10°/min was employed.

All stress-strain and stress relaxation measurements were made on an Instron model 1122. For the stress relaxation experiments, a fixed strain (generally $\leq 1\%$) was rapidly imposed and the stress relaxation was observed for a period of 10 minutes in contrast to following the complete stress relaxation behavior over several decades of time. From this 10 minute period the percent change in stress relaxation was determined and, in particular, measured as a function of the sub-T_g annealing time prior to initiating the test. While this time scale (10 minutes) is short relative to the complete relaxation curve, it has provided a good index of physical aging behaviors in past studies (1, 15-16). The consequences of using longer or shorter time periods for observing stress relaxation have been discussed elsewhere by two of the authors and hence will not be repeated here (17). All relaxation measurements were made at ambient as were the stress strain determinations. The Instron crosshead speed was low and maintained at 0.05 cm/min.

The liquid uptake (diffusion) measurements were made by casting or cutting 49 mm x 49 mm x 1.5 mm slabs of the material under investigation. These were then directly immersed within methyl ethyl ketone (MEK) and removed at a specified time, lightly blotted to remove MEK at the surface, and then weighed. The weight gain with immersion time was therefore determined. This time dependent absorption behavior was then considered with regard to the sub-T_g annealing storage time prior to immersion within MEK.

Results and Discussion

Linear Epoxy

For purposes of bridging the observed behavior in the epoxy networks with the past well known measurements on linear thermoplastics, we first present some of the physical aging characteristics of the linear counterpart to many of our Epon 828 based networks. Figure 1 shows the initial portion of the stress-strain curves for one of the linear epoxy materials measured at different sub-T_g annealing times in water where T_A was 23°C. From these data the effects of physical aging on this material are obvious. One notes in particular that the yield behavior becomes more pronounced with annealing time. Linear materials stored dry at 23°C also displayed very similar behavior to those presented above suggesting that the aqueous environment did not alter the recovery behavior. In addition, the initial slope of the stress strain curves increases indicating an increase in Young's modulus with annealing. In fact, when modulus is plotted with sub-T_g annealing time, a positive but distinct increase is noted which is linear in behavior. Indeed we have observed similar behavior in other quenched linear glasses (15, 17). Figure 2 shows the ten minute percent stress relaxation value for the linear epoxy material (stored dry) as a function of log annealing time for both linear samples and again linearity is noted as is the decrease in stress relaxation with log annealing time. In essence, all of these data indirectly support the well known fact that a quenched glass tends to densify (lose free volume) with annealing due to its initial nonequilibrium volume state. This decrease in volume (and enthalpy as well) limits molecular mobility which in turn affects the mechanical properties in the expected way, i.e., by basically shifting the relaxation processes to longer times. Our goal is not to determine these volume changes since many measurements of this type have been made by others (e.g., see other papers in this issue). However, we wish to point out the time dependent changes in properties that may be at least indirectly related to the nonequilibrium character of the material.

Network Epoxy

Similar measurements to those discussed above were conducted on the various network systems described earlier. Some of these data will now be discussed. Figure 3 shows a plot of Young's modulus for the two stage cured (Resin 1B) system, as determined after sub-T_g annealing in either a dry or an aqueous environment. It is noted that the modulus increases linearly with the logarithm of annealing time, in a similar manner to the linear epoxy. In addition, the presence of an aqueous environment upon this network system shows little, if any, change from the dry samples. This, of course, strongly implies that there is little uptake of water which would have plasticized the network and accelerated the time dependent changes. While not shown here, basically identical behavior was also observed for the one stage cured system (Resin 1A). This was expected in view of the fact that the

T_g values of the two samples were quite close to one another. Figure 4 shows the 10 minute stress relaxation percentage plotted against log annealing time . While some scatter exists, the linear trend is clear and is in agreement with past work from this laboratory (1, 15-17), as well as with the behavior of the linear epoxy data given above.

Figure 5 demonstrates the effect of sub-T_g annealing temperature. This shows the behavior of the 10 minute stress relaxation index for two quite different annealing temperatures. These data are for the one stage cured resin (Resin 1A) although the behavior of the two stage system is essentially the same. One observes that, as expected, the higher annealing temperature (closer to T_g) induces a faster rate of relaxation. (Note the test temperature was still 23°C.) While the data suggest that the 70°C annealing appears to induce an apparent equilibrium value after about 100 minutes, this is not truly the case. In short, it is only a consequence of the choice of a 10 minute "experimental window" as has been discussed by the authors elsewhere (17). The important point is simply that the slope and this rate of change in relaxation percentage with time, is higher for a higher sub-T_g annealing temperature. This observation is directly in line with past work an other sub-T_g annealing dependent parameters as again can be noted from the related papers given within this same issue.

The effect of thermally induced stresses due to temperature gradients upon quenching was studied with samples of Resin 1A. Test specimens were prepared with a range of thicknesses varying between 1 mm and 5 mm. This thickness variable would have the effect to change the thermal gradients upon cooling, thereby more likely inducing differences in internal stress effects. Should this be the case, the initial relaxation behavior might be expected to be different as implied from the work of Struik (18) and Broutman (19). Our results shown in Figure 6 suggest that within scatter of the relaxation data, no significant difference exists in either the initial stress relaxation rate or within the rate of change with sub-T_g annealing. Since actual internal stresses were not actually determined, it would be invalid to argue that these data confirm that internal stresses have no effect on influencing the non-equilibrium recovery process. However, they do at best imply that within the range of our experimental procedures, or those of others that may also vary sample thickness over a similar range, internal stress effects are probably not of great concern.

Since earlier studies have correlated the decrease in free volume during recovery to a decrease in transport properties, we undertook measurements of the time dependent sorption of MEK into some of the network samples. Figure 7A and 7B present two examples of the results for two different network systems -- one based on EPON 828 cured with NMA and the other being the Novalac type resin denoted earlier as WE_0. In short, the data clearly shows that as the degree of sub-T_g annealing increases prior to beginning the sorption experiment, the initial sorption rate is decreased. This, of course, is expected if the free volume "channels" or "holes" are becoming smaller or fewer in number with recovery. Hence, these data indirectly support the conjecture that there is a loss of free volume with annealing time. The papers by T. Smith and S. Chen in this same issue also provide additional direct evidence for this same conclusion. It should be noted that in Figure 7A the data are plotted against linear time in contrast to the square root of sorption time as is often done in view of possible Fickian behavior as observed in Figure 7B. Actually this short time data of Figure 7A also appears linear if replotted in this fashion. The point of importance is simply the decrease in slope with an increase in annealing time.

Figure 8 shows the change in sorption rate of the interacting penetrant with our earlier log annealing time behavior. This plot is based on the data given within Figure 7B and relates to the slopes of the earlier sorption results as a function of the log annealing time prior to the initiation of the sorption experiment. Indeed, the linear trend is again strongly suggested and is directly in line with many of our earlier discussions.

An additional point of interest was to add various types of rubber modifers to Resin 1A during curing. Recall that these modifiers were described earlier in this paper. Specifically, reactive short chain elastomers of the ATBN, PPO or PSX type were added during curing. The goal of this approach was principally to improve mechanical properties such as impact strength by inducing a second energy absorbing rubbery phase. Since the goals of this portion of the mechanical studies are not aligned with those here, the interested reader may obtain these results of this rubber modification on properties elsewhere (20). However, of pertinent interest here is to note if these modifiers alter the nonequilibrium recovery process. The answer for all three of these modifiers is that the process is not altered significantly as noted by the stress relaxation index parameter. Figure 9 is presented as one example of this behavior which shows the percent stress relaxation for Resin 1A containing 6.7% of the siloxane rubber with molecular weight of 2000. When these data are compared to the unmodified resin (see Figure 4) the reader will note very little, if any, difference. In short, this lack of influence on recovery behavior was noted for all of the three rubber types. This is similar to the observation of Ophir et al. (1) in their studies of CTBN rubber modified EPON 828 cured with NMA. Their conclusion, which also applies to our results is simply that if the rubber additive leads to phase separation and hence does not alter T_g of the epoxy matrix, the matrix will still display recovery with a similar manner to the unmodified resin. While not shown here, we have utilized DSC, dynamic mechanical and SEM to prove the existence of pronounced phase separation of the rubber and that little alteration occurs in the T_g value of the epoxy matrix. This latter point implies that nearly all of the rubber phase separates in contrast to solubilizing or becoming miscible with the matrix. Aging effects of the rubber modified system were also noted by stress strain tests. Representative data are shown in Figure 1. Again, the physical aging process was observed to be as expected.

Uniaxial Carbon Fiber Reinforced Epoxy

The results discussed thus far within this paper show that the network resins undergo physical aging in an analogous manner to linear thermoplastics. In light of these findings and also in view of the fact that many of these network glasses are being utilized as matrices for fiber reinforced composites, we wished to investigate the physical aging characteristics of these latter systems. While this latter project comprises a longer range portion of our studies, some initial findings will be presented here due to the important ramifications that are implied. Specifically, we investigated the 10 minute stress relaxation behavior for an uniaxial carbon reinforced epoxy. As would be anticipated, it was expected that the time dependent behavior would be directionally dependent due to the anisotropic character of the composite system. That is, measurement of stress relaxation along the fiber axis would be anticipated to be very small and likely independent of annealing time since the mechanical behavior is dominated by the stiffer fiber material (matrix and fibers acting in parallel). On the other hand, the reverse would be anticipated for the measurements made perpendicular to the fiber axis (matrix and fibers acting in series). Here the softer component (the matrix resin) would dominate the observed relaxation behavior and hence the composite was expected to be dependent upon annealing time. Indeed, as shown in Figure 10, this directionally dependent behavior is clearly observed as anticipated. (Note, due to the high fiber stiffness, a smaller strain level was used for these experiments.) The important point of these data is to recognize that composite systems employing a glassy matrix will physically age as should be expected. Certainly a simple crossply lay-up composite would not have shown significant physical aging by our stress relaxation test, for in this case the relaxation behavior would have been dominated by the fibers in both directions. However, it should be clear that the observed behavior following any stimulus imposed upon such a composite may be coupled to the response of the matrix as well as to the fiber, e.g., impact. Hence, recognition of physical aging of the matrix resin in quenched or rapidly cooled composites should be made and appropriate consideration given to design and long term applications. It must also be recognized that to note this behavior by a laboratory test, one must select a method whose results reflect the behavior of the softer matrix component. Finally, in view of the liquid absorption data presented within this paper, similar effects could well be anticipated for glassy composite matrices.

Concluding Remarks

It has been amply demonstrated that the physical aging process common to linear glasses is also readily observed within network glasses. This process, which extends from the nonequilibrium state induced upon quenching is due to imposed viscosity increases in going through T_g and may result in significant effects upon the final mechanical and permeation behavior. In general, the time dependent properties vary in a linear fashion with the logarithm of the sub-T_g annealing time. This log time dependence extends from the decrease in molecular mobility that results from a time dependent material densification as the true equilibrium state is approached. In view of the ever increasing use of glassy thermosets as direct adhesives, composite matrices, etc., it is strongly suggested that unless recognition of the physical aging process is made, prediction of long term properties and/or service behavior may be invalid if based on tests made very soon after curing. To achieve this latter goal is not a particularly simple task and may require analyses of the type discussed by Aklonis or by Matsuoka in this same issue.

Acknowledgement

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FIGURE CAPTIONS

1. Stress-strain curves for linear epoxy AEP-6 as determined after different sub-T_g annealing times as labelled. Sub-T_g annealing was at 23°C in water.

2. The percent of stress relaxation ocurring in 10 min. at 23°C and plotted as a function of the log sub-T_g annealing time. The data are for the linear epoxy AEP-6. A fixed strain value of 1% was used.

3. Young's Modulus E for Resin 1B plotted as a function of the sub-T_g annealing time. Data from both wet and dry samples are shown. (Test temperature = 23°C).

4. The percent of stress relaxation occuring in 10 min. at 23°C and plotted as a function of the log sub-T_g annealing time. The data are for Resin 1B. A fixed strain of 1% was used.

5. Percent of stress relaxation occuring in 10 min. at 23°C **and** plotted as a function of the log sub-T_g annealing time. The temperatures given represent different sub-T_g annealing temperatures.

6. Percent of stress relaxation occuring in 10 min. at 23°C and plotted as function of the log sub-T_g annealing time. The data are for three different sample thicknesses as given within the text. The fixed strain was one percent.

7. A) % weight gain of MEK within the Epon 828-NMA epoxy as plotted against immersion time. The different labelled times represent the sub-T_g annealing time <u>prior</u> to immersion within MEK.

   B) % weight gain of MEK within Resin WE_o as plotted against the square root of immersion time. The different times represent the sub-T_g annealing time <u>prior</u> to immersion within MEK.

8. The square root of % weight gain of MEK/min plotted against the log of sub-T_g annealing time for Resin WE_o.

9. % stress relaxation occuring in 10 min. at 23°C and plotted as a function of the log sub-T_A annealing time. The data are for the PSX rubber modified Resin 1A. The fixed strain was one percent.

10. % stress relaxation occuring within 10 min. at 23°C and plotted as a function of the log sub-T_g annealing time. The data are for the uniaxial fiber reinforced epoxy and the results are given for measurements determined parallel and perpendicular to the fiber axis. The fixed strain was 0.0025.

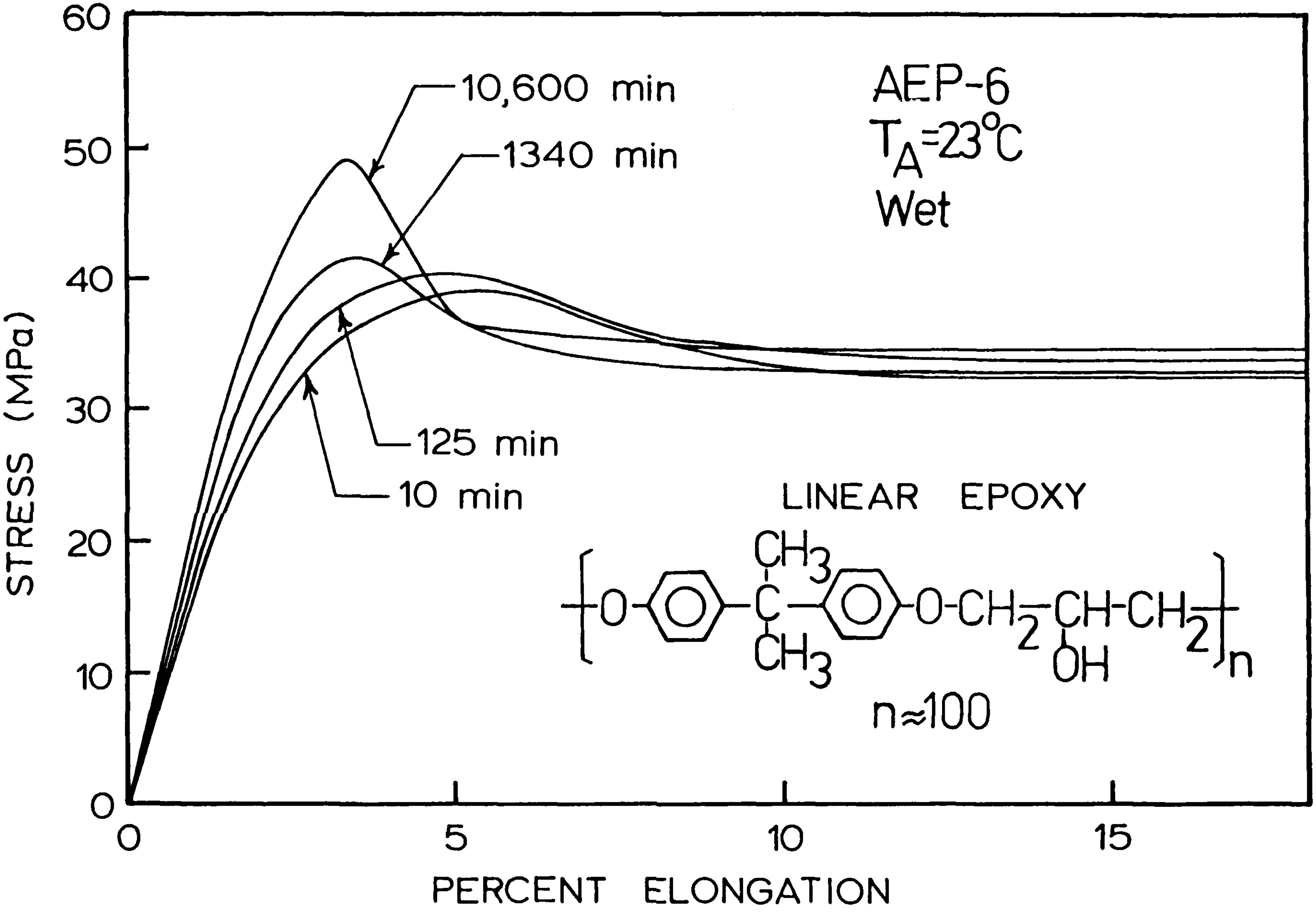

STRESS (MPa)
60
50
40
30
20
10
0
0
5
10
15
PERCENT ELONGATION
10,600 min
1340 min
125 min
10 min
AEP-6
T_A=23°C
Wet
LINEAR EPOXY
CH3
CH3
O
O-CH2-CH-CH2
OH
n
n≈100

FIGURE 1

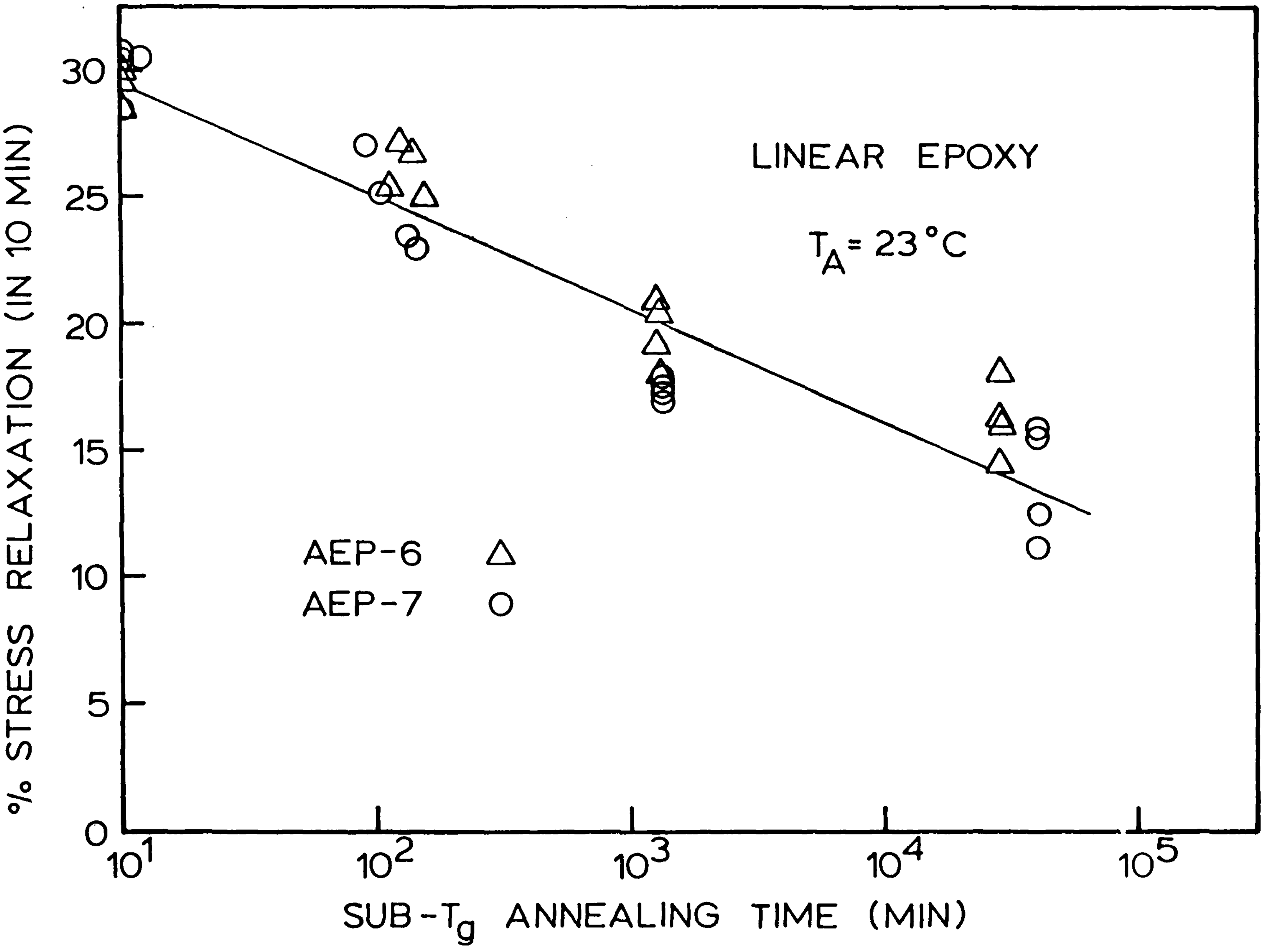

LINEAR EPOXY
$T_A = 23°C$
AEP-6 △
AEP-7 ○
% STRESS RELAXATION (IN 10 MIN)
0
5
10
15
20
25
30
10^1
10^2
10^3
10^4
10^5
SUB-T_g ANNEALING TIME (MIN)

FIGURE 2

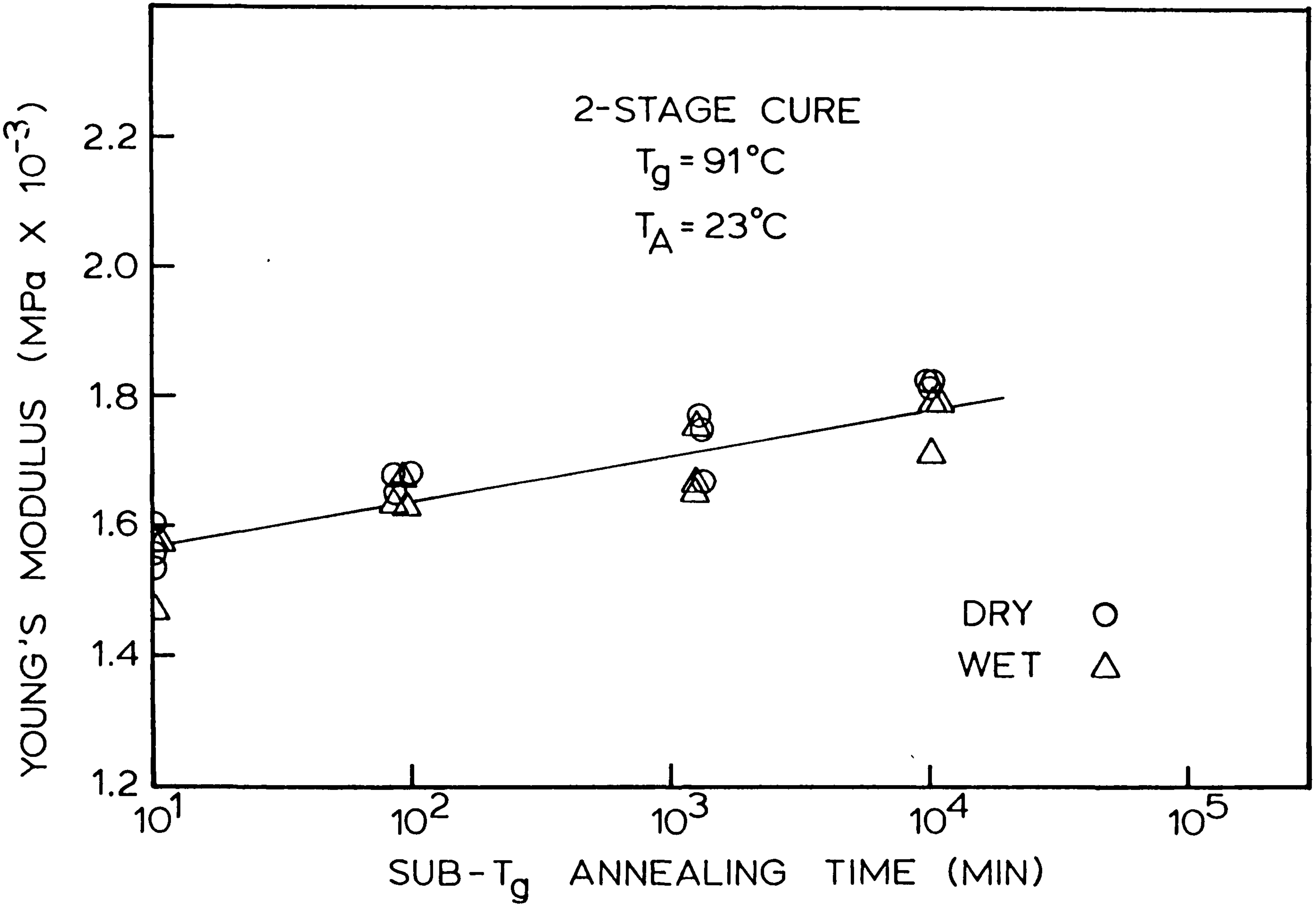

2-STAGE CURE
$T_g = 91°C$
$T_A = 23°C$
DRY ○
WET △
YOUNG'S MODULUS (MPa X 10^{-3})
1.2
1.4
1.6
1.8
2.0
2.2
10^1
10^2
10^3
10^4
10^5
SUB-T_g ANNEALING TIME (MIN)

FIGURE 3

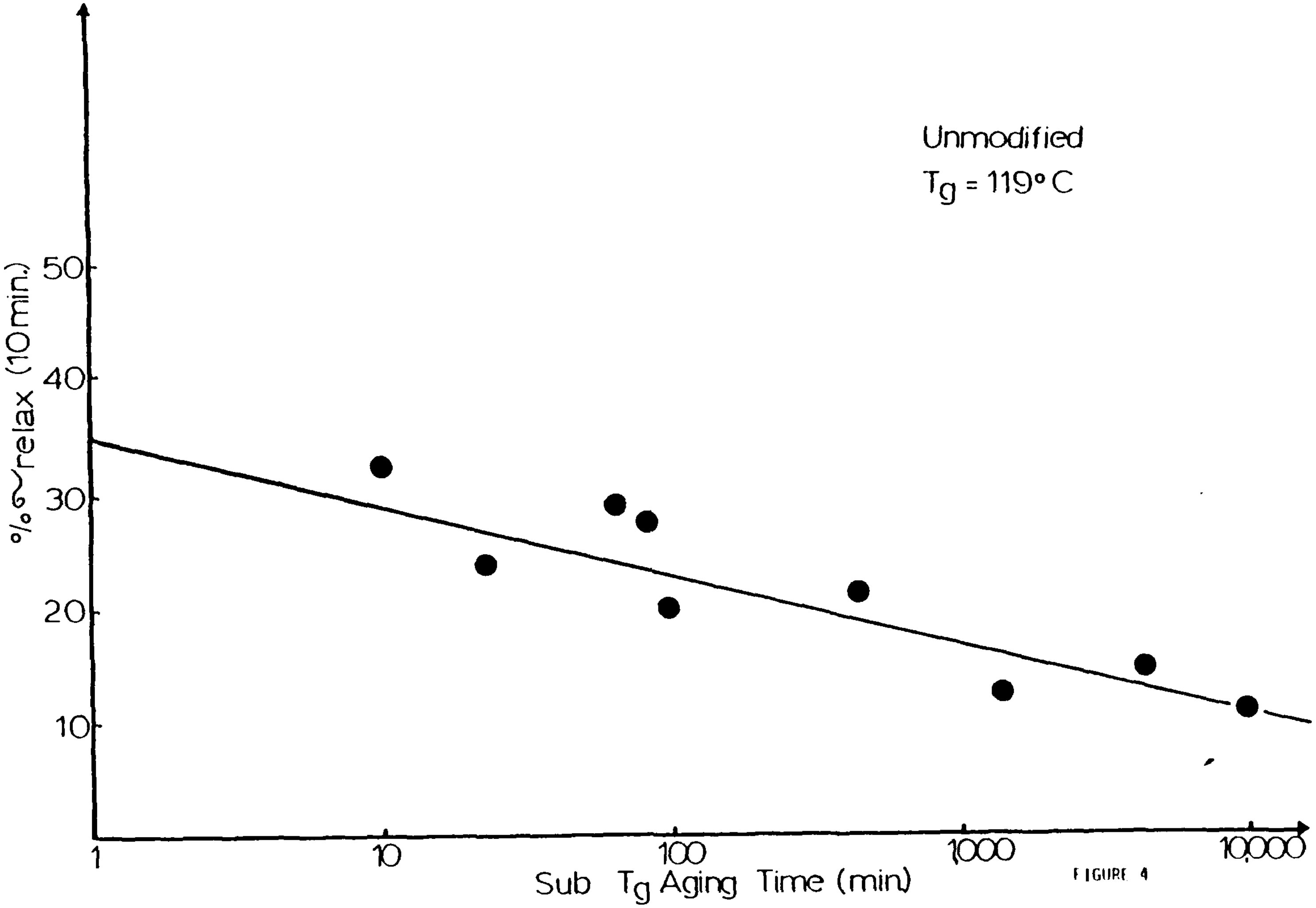

Unmodified
T_g = 119° C
% σ relax (10 min.)
50
40
30
20
10
1
10
100
1000
10,000
Sub T_g Aging Time (min)

FIGURE 4

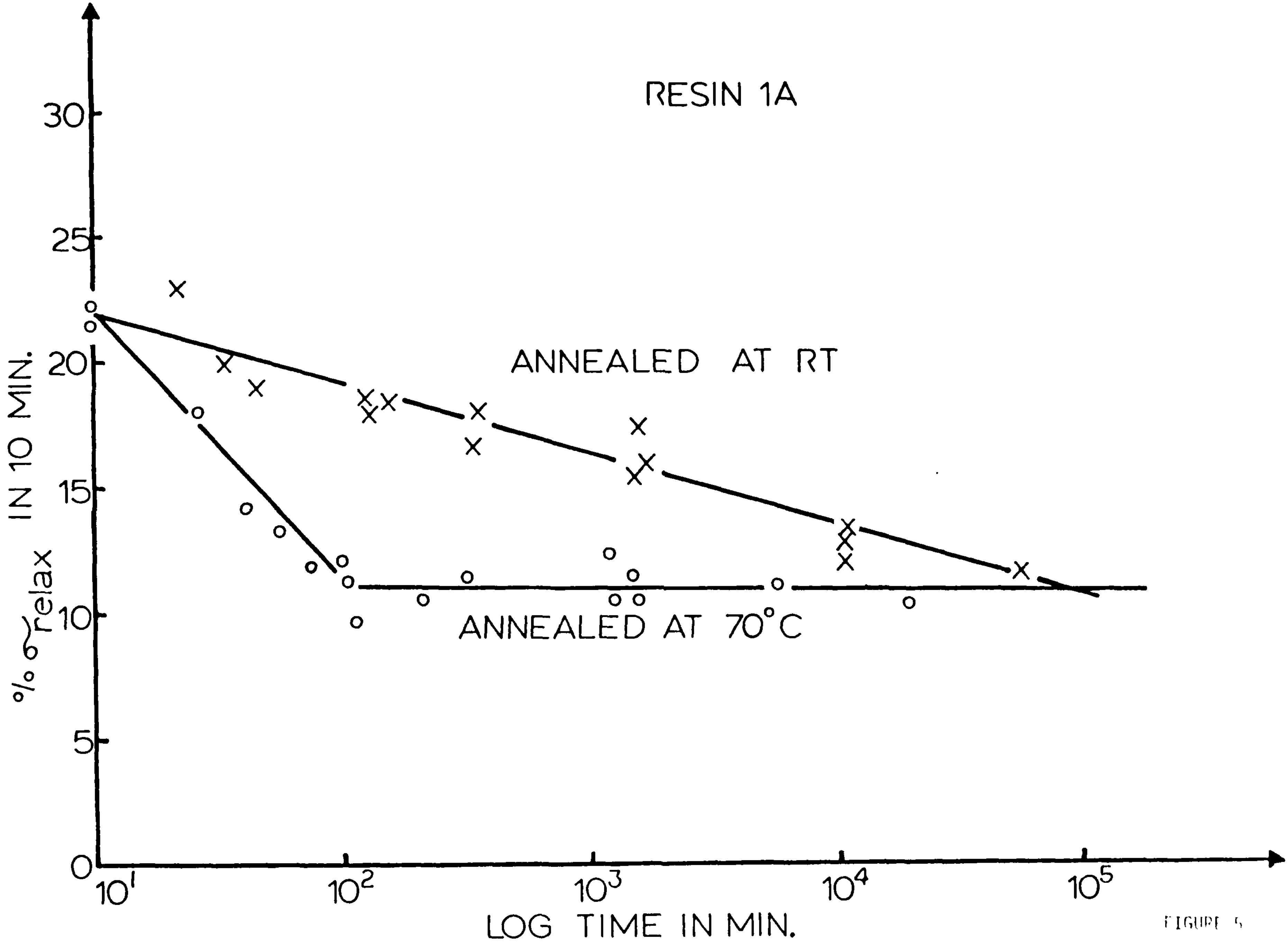

RESIN 1A
ANNEALED AT RT
ANNEALED AT 70°C
% σ_{relax} IN 10 MIN.
30
25
20
15
10
5
0
10^1
10^2
10^3
10^4
10^5
LOG TIME IN MIN.

FIGURE 5

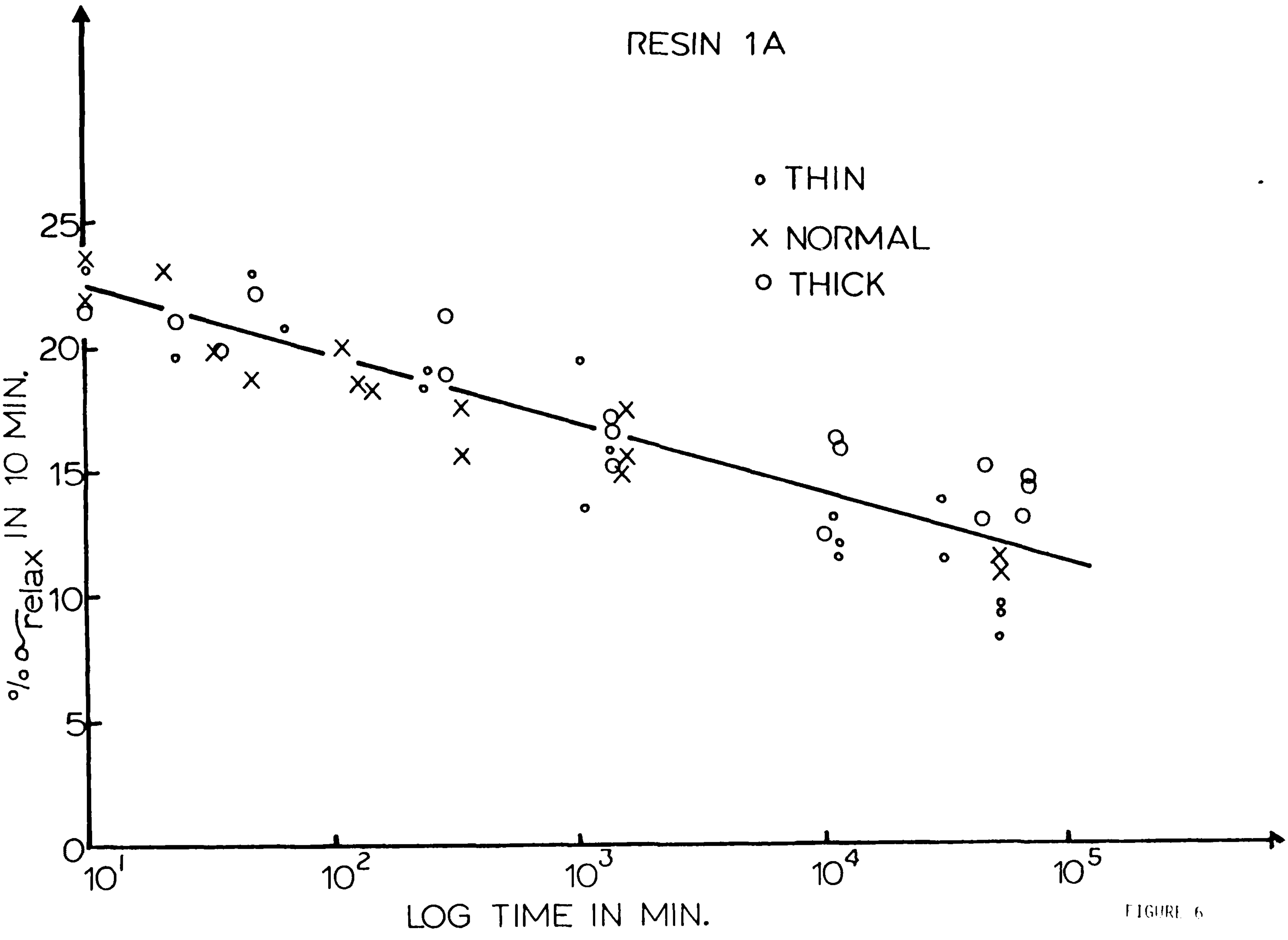

RESIN 1A
◦ THIN
× NORMAL
○ THICK
% σ relax IN 10 MIN.
0
5
10
15
20
25
10¹
10²
10³
10⁴
10⁵
LOG TIME IN MIN.

FIGURE 6

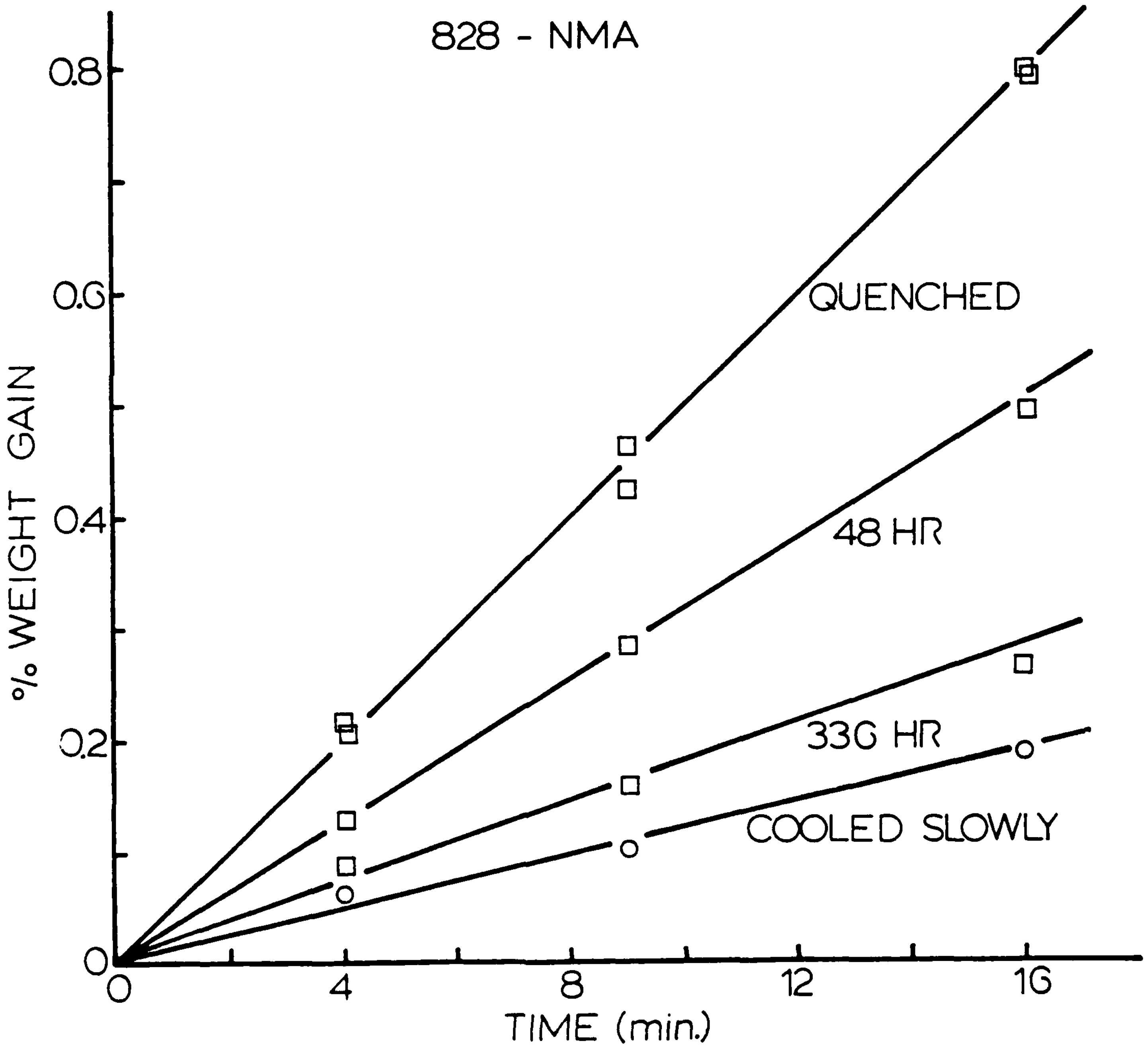

828 - NMA
QUENCHED
48 HR
336 HR
COOLED SLOWLY
% WEIGHT GAIN
0.8
0.6
0.4
0.2
0
0
4
8
12
16
TIME (min.)

FIGURE 7A

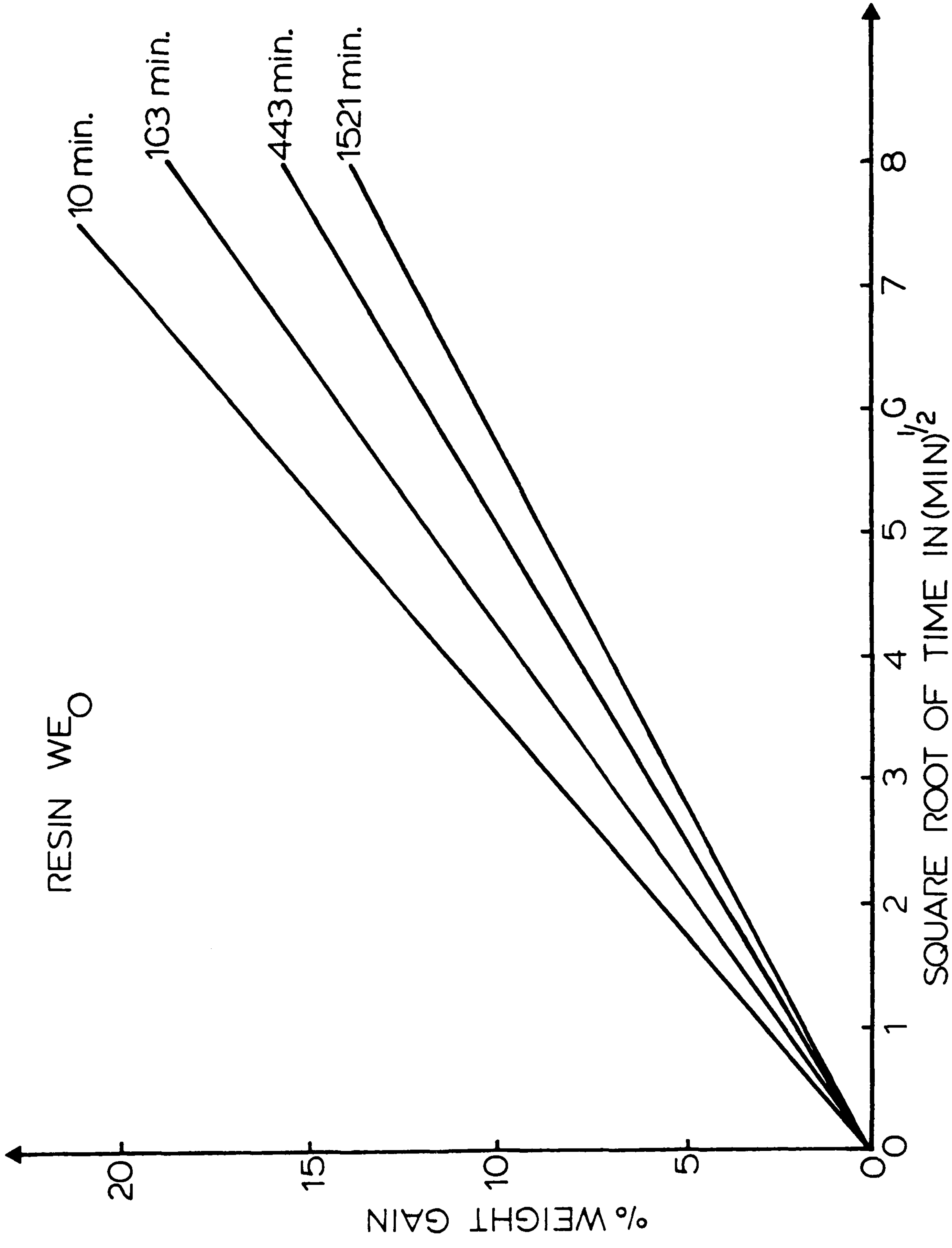

RESIN WE$_O$
10 min.
163 min.
443 min.
1521 min.
% WEIGHT GAIN
0
5
10
15
20
SQUARE ROOT OF TIME IN (MIN)$^{1/2}$
0
1
2
3
4
5
6
7
8

FIGURE 7B

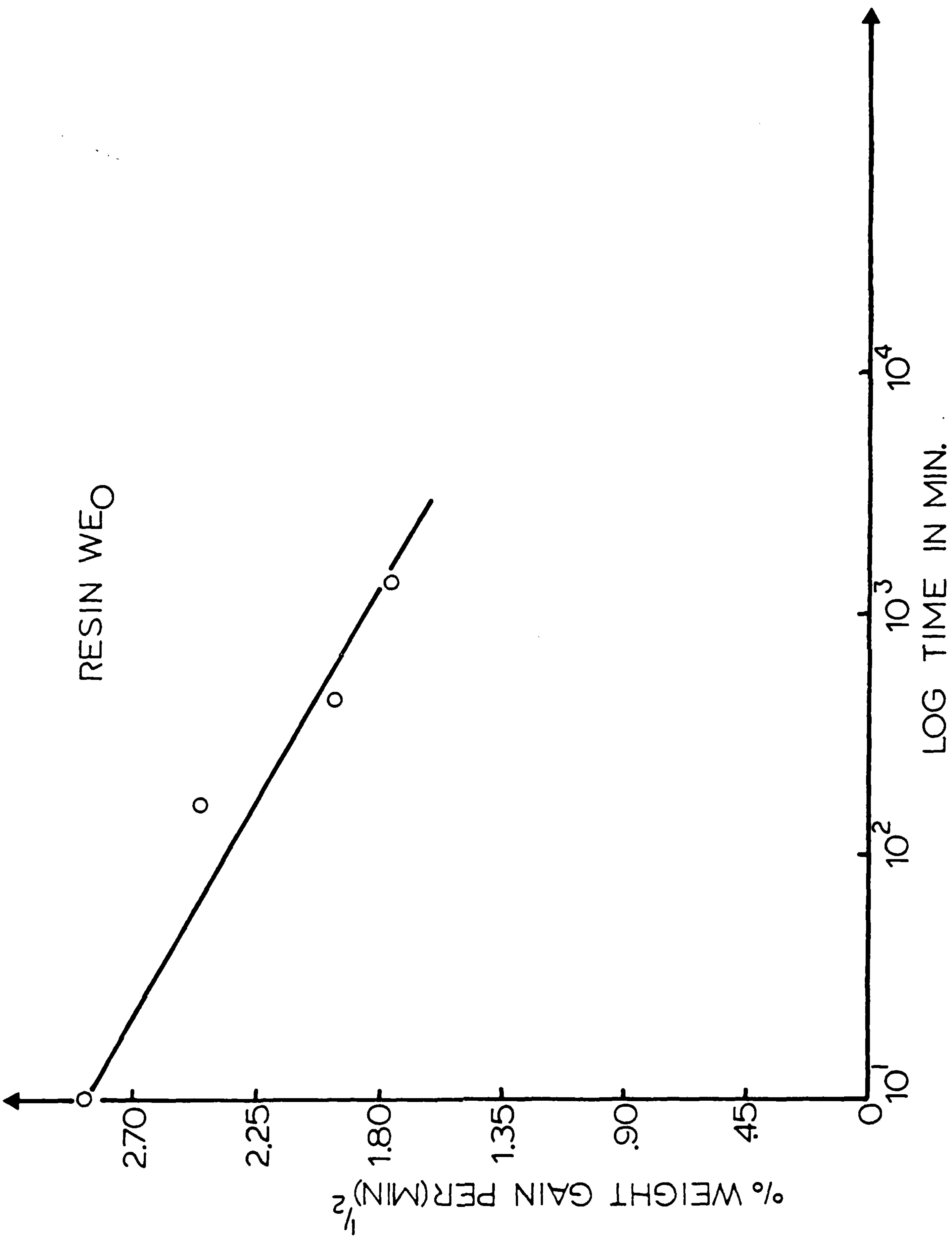

RESIN WE
% WEIGHT GAIN PER (MIN)^1/2
2.70
2.25
1.80
1.35
.90
.45
0
LOG TIME IN MIN.
10^1
10^2
10^3
10^4

FIGURE 8

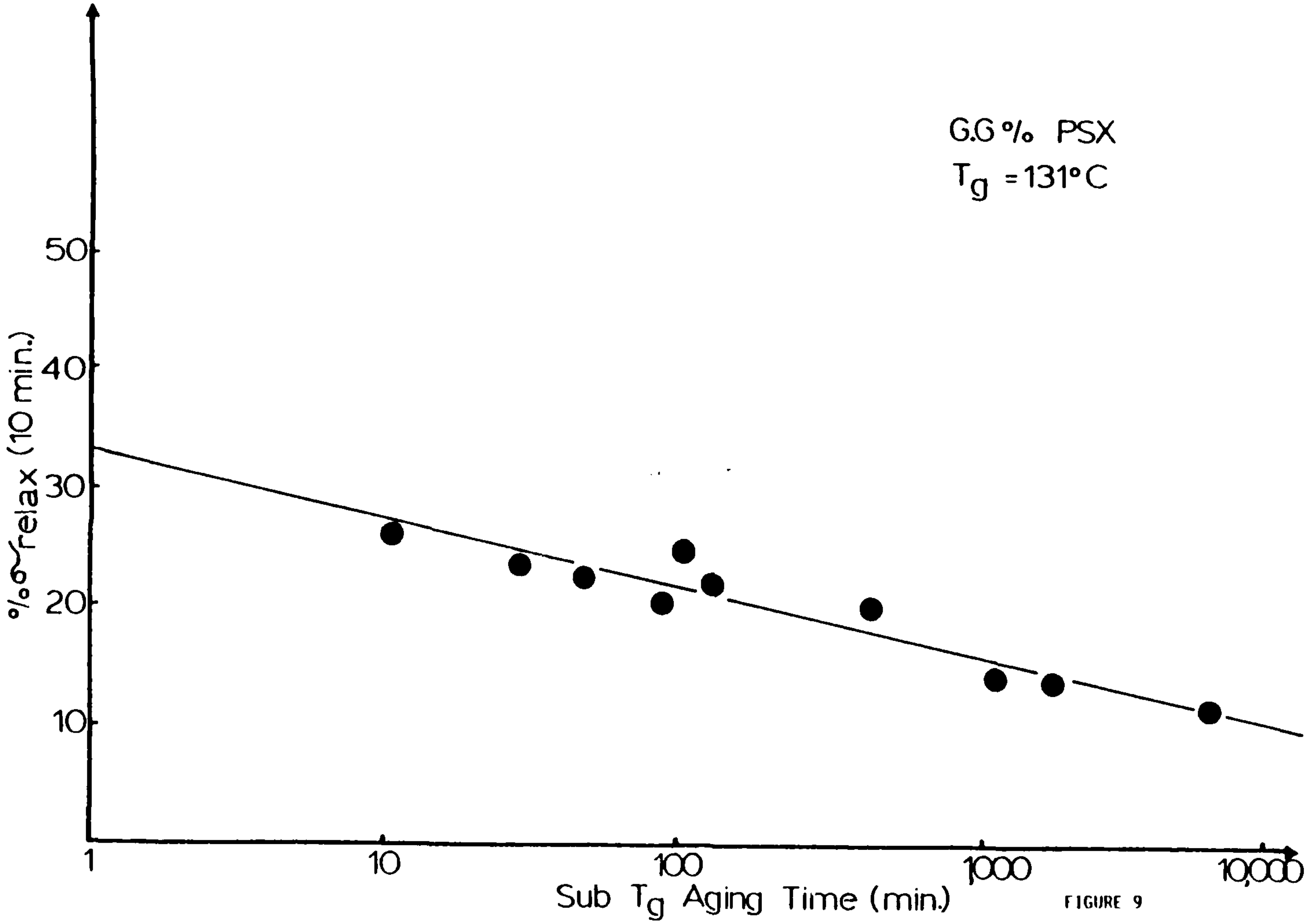
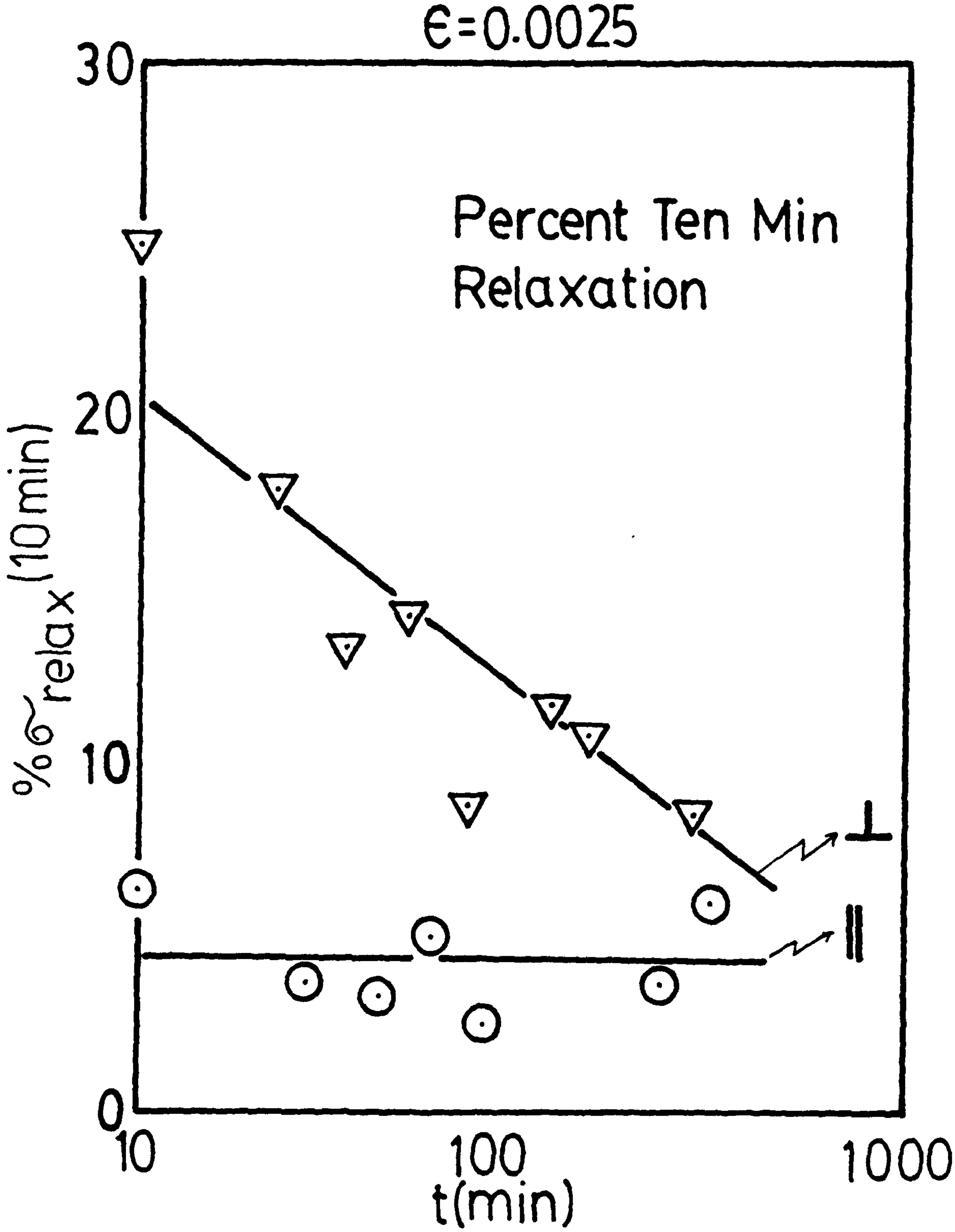

G.G% PSX
T_g = 131°C
%σ relax (10 min.)
50
40
30
20
10
1
10
100
1000
10,000
Sub T_g Aging Time (min.)

FIGURE 9



ϵ=0.0025
Percent Ten Min Relaxation
$\%\sigma_{relax}(10\,min)$
30
20
10
0
10
100
1000
t(min)
⊥
∥

FIGURE 10

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TECHNICAL REPORT NO. 3

Physical Aging of Linear and Network Epoxy Resins

by

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