SQT

(NASA-CR-169283) NONEQUILIBRIUM MATERIAL EFFECTS ON THE BEHAVIOR OF POLYMERIC COMPOSITE MATRICES AND THEIR RELATED COMPOSITES Final Report (Virginia Polytechnic Inst. and State Univ.) 37 p

HC A03

N82-31533

Unclas
G3/27 32318

FINAL REPORT

NASA CONTRACT NAG-1-78

NONEQUILIBRIUM MATERIAL EFFECTS ON THE BEHAVIOR OF POLYMERIC COMPOSITE MATRICES AND THEIR RELATED COMPOSITES

Submitted By

Garth L. Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-6496

April 2, 1982

Abstract

A brief review of the effects of physical aging on the material properties of some linear and network macromolecular glasses is presented. The free volume concept is used to describe this behavior. The effect of physical aging on properties of some uniaxial graphite/fiber epoxy resin composites is investigated using stress-relaxation in both tensile and flexural modes. The matrix polymers used for this study were Hercules 3501 and NARMCO 5208 resins both of which are based on a 4,4'-methylenedianiline derivative of epichlorohydrin with diaminodiphenylsulfone (DDS) as the curing agent. The matrix resin, as used in the practical application in composites, was found to be not fully cured and the glass transition of the network was found to be dependent on the curing schedule. The physical aging of the bulk crosslinked epoxy was found to depend on the sub-T_g annealing temperature, T_a, and the T_g of the resin. The physical aging of the composite, monitored by the stress relaxation method, was found to be dependent on the testing direction. When the test direction was perpendicular to the fiber direction (series model), the composite showed a considerable amount of stress relaxation in that it displayed a significant change in the percent stress relaxation with time. However, the value of the percent stress relaxation was found to be lower than that of the bulk resin. No aging effect was observed when the test direction was parallel (parallel model) to the fiber. Thus although the matrix does display changes in properties with time, the composite, depending on the test direction, may or may not provide evidence of physical aging.

INTRODUCTION

In principle any material that can undergo vitrification is susceptible to the later process known as physical aging. This phenomenon arises due to the simple fact that when a system is cooled from the liquid or rubbery state into the glassy state, it is difficult for the molecular system to maintain equilibrium as vitrification proceeds (1). This occurs because of the increase in viscosity as the glass temperature is approached which in turn limits the mobility of the molecules and their ability to acquire equilibrium packing and their lowest energy conformational states.

In essence it is possible that both an excess free volume (volume over and above that of the Van der waal's radii) as well as an excess enthalpy (due to nonequilibrium conformational states and excess volume) exist immediately following the vitrification process. The presence of this nonequilibrium state leads to the process of what is often called physical aging. While we will be addressing this process with regard to polymeric substances, it should be stated that it is not unique to only macromolecular systems. Indeed it is widely accepted that inorganic glasses physically age as do many of the low molecular weight organic systems which can also show vitrification. We will, however, focus our remarks on macromolecular systems where it has been within the last decade or so that considerable attention has been given to the physical aging process. More specifically, following this introduction, we will address the prominence of physical aging in high strength fiber-reinforced composites utilizing two epoxy matrix resins.

Early on, linear amorphous polymers such as those of polystyrene (1, 2), polymethylmethacrylate (3), polyvinylacetate (4), amorphous polyethylene terephthalate (PET) (1,5), and polycarbonate (6) have been demonstrated to display physical aging. More specifically physical aging can often be recognized as occurring by following the time-dependent changes within mechanical, sorption or dielectric properties. For example, Figure 1 presents the stress-strain curves for several amorphous PET samples that have undergone sub-T_g annealing at 23°C following rapid quenching. The sub-T_g annealing times range from 10 to 70,000 minutes (7, 8). From this figure it is clear that as aging progresses, the modulus, yield stress and characteristic draw behavior change considerably, thereby imparting an entirely new set of properties to the material.

Similar though not as dramatic changes have been observed in semicrystalline PET as well (9). The smaller change in behavior with sub-T_g annealing, however, arises from the fact that there is less amorphous material present to undergo physical aging as that particular component restores its equilibrium state.

The stress-strain behavior of linear high molecular weight epoxies also parallels those of the more common linear systems already denoted. Trends discussed earlier can be seen in Figure 2 which displays the stress-strain curves for one linear epoxy resin (AEP-6) that has been investigated by the authors (10).

Epoxy resins are more commonly crosslinked and these network glasses also undergo physical aging as has been first systematically demonstrated by work from the authors' laboratory (11). Epon 828 resin cured with nadic methylanhydride (NMA) is one such system. The two stress-strain curves for this material shown in Figure 3 indicate the very pronounced effect of a 56 day sub-T_g annealing carried out at room temperature (11). The data clearly indicate a significant difference in the deformation behavior. With specific regard to this paper, it should be recognized here that it is similar epoxy-based resins that serve as the matrix for many of the high strength resin composites of industrial interest.

Increases in moduli are rather consistently noted in materials undergoing the physical aging process. Consequently, aside from comparing entire stress-strain curves, one can generally demonstrate the physical aging process by plotting the modulus versus sub-T_g annealing time. Figure 4 displays an example of such a plot for a crosslinked epoxy resin (10). In addition, it shows that the effect of moisture on aging is rather insignificant for this particular system since the sub-T_g annealing was carried out both in the dry and wet states.

Returning to the origin of this nonequilibrium phenomenon, it should be realized that the excess volume and enthalpy addressed earlier will influence the given properties of the system at any given time. As indicated in Figure 5, as the system is cooled into the glassy state, the rate of cooling will influence the degree of nonequilibrium character and therefore the driving force for the system's approach to equilibrium (1). However, other factors, such as the sub-T_g annealing temperature, are important variables in regard to the rate at which a system may approach equilibrium. It is this time dependent shift toward equilibrium that produces changes in properties of the system due to the fact that both the enthalpy and the excess volume (free volume) is decreasing with time.

Selecting the variable of free volume as being indicative of physical aging one can demonstrate changes in free volume through absorption experiments. For example, Figure 6 shows a plot of the percent weight gain of methyl ethyl ketone (MEK) versus sub-T_g annealing time for samples of Epon 828 cured with NMA (11). It is noted from these weight gain data that the rate of MEK absorption is greatest for the samples with the smallest degree of sub-T_g annealing time thereby indicating a higher available free volume.

Stress relaxation tests can also be used as a means of monitoring the physical aging process. This concept can be understood simply from the fact that at a given temperature, a system will relax under an applied load at a rate that will be coupled to the available free volume (8, 12). The type of data that can be obtained from such an experiment is shown in Figure 7 along with the means of calculating the percent stress relaxation. Within our own laboratory, we have employed the method of stress relaxation to monitor physical aging (9-11). The stress relaxation duration that has been utilized is that of 10 minutes in contrast to the total stress relaxation curve. This time window is, of course, convenient but it does not provide the total picture of the time dependent changes in properties that may occur as has been discussed in previous papers (9-11). Such an approach, however, does yield a self-consistent body of data. For example, Figure 8 displays the percent stress relaxation occurring in 10 minutes versus the logarithm of sub-T_g annealing time for a particular crosslinked resin. These data were obtained on materials similar to those utilized in Figure 4 and again it clearly indicates that the effect of moisture plays a small role at best in terms of the physical aging process when contrasted to dry samples.

Finally Figure 9 presents some additional stress relaxation data for the same system but in this case the variable of sample thickness was investigated (10). It is noted that the data are independent of sample thickness and that again there is a linear behavior when this data is plotted as a function of the log of the sub-T_g annealing time. Had internal stresses been the cause of the change in the properties with time one would have expected to see differences for these samples. This is not to say, however, that internal stresses never contribute to time dependent behavior (13, 14) but rather that the data given in Figure 9 do not suggest this parameter to be of importance.

Now that the basis of physical aging behavior has been introduced and demonstrated for some rather common epoxy bulk resins, we will now direct our attention to epoxy based composites to note if the same or similar behavior occurs.

EXPERIMENTAL

Materials

Two uniaxial graphite fiber-reinforced epoxy composites were utilized in this study. Both of these systems were received from NASA/Langley. One of these was based on 8-ply specimens of a uniaxial graphite fiber composite utilizing Hercules 3501 resin -- one of the more common high strength composite resins. The two main constituents of the resin are the epichlorohydrin derivative of 4,4'-diaminodiphenyl methane (a tetrafunctional epoxy) and diaminodiphenylsulfone, DPS (also a tetrafunctional aromatic curing agent). The chemical structure of the epoxy and the curing agent are given in Figure 10. The epoxy apparently was not completely cured because the T_g of the resin was found to be around 84°C. The other graphite fiber composite used in this study was prepared using fiber/NARMCO 5208 resin, another well known composite resin. The curing of the latter system was carried out in our laboratory (after constructing specimens as described later) according to a schedule prescribed by NASA/Langley. The impregnated plys of graphite/NARMCO 5208 which were received in dry ice were warmed to room temperature and were then stacked in a uniaxial fashion (4 or 6 plys). They were then placed between Teflon sheets of 5 ml thickness, cut in the desired dimensions and directions and sandwiched between two flat metal sheets. The thickness of the top metal sheet was chosen so that the force exerted by the top sheet was around 10g/cm^2. The samples were heated for 4.5 hours at 149°C (300°F) after which the temperature of the oven was raised to 177°C (350°F) and kept there for an additional 1.5 hours. The samples were then taken out of the oven and quenched to room temperature in air. The bulk (pure) 5208 resin samples were prepared by the following procedure. Uncured resin which was received in dry ice and stored in a freezer was allowed to warm up to room temperature. A desired amount of the resin was weighed into a beaker then heated in a vacuum oven at 120°C and degassed for a period of 10-20 minutes until no gas evolved. The resin was then poured into a Dow Corning RTV 3110 silicone rubber mold which was preheated to 149°C. The curing was carried out at 149°C for 4.5 hours after which the temperature was raised to 177°C and kept there for an additional 1.5 hours. Quenching was done by placing the hot mold between two large metal pieces at room temperature. The samples were removed from the mold after they had cooled (approximately 1/2 hour). All the samples were stored in a desiccator prior to use.

The Hercules 3501 composite samples had to be cut after they were cured. To cut the samples, the sheet of the composite was sandwiched between two stainless steel dog-bone templates. The composite sheet was then sawed off around the templates using an ordinary electric saw. This was done to minimize formation of cracks in the samples. The samples were cut with the dog-bone axis in both the direction of the fibers (parallel, ||) and perpendicular to the direction of the fibers (perpendicular, ⊥). The size of the template was such that the final sample had a width of 0.65 cm and effective length of 4.0 cm.

The NARMCO 5208 composites were cut into appropriate dimensions prior to curing. To prepare samples for tensile studies, the sandwich of Teflon-composite-Teflon was placed between the dog-bone templates.

The sample was then cut by sliding a sharp razor blade around the templates. Samples were prepared again in the parallel and perpendicular directions. The effective size of these samples was the same as those prepared from Hercules 3501. The number of plys used in the parallel and perpendicular samples was 4 and 6, respectively, which resulted in respective thicknesses of 0.7 mm and 1.1 mm in the final samples following curing.

The size of the samples used for flexural tests was 7.5 cm x 2.5 cm. These samples were constructed from 4 plys which resulted in a sample thickness of ca 0.8 mm after curing. Samples for both parallel and perpendicular directions were cut prior to curing. Samples of pure resin were cured in rubber molds and had the dimensions 7.5 x 2.5 x 0.1 cm. All NARMCO and Hercules samples were annealed for 10 minutes at 200 and 100°C, respectively, quenched in cool water, quickly dried and aged within a vacuum desiccator.

Measurements

The thermograms of the samples were obtained using a Perkin Elmer DSC-2. The rate of scanning was 10°/min.

The stress relaxation measurements were made on an Instron Model 1122. The stress relaxation tests were done in the tensile mode, but for some samples the test was also performed in the flexural mode. For the stress or relaxation in the tensile mode, the sample was clamped between the jaws of the instrument so that effective initial length of the sample was 4.0 cm. A fixed strain (0.25 or 0.50) was applied rapidly (cross-head speed 10 mm/min) and the "initial" and the time dependent stress were monitored for a period of 10 minutes. The percent relaxation in 10 minutes was then calculated according to Figure 7. While the time scale of 10 minutes is short relative to the complete relaxation curve, it has provided a good index of physical aging behavior as discussed in past studies. Most of the stress relaxation tests were carried out at ambient conditions. The stress relaxation studies via the flexural tests were performed in the manner described below.

Flexural testing was performed using an Instron machine operated with a tensile load cell and fitted with two aluminum/stainless steel pieces. The lower and stationary piece formed a base and held two stainless steel rods 0.6 cm in diameter and 6.35 cm apart, center to center. The upper and mobile piece held a third stainless rod, also 0.6 cm in diameter and parallel to the two base rods. To run the flexural test, the mobile rod was lowered to a position below that of the two stationary rods in the base piece. As illustrated in Figure 11A, a sample was then placed above the single rod and below the pair of base rods. The geometry is then very similar to the common three-point bend test (15), the differences being the relative positions of the three "points" and the sample as well as the motion of the central point.

In the case of a composite material, it is important to note the orientation of fibers with respect to the direction of the flexural rods. Figure 11B illustrates the authors' notation for the two possible situations.

This test allows an accurate zeroing of samples in mechanical testing. With a sample in place between the rods, the mobile piece was raised at a crosshead speed of 10 cm/min. until a stress response was observed on the Instron's recording chart. The upper piece was then generally lowered 0.1 mm to ensure that no stresses were imposed on the sample prior to the beginning of testing.

Flexural stress-strain curves on samples aged 10 minutes (crosshead speed, 10 mm/min) showed that the behavior was linear to at least 6 or 7 mm central deflection for both the pure resin and the composites. Accordingly, 5 mm was chosen as a standard deflection to be sure that all testing was done in the linear region.

The flexural device was used to measure the ten-minute stress relaxation of NARMCO samples aged for various times. At a crosshead speed of 100 mm/min, samples were deflected to 5 mm in a deformation time of 3 seconds. This deformation was held for 10 minutes and the percent stress relaxation calculated.

The volume fraction of the resin in the graphite/NARMCO 5208 system was determined by removal of resin from an uncured composite using acetone as a solvent. Taking the density of the cured resin as 1.3 g/cc and that of graphite as 1.8 g/cc (both determined using a volume displacement method), the volume fraction of the resin was determined to be around 0.47.

The value of strain placed on bulk samples in the tensile relaxation experiment was 0.5 percent. The strain imposed on the composites in the perpendicular direction was chosen at 0.25 percent value. This was done taking into account a series model in which the deformation was assumed to be concentrated in the resin matrix. A strain of 0.25 percent was also applied to the composite in the parallel direction because at higher extensions considerable slippage of the samples occurred.

Results and Discussion

The mechanical properties and the aging behavior of the composites are dependent on the sub-T_g annealing temperature, T_a, relative to the transition temperature T_g of the resin. Since the rate of attainment of equilibrium is initially dependent on the temperature increment $\Delta T = T_g - T_a$, either a decrease in T_g and/or an increase in T_a would potentially result in a variation of aging behavior.

The glass transiton temperature of a fully cured bulk NARMCO 5208 resin (chemical structure of major constituent is given in Figure 10) is found to be around 240°C. The transition temperature of the resin in the composites is, however, far away from that of the fully cured state and is dependent on the curing condition employed in the preparation of the new composites. A comparison of the transition temperature of a composite prepared according to the NASA/Langley procedure to that of a resin which is essentially fully cured is made in Figure 12. The bulk resin, for example, which has been cured for 4.5 hours at 149°C and 1.5 hours at 177°C, displays an exothermic behavior above 180°C (just a few degrees above the highest curing temperature). This indicates that the sample is not yet fully cured and when enough thermal energy is supplied to the chains, the unreacted portions gain enough mobility to continue the reaction of the as yet unreacted species. The energy released from the subsequent chemical reaction is displayed as exothermic behavior. Thus the practical glass transition of such partially cured samples lies close to the highest curing temperature as described by Gillham (16). In order to study the effect of sub-T_g annealing on the physical aging behavior, the resin is generally heated for 5-10 minutes at 10-15°C above its T_g to erase past history and it is then quenched to the selected annealing temperature T_a. The time the sample is quenched is taken as time zero and thereafter the properties are measured against the sub-T_g annealing time (11). Since neither of our composites were fully cured, it was necessary to differentiate the effect of possible chemical aging from physical aging in our systems. One possible way of reducing chemical aging would be to fully cure the epoxy as done by Kong (17). Such a sample will not undergo further curing when it is heated to erase past histroy or when it is being aged. Unfortunately there are two problems associated with this manner of procedure. First, the curing procedure employed for preparation of a composite has been selected with optimization of the material properties. That is, under that specific curing procedure, and therefore a given apparent T_g of the resin, the material properties of the system may be most desirable when the fully cured condition is not achieved. For example, possibly further curing may result in a more brittle system and therefore the aging study of such a system may not be relevant to practical applications.

Secondly, when a system is fully cured its T_g becomes higher and therefore for a given ΔT one has to choose a higher annealing temperature. Moreover, if the system is fully cured, it does not guarantee that no other chemical reactions can occur. Indeed we have observed that annealing at above 120°C for a period of one week, even in vacuum ($P_{air} \leq .5$mmHg), resulted in a noticeable discoloration of bulk NARMCO 5208 in the first 0.2 - 0.5 mm of the sample thickness. Because of these complications, it was decided to study the aging behavior of these composites prepared according to the "standard" prescribed procedure. To investigate the effect of possible chemical aging, a sample of NARMCO 5208 resin which was cured according to the prescribed schedule, T_g ~185°C, (Figure 12, curve A) was heated for 10 minutes at 200°C (about 15°C above T_g). In this way we introduced a heating cycle which was needed to erase the past history of the sample. A DSC rerun of this sample shows that the apparent T_g of the sample had been raised to 200°C (as expected due to further curing). However, when such a treated sample was aged for 1 week at ambient or even when it was aged for that period at 100°C no noticeable changes in the thermogram of the sample were apparent (Figure 12, curve C). Therefore chemical aging of the sample under those conditions was considered negligible. Therefore aging of the NARMCO samples followed a 10 minute pre-treatment of the composite at 200°C.

The effects of sub-T_g annealing temperature on physical aging are illustrated in Figure 13. Bulk samples of NARMCO 5208 which had been treated identically and, therefore, had the same T_g, 195-200°C, were aged at ~25°C (T_R) and 100°C (T_{100}). It should be recalled that, as indicated before, this 100°C sub-T_g annealing does not cause any significant change in the chemical structure of the polymer and therefore a difference in mechanical behavior is related to physical aging of the resin. At early aging times (for example, 10 or 100 minutes), the samples at higher sub-T_g annealing temperature (100°C) display lower percentages of stress relaxation than samples stored at T_R. This indicates that a sample aged at a higher annealing temperature has densified (or has lost free volume) more than a sample aged at a lower temperature during the short aging periods used here. At longer aging times (for example, 10,000 minutes), the percentages of stress relaxation in samples aged at T_R and T_{100} have apparently become closer in value to each other. Therefore the data in Figure 13 indicated that at an early aging time, the sample at the higher sub-T_g annealing temperature has come closer to its true equilibrium state than the sample at the lower annealing temperature. However, the rate of aging (that is the slope of lines in Figure 13) is higher for the sample at the lower annealing temperature. Thus it is conceivable that at very long aging times, for example 10^6 minutes, samples aged at T_R may show more embrittlement than samples aged at T_{100}. To explain this phenomenon we will utilize the volume-temperature plots given in Figure 14. Let us assume that the resin sample is cooled down from somewhere above T_g. Once the temperature of the sample is lowered below T_g, the volume of the resin will follow the solid line (nonequilibrium) and, at any given temperature, will deviate from the equilibrium volume (broken line in Figure 14A & B). Initially the sample would be either at point 1 or 2 depending on whether the annealing is done at 100°C or at T_R = 25°C. Figure 14A represents the volume state of the sample at *an early time*. That is after a short aging period the sample annealed at the higher temperature will be at the point A_{100} and the sample at T_R will be at point B_{25}. The larger decrease in volume for the sample at the higher annealing temperature is due to the fact that at higher temperatures more thermal energy is available for the molecules to undergo Brownian motion and thus more readily approach equilibrium.

The lower the temperature (i.e. at 25°C) the less thermal energy is available to overcome viscous forces even though at this temperature the volume of the sample is farther away from its equilibrium state. Thus when the sample at 100°C is quenched in cold water after a short period of aging (for example, 10 min) in order to determine its stress relaxation, the volume decreases following a path that we will presently assume is parallel to the line between points 1 and 2. After this short annealing time, the sample aged at 100°C has densified to a greater extent and consequently has lost more volume (or free volume) than the sample aged at T_R for the same period of time (points A_{25} and B_{25} in Figure 14A.) The sample aged at 100°C will therefore show a lower percentage of stress relaxation than one aged at T_R because the lowering of free volume restricts the mobility of macromolecular segments. At a longer aging time (see Figure 14B) the sample at the elevated temperature T_{100} has come very close to its equilibrium volume, whereas the sample at T_R is still very far away from its equilibrium volume state and therefore continues its densification process. That is, at a longer sub-T_g annealing time, the volume (or free volume) occupied by a sample aged at T_R (B'_{25} in Figure 14B) and the volume taken up by the sample aged at T_{100} and quenched to 25°C (A'_{25}) are close to each other.† This means that at longer aging times both samples may show similar behavior as suggested by the data in Figure 13.

To elaborate on the above discussion, a schematic representation of the dependence of the volume change, $|\Delta V| = |V_i - V_t|$, is shown in Figure 14C where V_i is the initial volume of the glass after quenching to a given temperature and V_t is the volume at any given time at that temperature. Figure 14C presents changes in ΔV from time zero to infinity. This time-line can be broken into three regions, two of which are, at present, experimentally inaccessible to us. Data given in Figure 13 indicates that in the first ten minutes of aging those samples aged at T_{100} lose free volume much more quickly than those aged at T_R, presumably because of the higher thermal energy available at T_{100}. We begin to measure stress relaxation at 10 minutes, at which time the T_{100} samples have considerably less free volume than the T_R samples and show correspondingly lower values of percent stress relaxation. Within the time frame of the

---

†The reader realizes that once a sample is quenched to T_R from T_{100} it starts to undergo aging at this lower temperature. However, since the stress relaxation test is done almost immediately after quenching the sample to T_R (aged not more than 1-4 minutes), such aging should be insignificantly small and is therefore not considered here.

experiment, 10 to 10,000 minutes, those samples aged at T_{100} are already approaching their equilibrium free volume whereas those samples aged at T_R are still losing free volume at an appreciable rate, producing greater decreases in stress relaxation with time, that is, physically aging to a higher degree. As shown by extrapolations beyond 10,000 minutes in Figure 14C, T_{100} samples are nearly at their equilibrium volume at very long times. The T_R samples, however, continue to lose free volume at a greater rate, the end result being that their final free volume at infinite time will be significantly smaller than the *equilibrium* free volume of samples aged at T_{100}. In regard to mechanical properties for the case in point, one might anticipate that a sample aged at T_R for infinite time will be much more brittle (at T_R) than one aged at T_{100} for the same amount of time but tested at T_R.

Having discussed the aging properties of the bulk resin, the aging behavior of the composite can now be considered. A comparison of the percentage of stress relaxation in the tensile mode of carbon fiber/NARMCO 5208 composites has been made to that of the bulk resin as shown in Figure 15. The sub-T_g annealing has been done at room temperature ($\sim$25°C). The percentage of stress relaxation for the uniaxial composite is expected to be dependent on the test direction relative to that of the fiber axis. We have performed the test in both the direction perpendicular to the fiber axis ($\perp$) and parallel to the fiber axis ($\parallel$). Although the pure resin shows a considerable amount of aging with time, the composite may or may not display aging, depending on the test direction. In the test carried out in the direction perpendicular to the fiber axis ($\perp$), the samples show a distinct change in properties with time. This is because in this direction the composite behaves with the matrix and fibers in series. That is, while the graphite matrix may not show any change in properties with time, because the resin does have time dependent characteristics, the system as a whole would show kinetic effects. The absolute value of the relaxation for the perpendicular sample at any given time is approximately half of that for the pure resin. This is probably due to the fact that the volume fraction, ϕ, of the resin in the NARMCO composite is also about one half ($\phi_{resin} = 0.47$).

The stress relaxation of the composite in the fiber direction is noted to be very small. Moreover it is time independent. This is due to the fact that in the parallel direction, mechanical properties are dominated by the stronger graphite fibers. That is, although the resin does undergo physical aging, the composite does not change properties with time in this direction. Even the small percentage of stress relaxation exhibited in the parallel direction is believed to be primarily due to the small slippage of the extremely rigid samples in the grips of the sample holders.

The effects of aging on the tensile stress relaxation of graphite/Hercules 3501 composites are shown in Figure 16. The tests are again run in the parallel and perpendicular direction. The resin used in this composite has basically the same chemical structure as shown in Figure 10. The glass transition of the resin is, however, much below that of NARMCO 5208 material and is around +85°C. The exact reason for the lower transition of this resin has not been disclosed to us but it could be due to a lower concentration of co-catalyst and/or less severe curing conditions. Whatever the reason, the resin is less fully cured and therefore has a lower transition as discussed earlier. The composite shows basically the same trend as the NARMCO system in that it does not display any change in property with time when measured in the direction of the fiber (i.e. parallel). The stress relaxation behavior of the sample in the perpendicular direction is again time dependent indicating that aging properties of the resin are displayed in this testing direction.

The results of determining physical aging using the flexural test are given in Figure 17. The samples were bent using a three-point set-up and the initial stress and the stress after a lapse of 10 minutes were recorded. The testing was again done in two directions, "Across" and "Between", which correspond resoectively to parallel and perpendicular tensile tests (see Figure 11B). The results from this test not only support the earlier tensile results, but in respect to practicality, the ease of measurement as well as the accuracy of the results supersede the earlier tensile tests. The bulk NARMCO 5208 (pure) shows almost identical aging behavior to that of the tensile tests (compare Figures 15 and 17). In the flexural test in which the composite is bent against the fibers (direction A), which corresponds to the tensile test in the parallel direction, the sample displays zero relaxation which does not change with time. This is expected because in this direction the properties are controlled by the strong time independent graphite fibers which dominate the properties under these conditions. This result indicates that the small relaxations obtained in the tensile mode for samples in the parallel direction at all the aging times were probably due to the slippage of samples from the grips of the clamps. In the opposite direction (i.e. direction B), which corresponds to the perpendicular direction of the tensile test, the sample clearly shows physical aging. This is again due to the fact that in the testing direction the resin (matrix) plays an important role and thus its aging behavior becomes apparent. The results of the tests in this direction are identical to that obtained via the tensile test (compare B in Figure 17 to that perpendicular in Figure 15) and again the absolute value of relaxation at any given time is approximately one-half of that of pure resin. As mentioned earlier, this lower percentage stress relaxation of the composite is principally due to the fact that this composite contains about half as much resin (ϕ_{resin} = .47). However, the fact that the rate of aging (slope of the line B or slope of perpendicular test direction in Figures 17 or 15, respectively) is different could be related to the difference in the morphology of the resin in the composites. Such a difference could be due to the nature of the gelation front in the pure resin as compared to that in a composite matrix as recently discussed (18).

SUMMARY

Physical aging of the resin in graphite epoxy based composites affects the material properties of the matrix. This physical aging behavior, which is dependent on the variation of the free volume of the polymer resin with time, can be most noticeable when the testing is done in an appropriate direction. If the directional effect is not noted, a test might indicate no change in a property with time, whereas in actuality the resin has undergone aging and other important properties of the composite such as its toughness or impact resistance may also be affected in an undesirable manner. Stress relaxation in both the tensile and flexural modes provides a means of easily monitoring physical aging provided an appropriate testing direction has been chosen.

REFERENCES

1. S. E. B. Petrie, in Polymeric Materials: Relationship Between Structure and Mechanical Behavior, E. Baer and S. V. Radcliffe, eds. American Soc. for Metals, Metals Park, OH, Chap. 2 (1975).
2. S. Hozumi, Polymer J. 2, 756 (1971).
3. L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, Amsterdam, The Netherlands (1978).
4. A. J. Kovacs, Fortschr. Hochpolym. Forsch., 3, 394 (1963).
5. R. M. Mininni, R. S. Moore, J. R. Flick and S. E. B. Petrie, J. Macromol. Sci., Phys., B8, 343 (1973).
6. A. H. Chan and D. R. Paul, Polym. Eng. Sci., 20, 87 (1980).
7. M. Tant and G. L. Wilkes, Polym. Prep., 20(2), 535 (1979).
8. M. Tant and G. L. Wilkes, Polym. Eng. Sci., in press.
9. M. Tant and G. L. Wilkes, J. Appl. Polym. Sci., in press.
10. E. S. W. Kong, G. L. Wilkes, J. E. McGrath, A. K. Banthia, Y. Mohajer, and M. R. Tant, Polym. Eng. Sci., in press.
11. Z. H. Ophir, J. A. Emerson and G. L. Wilkes, J. Appl. Phys., 49, 5032 (1978).
12. I. M. Ward, Mechanical Properties of Solid Polymers, Wiley-Interscience, London, Chap. 7 (1971).
13. L. C. E. Struik, Polym. Eng. Sci., 18, 799 (1978).
14. L. J. Broutman and S. M. Krishnakumer, Polymer Eng. Sci., 16, 74 (1976).
15. L. E. Nielsen, Mechanical Properties of Polymers and Composites, Vol. 1, Marcel Dekker, Inc., NY (1974).
16. J. K. Gillham, Org. Coat. Plast. Chem., Prep. 44, 185 (1981).
17. E. S. W. Kong, manuscript submitted, J. Appl. Phys.
18. Hirschbuehler, K. R., Abst. Critical Review, Characterization of Comp., MIT, June 1981.

FIGURE CAPTIONS

Figure 1. Stress-strain curves of amorphous PET aged at room temperature for 10, 90, 1,000, 10,000 and 70,000 min. Note changes in yield stress, modulus, and characteristic draw ratio. References 7 and 8.

Figure 2. Stress-strain curves for a linear high molecular weight epoxy (AEP-6) aged at room temperature for 10, 100, 1,300 and 10,000 min. Note changes as per Figure 1. Reference 10.

Figure 3. Stress-strain curves for Epon 828 resin crosslinked with nadic methyl anhydride and aged at room temperature for 10 min. and 56 days. Reference 11.

Figure 4. Modulus vs. log time plots for Epon 828 crosslinked with PACM-20 by a two-stage curve. No significant differences are noted between "dry" samples and those subjected to moisture. Reference 10.

Figure 5. Schematic plots showing changes in enthalpy and volume with changes in temperature. Dotted line indicates the equilibrium state, which is achieved only if the material is cooled infinitey slowly. T_2 is the temperature. Reference 1.

Figure 6. Plots of percent weight gain of methyl ethyl ketone vs. time immersed in MEK for an Epon 828 resin cured with PACM-20. The rate of MEK uptake is reduced with aging time as a result of decreases in free volume. Reference 11.

Figure 7. Schematic of a stress relaxation curve in which the stress needed to sustain a particular deformation decays with time. The calculation for percent stress relaxation is described in the figure.

Figure 8. Plot showing the linear decrease in percent stress relaxation with log aging time for Epon 828 cured with PACM-20 in a one-stage reaction. It is seen that the physical aging behavior of this material in the presence of moisture does not differ markedly from that in a dry environment.

Figure 9. Plot of percent stress relaxation vs. log aging time for Epon 828 cured in one stage with PACM-20 and prepared in samples of different thicknesses. All data points fall on essentially the same line, suggesting that internal stresses did not significantly influence the natural physical aging in this case. Reference 10.

Figure 10. Chemical structures of major constituents of NARMCO 5208 and Hercules 3501 resins.

Figure 11A. Schematic drawing of the flexural test device including sample shape, sample and rod positions, and motion of the rods.

Figure 11B. Schematic drawing showing the authors' notation for the orientation of test device rods and fiber direction in flexural test samples.

Figure 12. DSC thermograms of NARMCO 5208 resin. The curing schedule and the thermal history of samples are described in the figure. The heating rate is 10°C/minute.

Figure 13. Effect of annealing temperature on the aging behavior of bulk NARMCO 5208 resin. The tests are in the tensile mode and $\epsilon = 0.5\%$.

Figure 14A. A schematic representation of volume-temperature behavior of a resin after a short annealing time. Points 1 and 2 refer to volumes of the glass at 100°C and T_R (25°C), respectively, immediately after it is quenched from T_g.

Points A_{100} and B_{25} refer to volumes of the glass after a short period of time at 100 and 25°C. Point A_{25} is the volume of the polymer which was aged at 100°C immediately after it was quenched to T_R. T_2 is the equilibrium second order transition temperature of the resin. (The length of the arrows is proportional to the changes in volume).

Figure 14B. The same as 14A except after a longer annealing time. Prime is used in A'_{100}, A'_{25} and B'_{25} to indicate longer annealing times.

Figure 14C. The dependence of the absolute value of the change in volume of the resin, $|\Delta V|$, with time at 100°C and room temperature, $|\Delta V| = |V_i - V_t|$; V_i is the volume of the polymer immediately after it is quenched and V_t is the volume at time t.

Figure 15. A comparison of aging behavior of bulk NARMCO 5208 resin to that of the graphite fiber composite in the parallel and the perpendicular directions. The aging was done at room temperature; $\epsilon = 0.5\%$, and 0.25%, respectively, for the bulk and the composite. The tests are in the tensile mode.

Figure 16. A comparison of aging behavior of graphite fiber/Hercules 3501 composite in the parallel to that in the perpendicular direction. The tests were done at room temperature with $\epsilon = 0.25\%$.

Figure 17. A comparison of the physical aging of bulk NARMCO 5208 resin to that of its graphite fiber composite. The tests were done in the flexural mode in directions against the fiber (A) and along the fiber (B) (See Figure 11 for further description of notation).

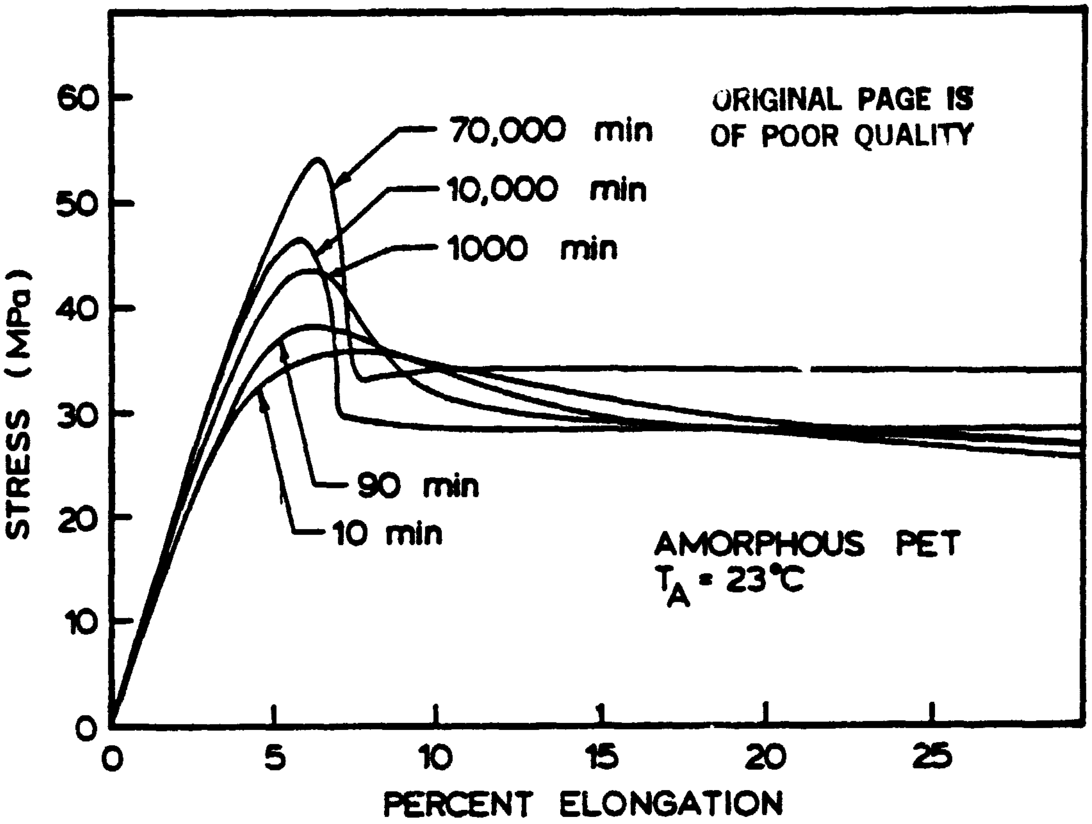

60
50
40
30
20
10
0
STRESS (MPa)
0
5
10
15
20
25
PERCENT ELONGATION
70,000 min
10,000 min
1000 min
90 min
10 min
AMORPHOUS PET
$T_A = 23°C$

Fig. 1

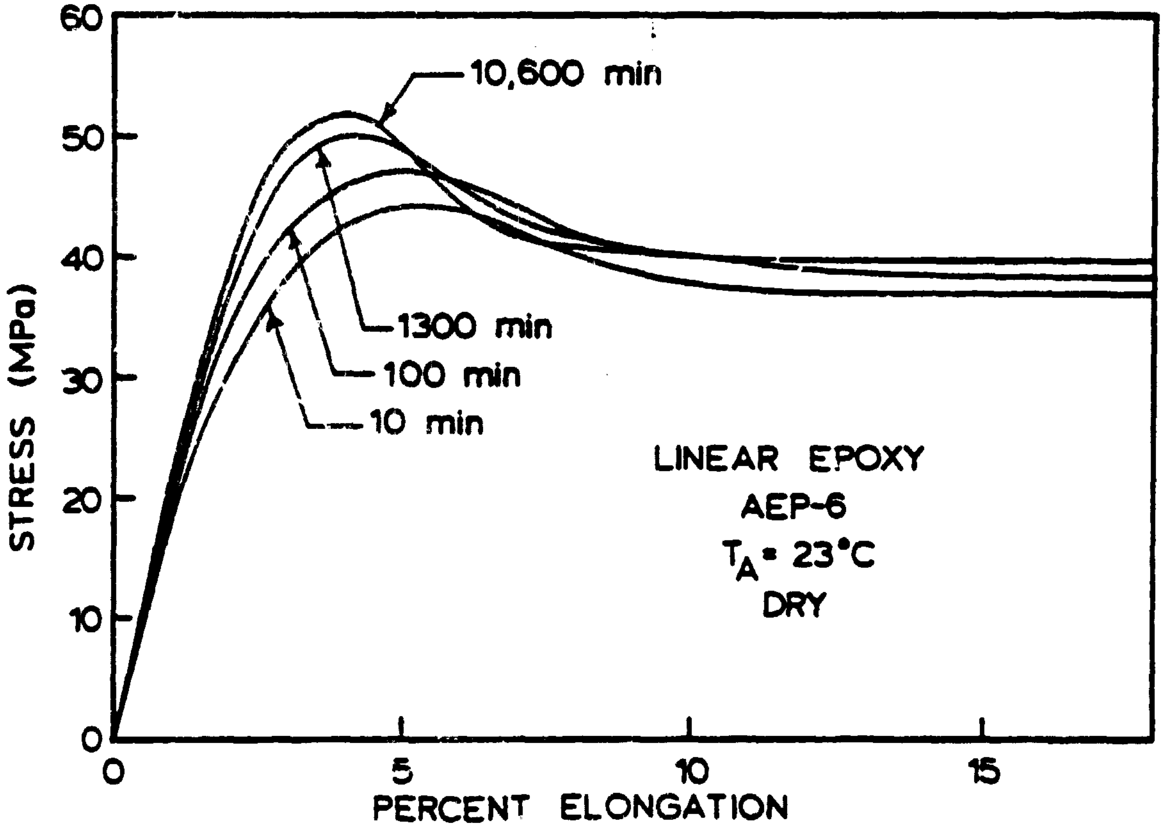

60
50
40
30
20
10
0
STRESS (MPa)
0
5
10
15
PERCENT ELONGATION
10,600 min
1300 min
100 min
10 min
LINEAR EPOXY
AEP-6
$T_A = 23°C$
DRY

Fig. 2

Fig 3

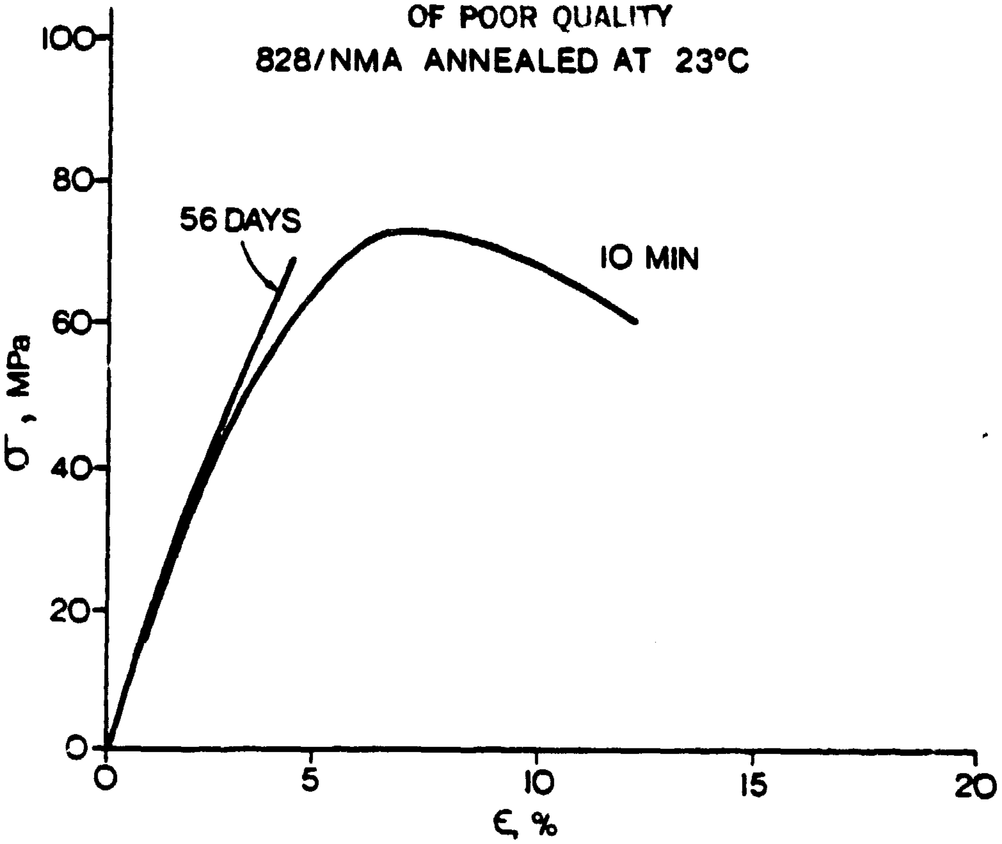

828/NMA ANNEALED AT 23°C
56 DAYS
10 MIN
σ, MPa
0
20
40
60
80
100
0
5
10
15
20
ε, %

Fig 4

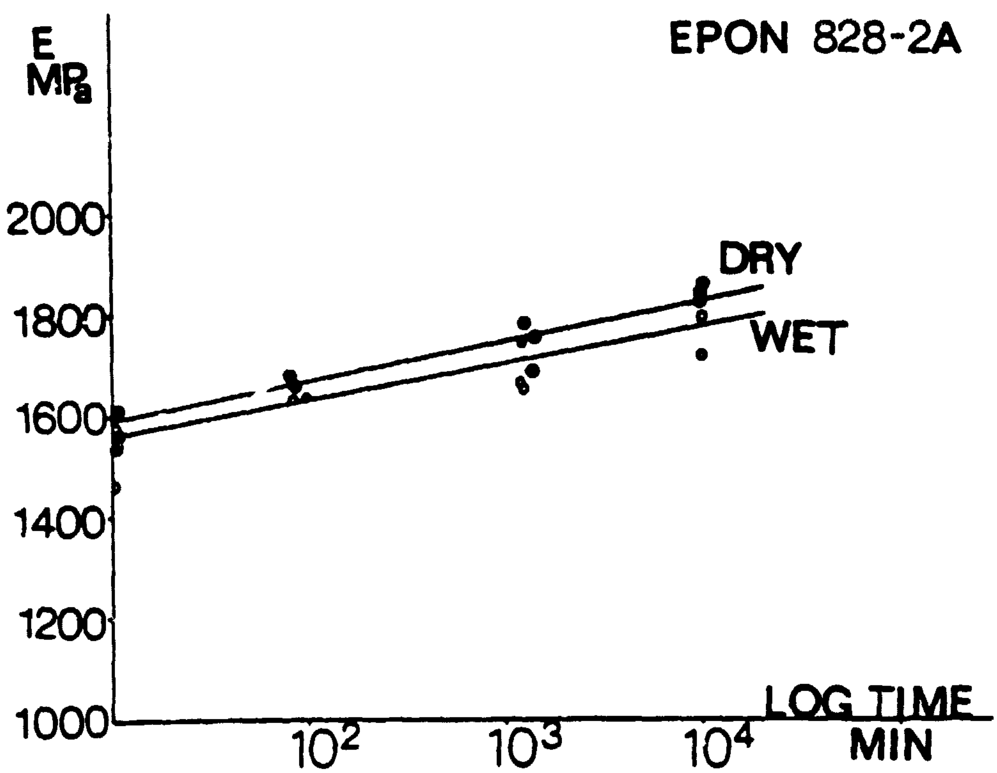

EPON 828-2A
E
MPa
2000
1800
1600
1400
1200
1000
DRY
WET
LOG TIME
MIN
10^2
10^3
10^4

Fig 5

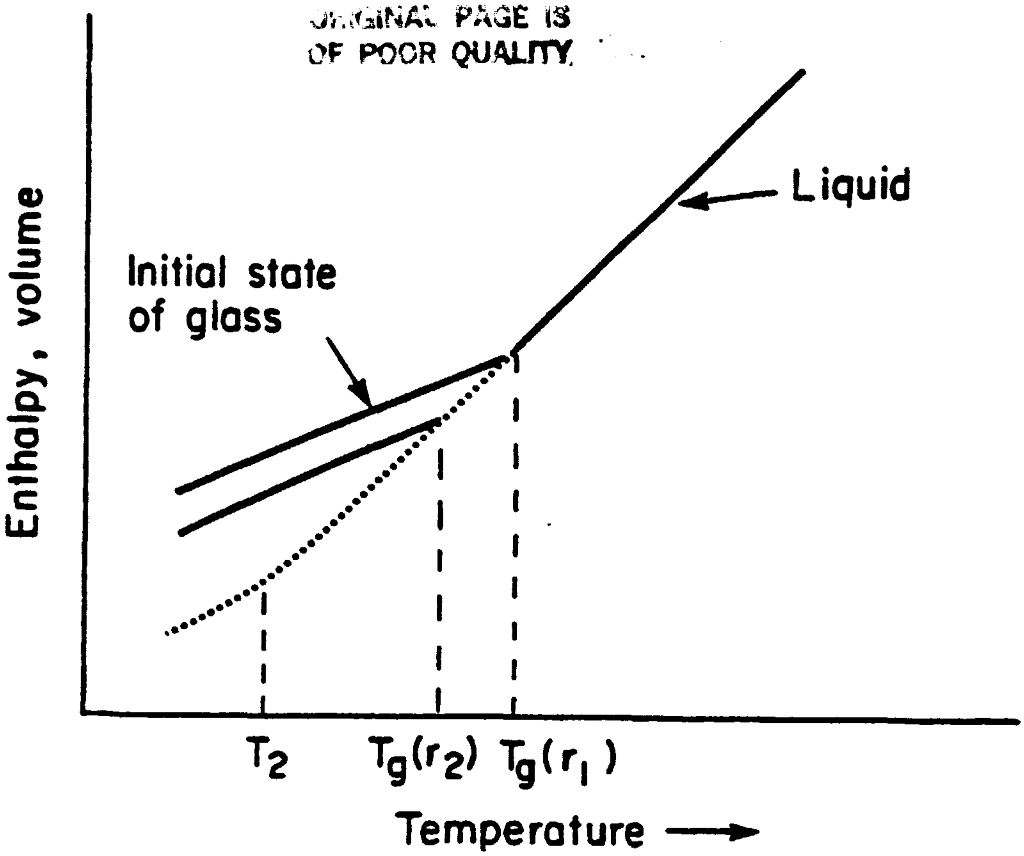

Liquid
Initial state of glass
Enthalpy, volume
T_2
$T_g(r_2)$
$T_g(r_1)$
Temperature →

Fig 6

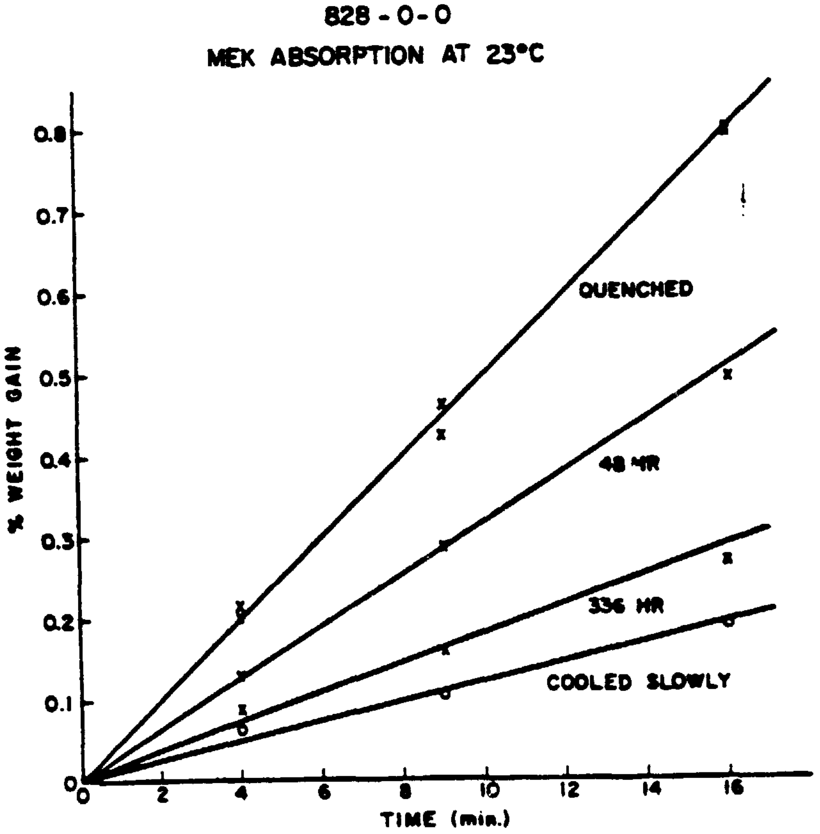

828-0-0
MEK ABSORPTION AT 23°C
% WEIGHT GAIN
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
QUENCHED
48 HR
336 HR
COOLED SLOWLY
0
2
4
6
8
10
12
14
16
TIME (min.)

Fig 7

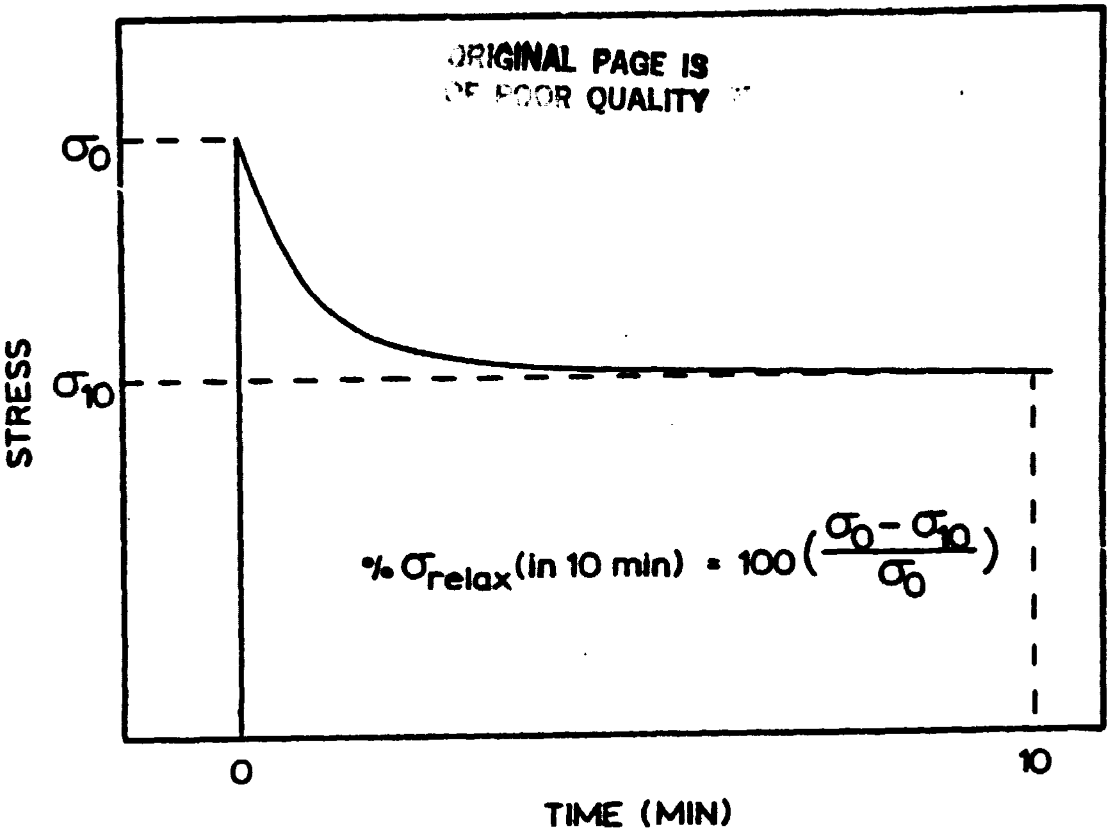

σ_0
σ_{10}
STRESS
$\% \sigma_{relax}(\text{in 10 min}) = 100\left(\frac{\sigma_0 - \sigma_{10}}{\sigma_0}\right)$
0
10
TIME (MIN)

Fig 8

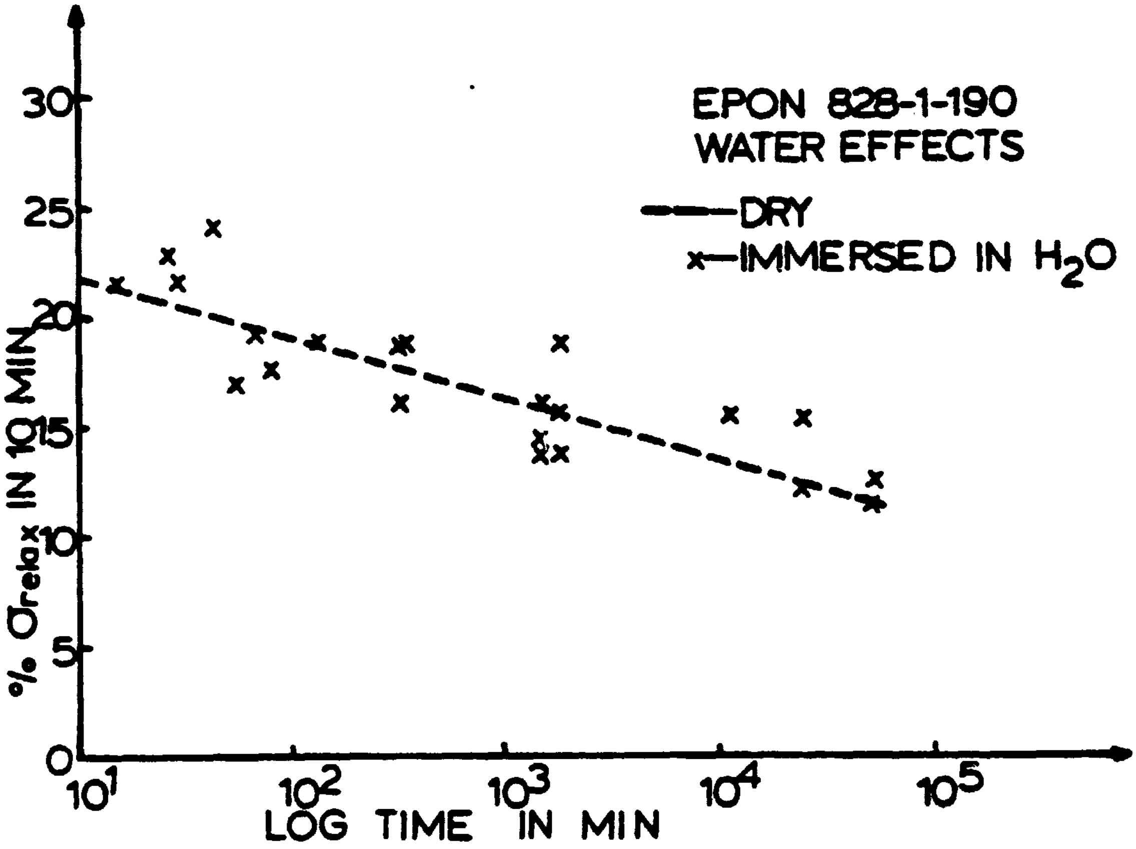

EPON 828-1-190
WATER EFFECTS
DRY
x—IMMERSED IN H_2O
30
25
20
15
10
5
0
% σ_{relax} IN 10 MIN
10^1
10^2
10^3
10^4
10^5
LOG TIME IN MIN

Fig 9

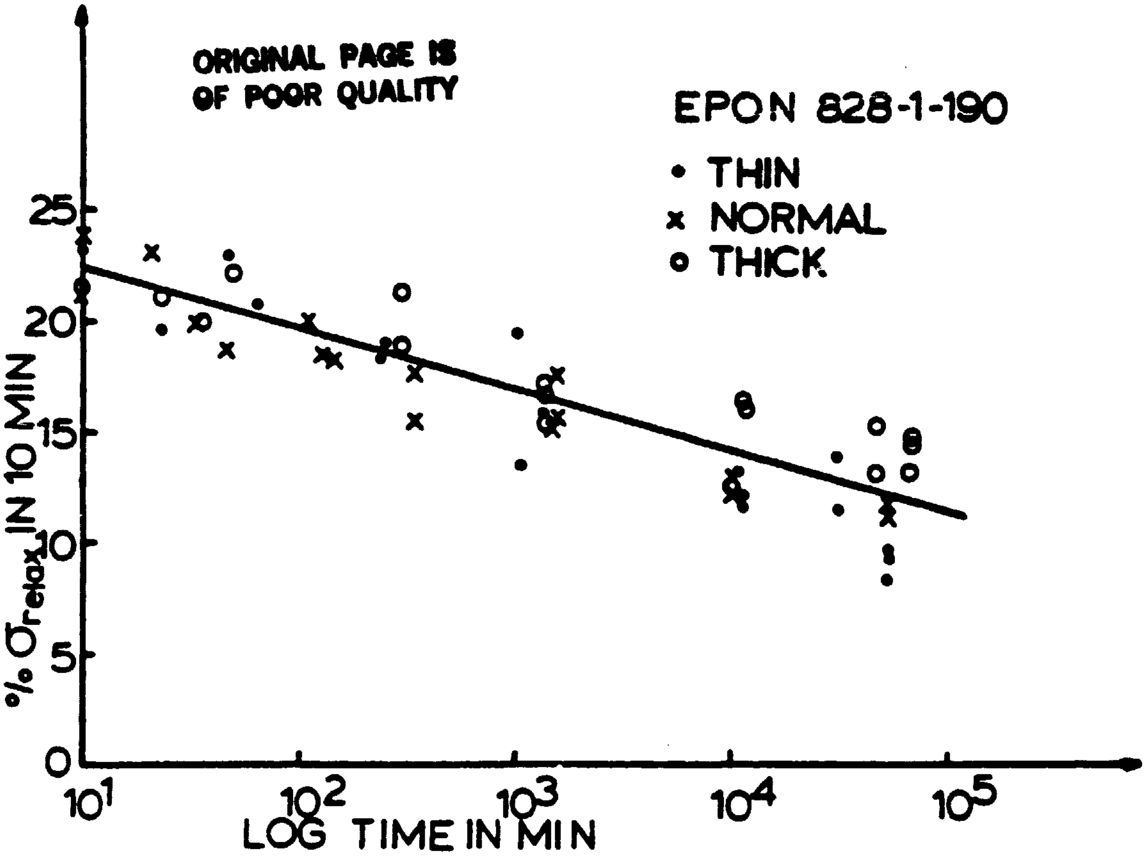
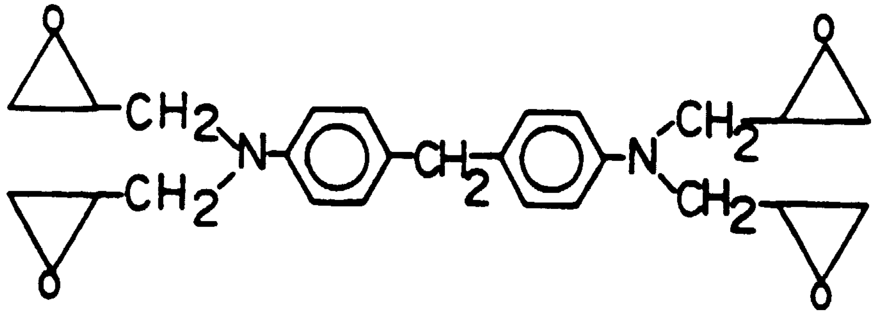
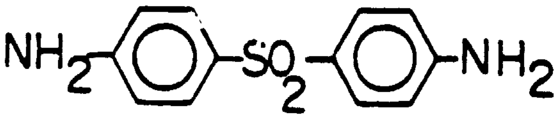


Fig 10

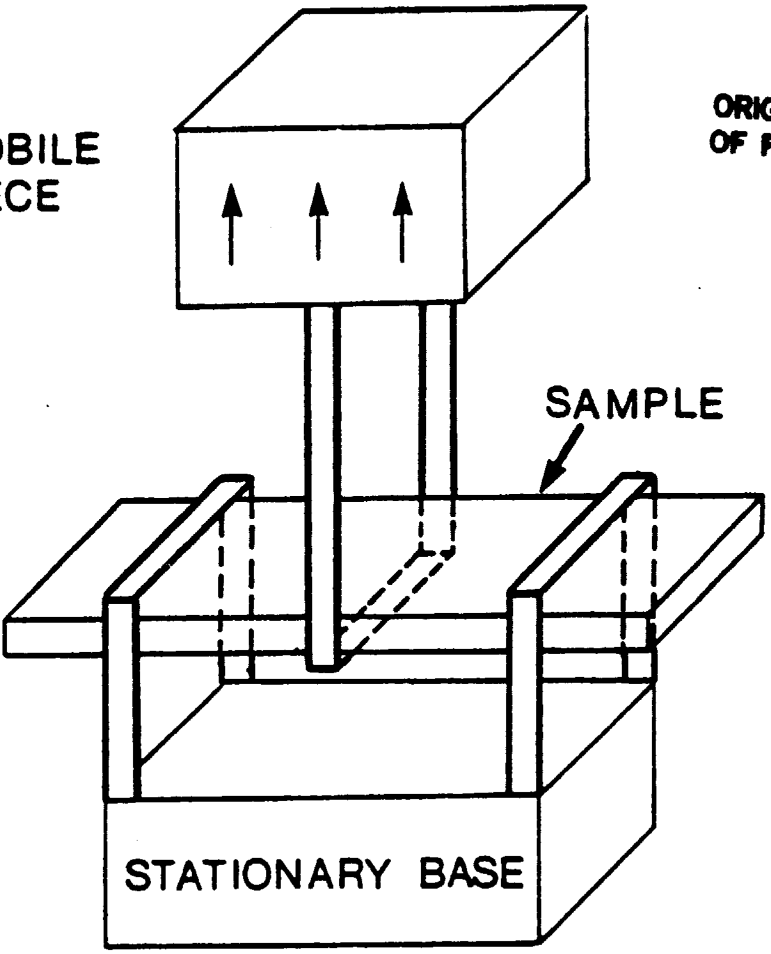
NARMCO 5208





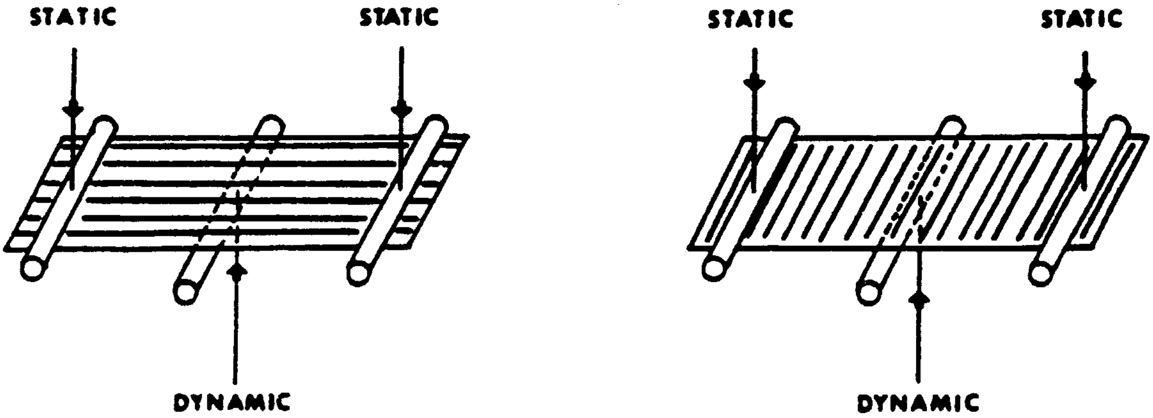
DDS

Fig 11A



FLEXURAL TEST

Fig 11B



Across -- A

Between -- B

Fig 12

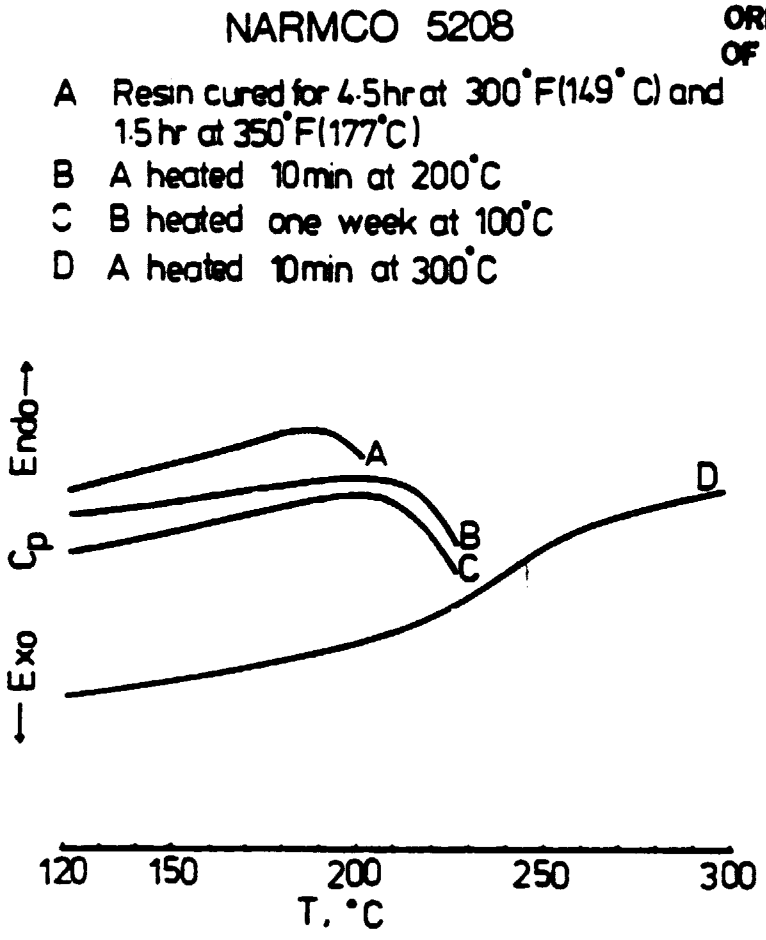

NARMCO 5208
A Resin cured for 4.5hr at 300°F(149°C) and 1.5 hr at 350°F(177°C)
B A heated 10min at 200°C
C B heated one week at 100°C
D A heated 10min at 300°C
Endo→
C_p
←Exo
A
B
C
D
120
150
200
250
300
T, °C

Fig 13

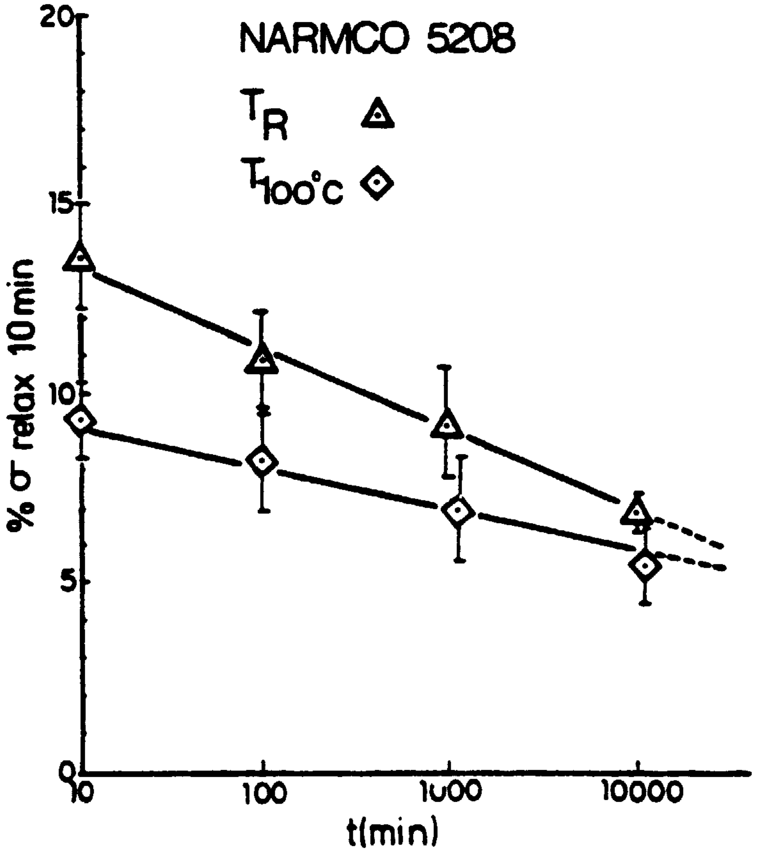

NARMCO 5208
T_R △
$T_{100°c}$ ◇
% σ relax 10min
20
15
10
5
0
10
100
1000
10000
t(min)

Fig. 14

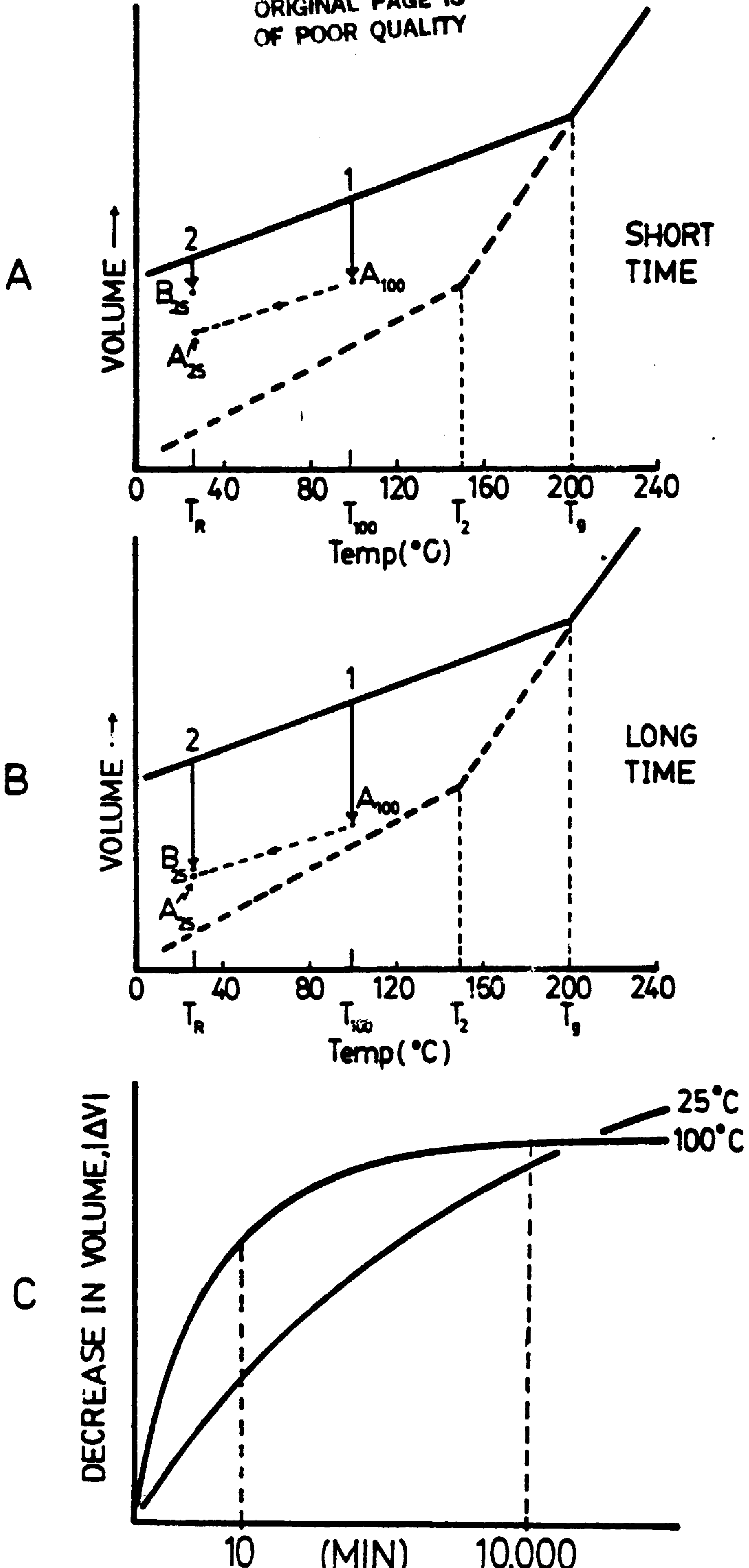

A
VOLUME
1
2
B25
A100
A'25
SHORT TIME
0
40
80
120
160
200
240
TR
T100
T2
Tg
Temp(°C)
B
VOLUME
1
2
A100
B25
A'25
LONG TIME
0
40
80
120
150
200
240
TR
T100
T2
Tg
Temp(°C)
C
DECREASE IN VOLUME, |ΔV|
25°C
100°C
10
(MIN)
10,000

Fig 15

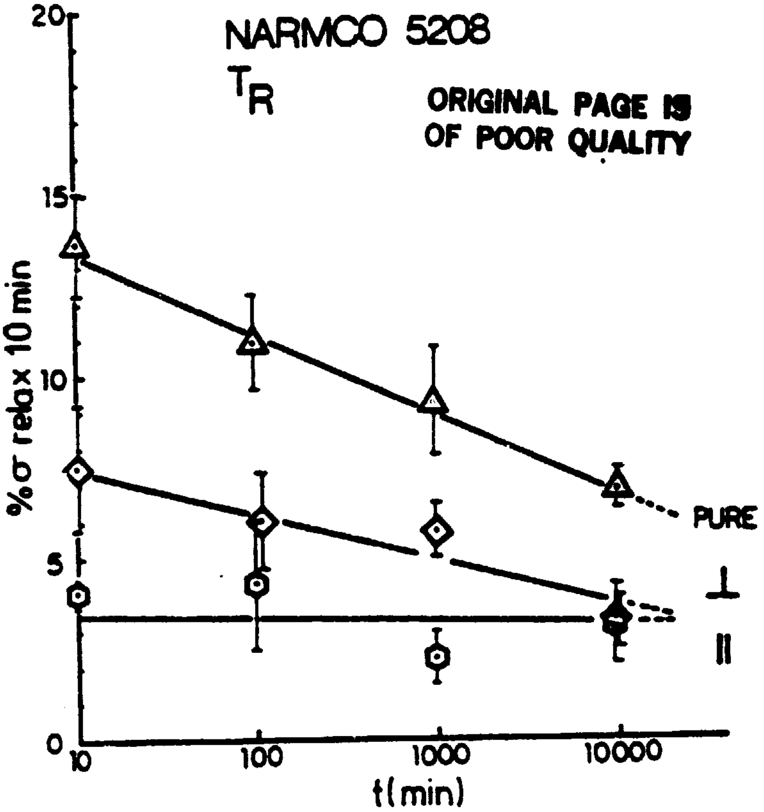
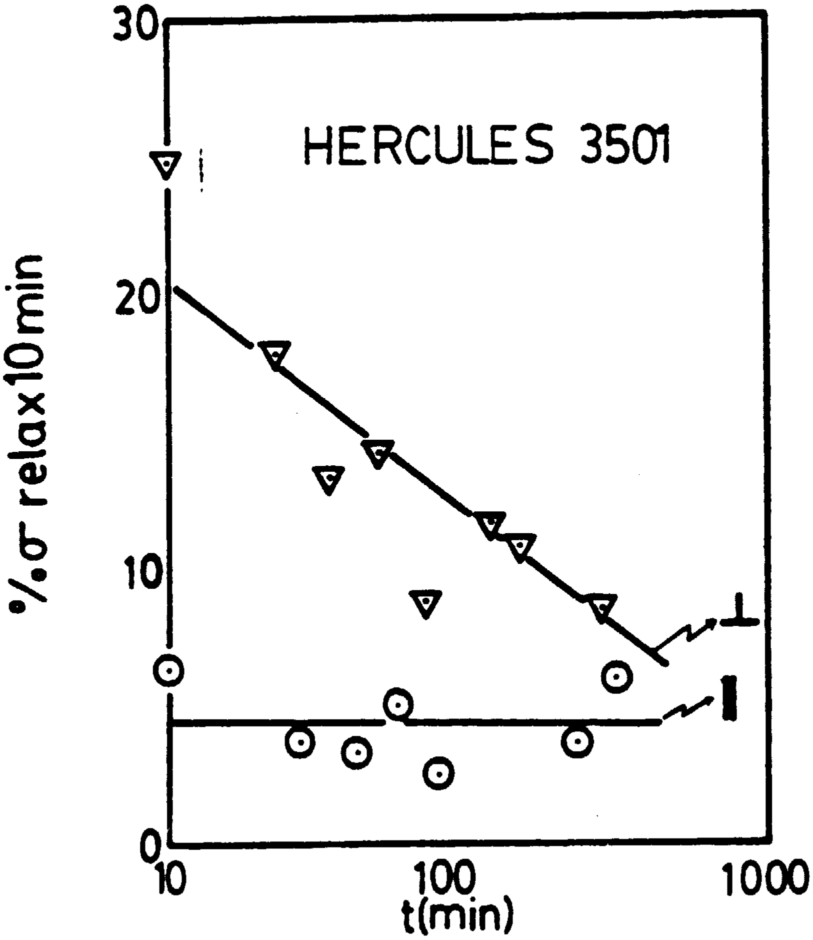

NARMCO 5208
T_R
20
15
10
5
0
%σ relax x 10 min
PURE
⊥
∥
10
100
1000
10000
t(min)

Fig 16


HERCULES 3501
30
20
10
0
%σ relax x 10 min
⊥
∥
10
100
1000
t(min)

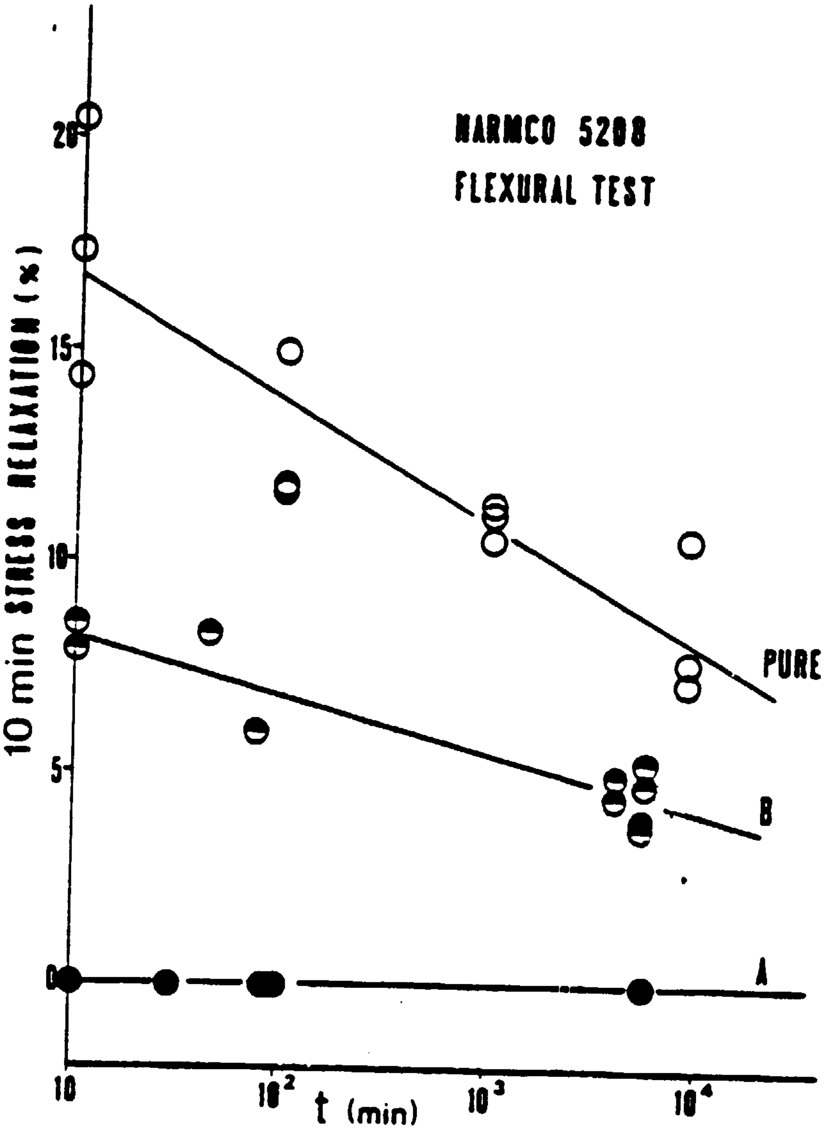

NARMCO 5208
FLEXURAL TEST
10 min STRESS RELAXATION (%)
20
15
10
5
0
PURE
B
A
10
10^2
t (min)
10^3
10^4

Fig 17