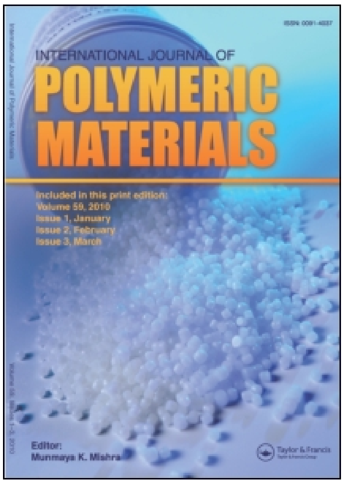

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A. I. Isayev[a]; D. Katz[a]
[a] Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel

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Large Amplitude Cyclic Deformation of a Crosslinked Epoxy Resin in the Transition Zone

A. I. ISAYEV and D. KATZ

Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel

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Absolute values of complex dynamic shear modulus at different frequencies and deformation amplitudes in the transition zone from glassy state to rubbery state were measured for an epoxy resin cured with diethylenetriamine. A sharp decrease of the modulus, truncation of the glassy state region and shifting of the transition zone to lower temperatures have been observed as an effect of large amplitude deformations above certain critical values. The maximum in the modulus values decrease and the minimum of the critical amplitude both take place at glass transition temperature. The values of the maximum and the minimum, as well as the temperature when they occur, depend upon frequency. The transition temperature, determined by the point of intersection of straight lines which express the modulus temperature relation in the glassy state and in the transition zone, can be frequency independent at large deformation amplitudes, contrary to the known behavior of the polymers at small deformation amplitudes. The time required for obtaining the modulus equilibrium value at a given deformation frequency and amplitude was measured. This period decreases by more than three orders of magnitude with the increase of temperature within the transition zone. The observed modulus decrease seems to be due mainly to thixotropic nature of the investigated polymer.

INTRODUCTION

Crosslinked epoxy resins are used extensively as polymer matrices in composite materials, adhesives in aircraft industry, insulators in the large magnetic accelerators and other engineering applications. In many cases epoxy resins are subjected to cyclic loading, varying in a wide range of frequency and amplitude and measurement of dynamic properties is a suitable means to characterize the behavior of the materials in these conditions.

Many studies were devoted to the definition of dynamic properties of the epoxy resin subjected to strains with small amplitudes.[1-12] These investigations were mainly carried out in order to find transition temperatures, the effect of fillers, curing agents and plasticizer concentrations as well as the filler–matrix interaction on the material properties. They serve also to define the influence of environment and heat treatment, as well as the relationship between dynamic properties in torsion, flexure and tension, on static strength of the system.

It can be expected that the properties of an epoxy resin will change at the increase of the deformation amplitude. To the best of our knowledge, existing literature which deals with the effect of large amplitudes on the dynamic properties of polymers, refers to the fluid and high-elastic states of some thermoplastic materials[13-17] and to a few filled and unfilled solid polymers and rubber vulcanizates described in the work of Payne[18] and the monographs of Ferry[19] and Nielsen.[20] Recently, some work was published on the behavior of polymers in their glassy state when subjected to dynamic loading with large amplitudes; the investigated samples were polycarbonate (PC), polymethylmethacrylate (PMMA)[21,22] and a carbon fibre reinforced epoxy resin (CFRE).[10] It was shown for CFRE, that the dynamic properties depend on the amplitude of the shear stress in cracked samples in the whole range of stress amplitudes. In uncracked samples there is no dependence up to a stress of 5×10^7 dyne/cm^2, which is the top limit of amplitude used in this work.

The aim of this study is the definition of viscoelastic behavior of a cross-linked epoxy resin in the transition zone from the glassy to rubbery state at cyclic deformation with large amplitudes. Results of this investigation together with existing literature data for other polymers will contribute to further understanding of the behavior of polymers in their different physical states.

EXPERIMENTAL

Materials and sample preparation

The Epoxy resin used for this study was EPON Resin 826, a product of Shell Chemical Co., cured with diethylenetriamine (DETA), a product of E. Merck. The component ratio of resin to curing agent was 6.75 g to 1 g respectively, as used by Katz and Buchman.[24] The resin and hardener were mixed, degassed in a vacuum chamber for about 15 minutes, and cast into the sample casting mold. The mold containing the mixture was heated for 15 minutes at 35°C and then for two hours at 105°C.

In order to prepare the required sample, a simple device was designed, in which the casting was carried out in a circular clearance, formed between glass surfaces. To avoid sticking of the crosslinked epoxy resin to the glass surfaces, the latter were dipped in a 1/1 mixture of dimethyldichlorsilane/carbontetrachloride, dried afterwards for 15 minutes in air and heated for 4 hours at 150°C.

At the end of the curing process, a tube with dimensions $l = 44$ mm, $R = 4.975$ and $r = 4.025$ mm was obtained. The tube was cut to the length of 16 mm and installed in the grips of the testing apparatus. The internal surface of the grips was coated beforehand with the same resin–hardener mixture and a curing process carried out in the same conditions as those of the sample preparation assured a firm hold of the sample in the grips.

Instrumentation

Dynamic apparatus In order to carry out the study, a special apparatus was designed and built and the diagram of this device is shown in Figure 1. The apparatus consists of a working unit, a thermostat, a system for oscillation recording and an arrangement for change of the environmental conditions. The working unit consists of upper (1) and lower (2) grips, with circular channels 5 mm long, in which the sample (3) is inserted and glued to the internal surfaces of the grips. The length (L) of the working part of the sample

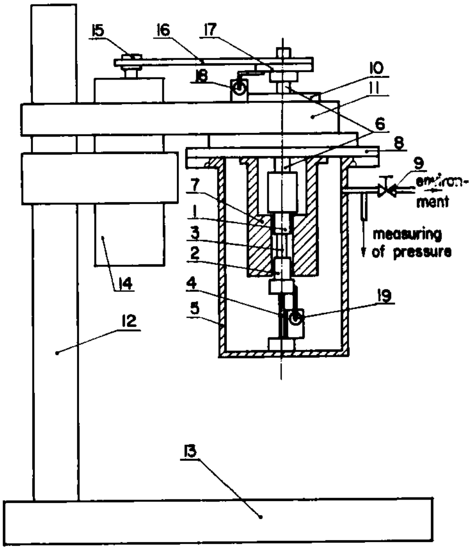

FIGURE 1 Schematic diagram of the dynamic testing apparatus.

is 6 mm, the outer (R) and inner (r) radii of the sample are 4.975 mm and 4.025 mm, respectively. A tubular shape was chosen for the sample in order to ensure the uniformity of deformation and stress through its cross section, a factor which is important when shear oscillation with large amplitudes are induced.[14-16] In the sample of the above mentioned dimensions, the uniformity of the deformation field was higher than 80%.

The lower grip is connected to the upper end of a torsion bar (4), which has a constant rigidity of 80 Nm/rad. and the lower end of the torsion bar is fastened to the bottom of the vessel (5). The axial arrangement of the working unit is ensured by installing a travelling shaft (6) instead of the lower grip.

The thermostating system consists of a compact electric oven (7), located inside the vessel (5) and fastened to the flange (8) of the apparatus. An Eurotherm temperature controller keeps the temperature constant within $\pm 1°$C.

The system for the environment variation consists of the vessel (5), which can be connected through a valve (9) to a vacuum pump on the outside atmosphere, or to an inert or another gas supply. The sealing of the travelling shaft (6) is ensured by use of an Edwards vacuum seal shaft (10), fixed to the flange (8). The flange is inserted in a holder (11) attached to the column (12). The base (13) is equipped with dampers.

Forced harmonic oscillations are induced by means of a motor (14) and an eccenter mechanism, which transforms the rotary motion of the motor into oscillatory motion of the upper grip of the sample. The motor with a speed controller was manufactured by the Minarik Electric Company. The eccenter mechanism consists of a removable eccenter (15) and a lever (16) connected with the shaft (6) through flange (17). The frequency (ω) of the oscillation can be smoothly varied between 1–40 Hz and the amplitude discreetly changed in the range 4×10^{-4} to 4×10^{-2} rad.

The oscillations are recorded with the aid of two displacement transducers (18, 19), made by Hewlett Packard. The transducers are connected to the upper and lower grips of the sample, respectively and the signals are displayed on an oscilloscope screen.

The dynamic properties, namely the absolute value of the complex dynamic shear modulus $|G^*|$, the storage modulus G' and the loss modulus G'' are determined by the following equations,[15] used for a tubular sample:

$$|G^*| = \frac{\tau_0}{\gamma_0} = \frac{(C - Iw^2)\theta_1}{\pi\gamma_0(R^2+r^2)(R-r)} \tag{1}$$

$$G' = \frac{\tau_0(\theta_2 \cos\phi - \theta_1)(R+r)}{2L\gamma_0^2} \tag{2}$$

$$G'' = \frac{\tau_0\theta_1 \sin\phi(R+r)}{2L\gamma_0^2} \tag{3}$$

where τ_0 and γ_0 are the amplitudes of the stress and of the deformation, respectively, θ_1 and θ_2 are the amplitudes of the oscillation of the lower and upper ends of the sample, respectively, ϕ is the phase angle between the oscillations of the upper and lower ends of the sample, I is the inertia moment of the lower grip, which is 1.3×10^{-5} kgm^2, R and r are the outer and internal sample tube radii and L is the sample length between grips.

The deformation amplitude is determined by the formula for the addition of harmonic oscillations:

$$\gamma_0 = \frac{R+r}{2L}(\theta_1^2+\theta_2^2-2\theta_1\theta_2 \cos \phi)^{\frac{1}{2}} \tag{4}$$

The following experimental procedure was applied for testing of the samples: while a harmonic torsion oscillation with a constant frequency and amplitude was imposed on the upper end of the sample, the oscillation amplitudes of the upper and lower ends of the sample (θ_1 and θ_2) and the phase angle between them were measured. Equations (1)–(4) were used to calculate the dynamic properties.

Analysis of crosslinking density

By use of the Cluff–Gladding–Pariser method,[23] the average molecular weight of the resin network chain M_c was calculated from results obtained in compression testing of the strained and unstrained samples swollen to equilibrium. The swelling was carried out at room temperature in 1 : 1 acetone/water solution.

Microscopic observation

In cases of fracture of the sample photomicrographs of the fracture surfaces were prepared by use of an Electron Scanning Microscope JSM–U3 JEOL, Japan. The fracture surface of the sample was coated in vacuo with a thin layer of Pd–Au, prior to the introduction into the microscope.

RESULTS AND DISCUSSION

A. Linear behavior

In order to understand the processes which are taking place in the material subjected to cyclic deformations with large amplitudes, it is necessary to know the temperature ranges of the basic physical (rheological) states of the material. This can easily be attained in most cases by interpretation of results obtained from dynamic measurements, when small amplitudes are applied and when the polymer structure remains unchanged during the experiment. Because of experimental difficulties to distinguish between the real and imaginary components of the complex dynamic shear modulus G^*, which are due in our investigation to errors in the definition of the phase angle between stress and strain, only the temperature dependence of absolute values of $|G^*|$ was investigated in this study. Data for four frequencies: 1, 10, 20 and 40 Hz are presented in Figure 2 for the region of the linear behavior of the material. For cases in which the linear range could not be defined due to experimental limitations, values of $|G^*|$ were determined from amplitude dependence of the logarithms of $|G^*|$; this was done by extrapolating values of the latter obtained at the lowest deformation amplitudes, to the zero amplitude. As it can be seen in Figure 2 the behavior of the material was different in two temperature ranges. In low temperatures, when the polymer was in its glassy state, the value of $|G^*|$ was almost temperature independent and it did not change significantly with frequency within a wide range of frequencies. At higher temperatures, a marked transition zone between the glassy state and the rubbery region can be seen. In this zone, with the increase of temperature a sharp fall can be observed in the values of $|G^*|$ and a small shift of the curve $|G^*|$ versus T occurs in the direction of higher temperatures with the increase of loading frequency. A change in frequency by a factor of

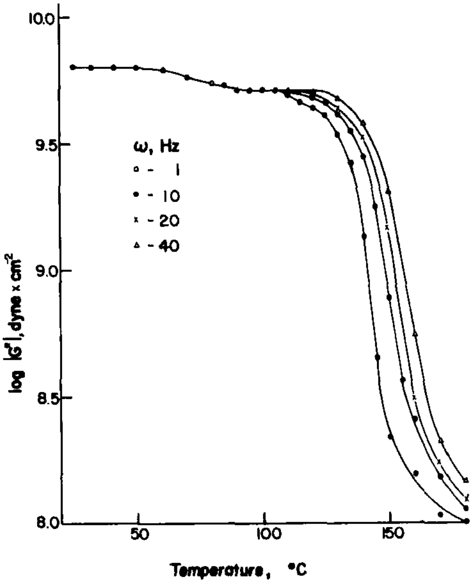

FIGURE 2 Dependence of absolute values of complex dynamic shear modulus $|G^*|$ in the range of linear behavior on temperature at different frequencies for the EPON Resin 826–DETA system.

40 caused a shift of the transition zone of the epoxy compound by approximately 12°C. This result is in good agreement with the accepted empirical rule, which says, that an increase in frequency in dynamic measurements by one decade leads to a shift of the transition zone by approximately 7°C.[25] It can be seen, that the transition zone, which is of particular interest in our study extends to temperatures above 110°C. Preliminary experiments, carried out with deformation amplitudes increasing up to 2% showed at lower temperatures no dependence of the values of $|G^*|$ on γ_0, which is in full agreement with the results of the work of Adams *et al.*[10]

B. Non-linear behavior

Transition process In most general conditions, when dynamic loadings with large amplitudes were applied to the polymers, the values $|G^*|$ of the material were a function of four variables: frequency ω, deformation amplitude γ_0, time of the applied deformation t and temperature T. In order to understand the behavior of the material in its transition zone, when it was subjected to the action of cyclic strains with large amplitudes, it is necessary first to clarify the role of the time factor in the experiment. This approach presents the possibility to consider the equilibrium states of the material only. The amount of information in literature which deals with the above problem is, to the best of our knowledge, not systematic and some of the data are contradictory. For example, in the work carried out on polymethylmethacrylate (PMMA) and polycarbonate (PC) in their glassy state[21] the transition process, till the polymer reached an equilibrium state lasted at least half an hour from the moment of the stress application. In another investigation of PC[22] in its glassy state, it took only 4 minutes to complete the same process. In a work by Maxwell and Guimon[26] devoted to the determination of the limit of linear viscoelasticity for different polymers in their glassy state when subjected to flexure oscillations, the existence of a transition process was not mentioned at all. Based on data by Faytelson and Tsiprin[13] for filled polyethylene melts the transition period is one minute. According to other sources for thermoplastics in their fluid and high elastic state[14,15] and for vulcanized rubber[7] the above mentioned transition process does not exist; this is probably due to the fact that the transition process ended during the first oscillation cycles and was not observed.

Data regarding the duration and nature of the transition process caused by the action of cyclic deformation with large amplitudes, as observed in our study of the investigated epoxy compound, is presented in Figure 3. It shows the relation between values of $|G^*|$ and time of the applied cyclic deformation, for different temperatures, frequencies and deformation amplitudes. It follows from Figure 3, that for each frequency and amplitude,

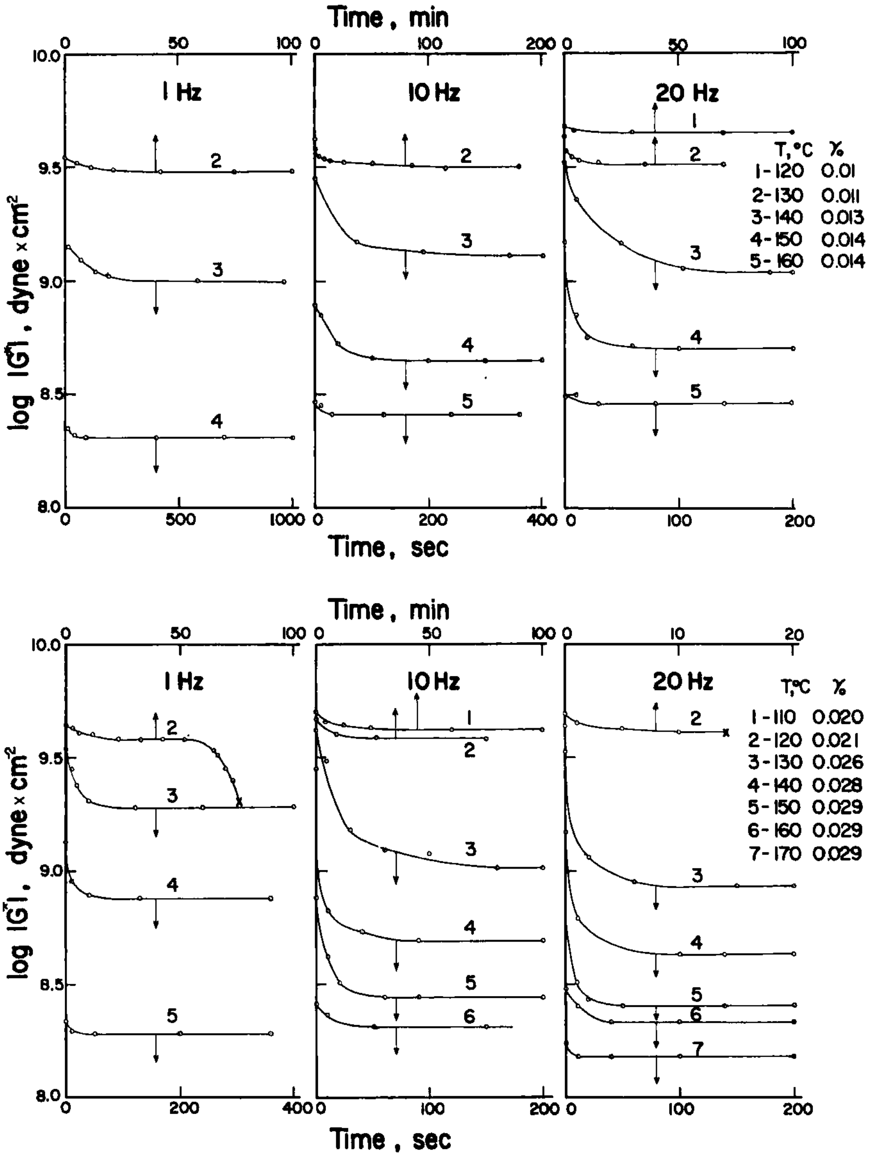

FIGURE 3 Dependence of value $|G^*|$ on time of applied deformation at different temperatures, frequencies and deformation amplitudes.

an equilibrium value of $|G^*|$ exists at a certain temperature. The most considerable changes of the values of $|G^*|$ are observed in the initial period of loading. Later these changes are diminishing and eventually the value of $|G^*|$ reaches an equilibrium. It is difficult to determine the time t_s required for reaching the equilibrium values of $|G^*|$; however, we attempted to do it and obtained a semi-quantitative dependence between the time t_s, and the reciprocal value of temperature at two deformation amplitudes in the frequency range 1–20 Hz (Figure 4). A considerable scattering of data can be seen, a fact which is caused by error in the definition of t_s and probably also by the statistical dispersion in the occurrence of the transition process.

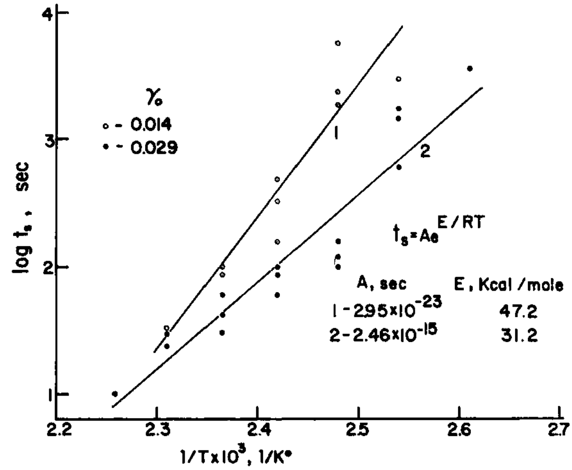

FIGURE 4 Dependence of duration of the transition process on reciprocal values of temperature at two deformation amplitudes in frequency range 1–20 Hz.

Lines 1 and 2 in Figure 4 represent values calculated according to the method of the last squares. As seen in Figure 4, the frequency of oscillation in the range of 1–20 Hz does not influence the duration of the transition process, while the deformation amplitude affects it. When the deformation amplitude is small, the transition time t_s becomes relatively long. However, the temperature is a very essential factor in this process and it affects exponentially the duration of the transition process. In the temperature range 110–170°C, which corresponds to the transition region from glassy to rubbery state, the values of time t_s may change by 3 decades; from ten minutes for lower temperatures to a few seconds at higher temperatures. Hence, it becomes clear why in investigations dealing with the effect of large amplitudes on properties of polymeric systems in their fluid and rubbery states, no attention was paid to the time dependence of the transition processes: in those physical states the differences in the transition period may become unnoticeable during the first cycles of oscillation. On the other hand, as seen in Figure 4 while approaching the glassy state, the investigated transition period t_s extends for tens of minutes. The existence of longer transition periods can be attributed to small changes occurring in the physical structure of the polymer and to the essential moderation of the relaxation processes in the material in the glassy state, due to relatively slow response of the macromolecular chains.

It can be assumed, that the observable effects of the reduction of modulus $|G^*|$ are mainly of thixotropic nature. When samples previously subjected to large amplitude deformations were subjected again after certain periods of rest to small strains at the same frequency the value of $|G^*|$ was almost fully recovered. The measurement of molecular weight between crosslinks, M_c, executed according to the Cluff–Gladding–Pariser method showed for samples with a dynamic loading history, as compared with samples which were not deformed, an increase in M_c up to 10% only, which is within the error range of the experiment. In some cases, which are marked on Figure 3 by crosses at the low temperatures ($\leqslant 120°C$) shear fracture has been observed on the samples (Figure 5a). Typical photomicrograph of a fracture sample surface obtained by means of optical and scanning electron microscopes are shown in Figures 5b and 5c. The rupture occurred at the angle of 45°C to lateral axis of the cylindrical surface of the sample, as well known phenomenon characteristic for shear rupture of materials.[27] Fracture surfaces covering all the length of the sample between the grips were noticed in these cases. At the moment of fracture, a distortion in the sinusoidal shape of the stress-time curve was observed on the scope. The problem of shear fatigue of epoxy compounds demands additional investigation and in this work it was not considered. At temperatures above 130° C no sample failure was observed, and this can be probably attributed to the easiness of "defects healing" due to softening of the material subjected to deformation and which has shorter relaxation times in these temperatures.

Equilibrium properties

In order to investigate the nature of the equilibrium modulus $|G^*|$, its dependence on deformation amplitude, frequency and temperature was studied. In Figure 6, which presents the experimental results, two ranges of viscoelastic behavior of the polymer can be distinguished: a linear one, corresponding to small deformation amplitudes and a nonlinear one—for large amplitude deformations. It can be seen that in the nonlinear range, the value of $|G^*|$ decreases significantly by more than an order of magnitude, at deformations of 0.02–0.03. This is an undesirable effect, since it may cause considerable creep of the materials as a result of simultaneous action of

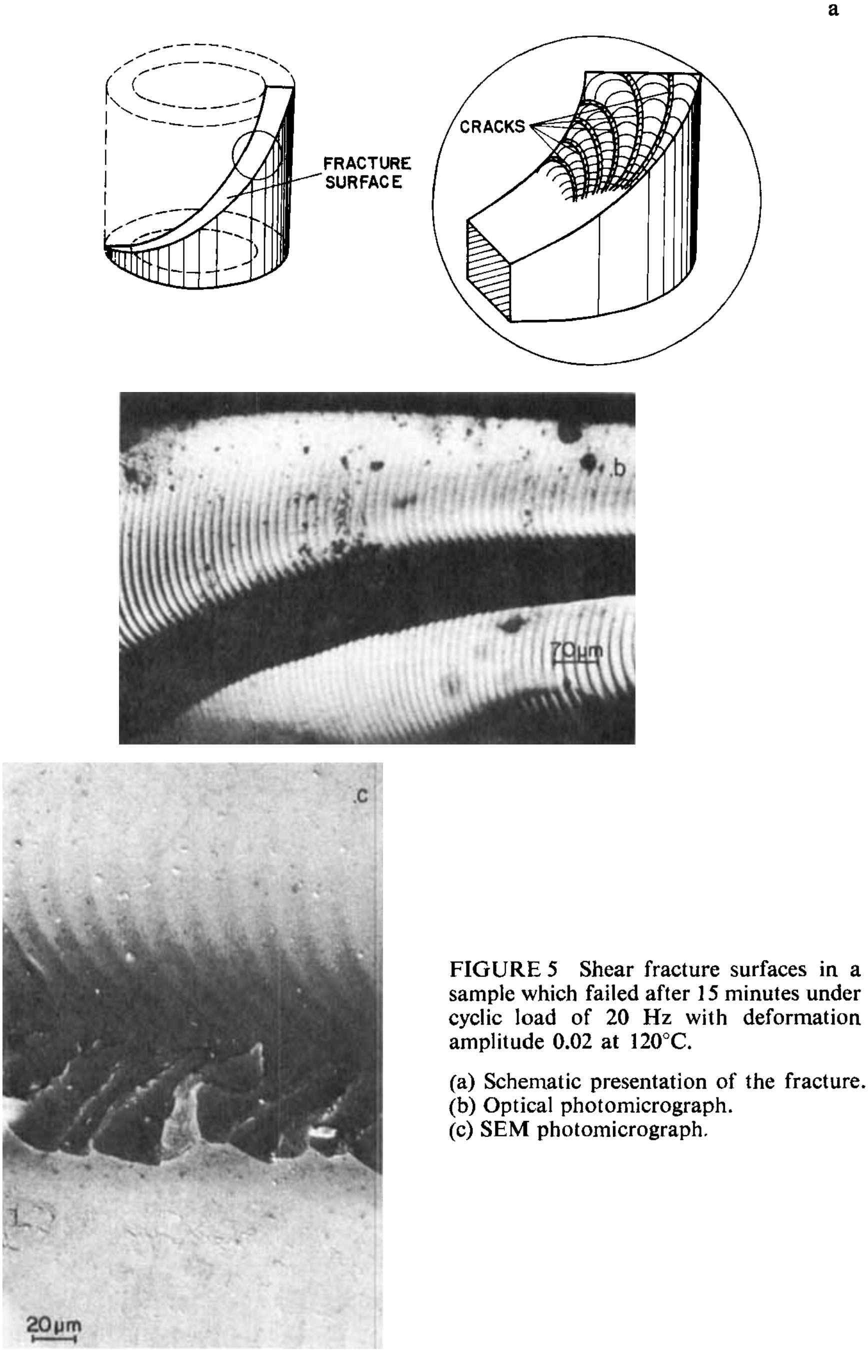

FIGURE 5 Shear fracture surfaces in a sample which failed after 15 minutes under cyclic load of 20 Hz with deformation amplitude 0.02 at 120°C.

(a) Schematic presentation of the fracture.
(b) Optical photomicrograph.
(c) SEM photomicrograph.

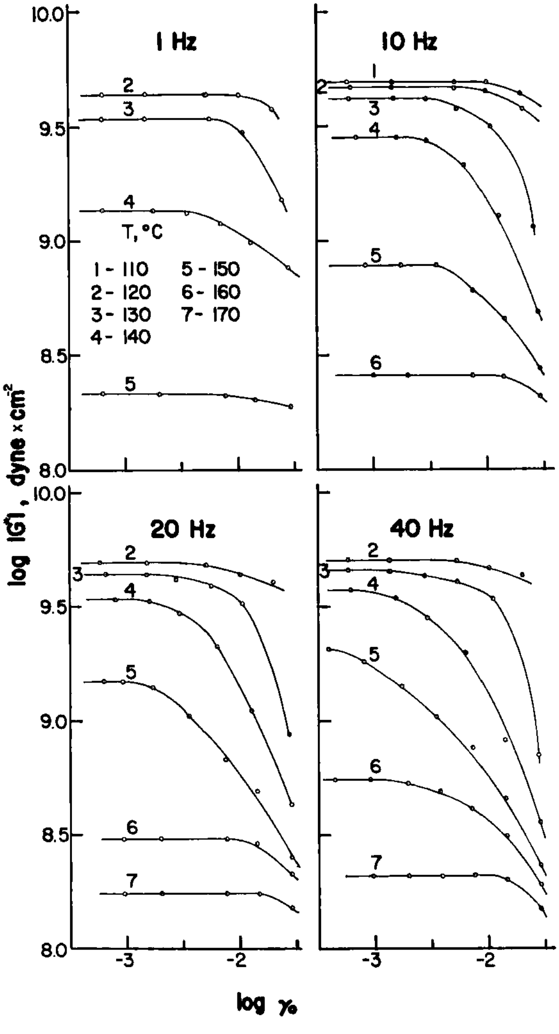

FIGURE 6 Dependence of the value $|G^*|$ on deformation amplitude at different temperatures and frequencies.

static and dynamic loads and failure may occur. Apparently, this effect is not due to shear heating of the material. As shown by Davis and Macosko,[21] at the deformation amplitude of 0.04, the maximum temperature rise was less than 2°C for PMMA and 1°C for PC. It follows from the data presented in Figure 6, that as a result of cyclic deformation the transition region between the glassy and rubber state can shift. This change in the location of transition region is clearly seen in Figure 7, in which the temperature

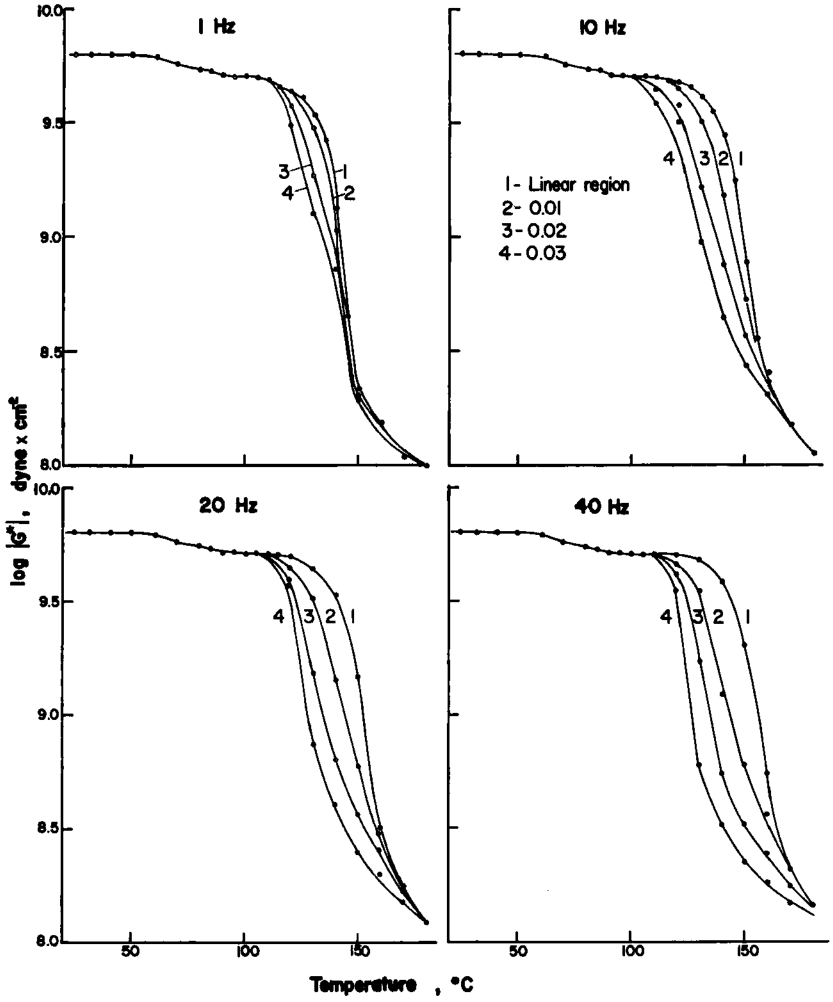

FIGURE 7 Temperature dependence of value $|G^*|$ at different deformation amplitudes and frequencies.

dependence of the modulus $|G^*|$ at different deformation amplitudes and frequencies is presented. The most important result seems to be the fact that at large deformation amplitudes, the shift of the whole transition zone occurs in the direction of lower temperatures probably due to softening of the materials because of the breakdown of some physical bonds in the network structure. In other words, the large deformation amplitude truncates the glassy state of the epoxy compound and consequently restricts the temperature range of the material usability. Those amplitudes, large enough to affect the nature of the transition region close to T_g, were not sufficient to introduce serious changes in the behavior of the polymer in its transition region close to its rubbery state. It is known,[15] that an observable change in dynamic properties of a polymer in its rubbery state requires deformations of at least a few tens of percent. Similarly, for polymeric systems in fluid states, the limit to linear behavior is set by deformation amplitudes of unit.[14-17] It is clear, from what was said above, that the definition of large amplitudes must be related to the physical state of the polymer and for different physical states, the limit of linear behavior shown by the material subjected to oscillatory loadings can shift a thousand and more times on the deformation scale.

Relation between T_g and material sensitivity to deformation amplitudes

There are two possibilities for evaluation of the material sensitivity to cyclic deformations. The first one is to define it by means of the critical deformation amplitude γ_0^{cr}, at which the transition from linear to nonlinear range of deformation occurs. However, because the characteristic point of transition can not be defined well enough when the dependence of dynamic characteristic on deformation amplitude is investigated, the usually accepted γ_0^{cr} is the deformation amplitude, at which a certain property has changed by a small percent. For instance, in the work by Davis and Macosko,[21] the value γ_0^{cr} was chosen as equal to γ_0 at a dynamic modulus change of 5%. In our investigation, the value γ_0^{cr} was assumed to be equal to γ_0 when the modulus $|G^*|$ was reduced by 10%.

The second possibility is evaluation of the relation between two values of $|G^*|$ measured at two markedly different deformation amplitudes. The sensitivity of the material to cyclic deformation was found by the use of data describing the ratio between the modulus $|G^*|$ measured in the linear range and at a deformation amplitude equal to 0.03. In one of the earlier works,[21] the sensitivity of a polymer was evaluated by presenting its dynamic characteristics in the nonlinear range in the form of series including even powers of the deformation amplitude. In this case, because of small nonlinear effects, consideration of only two terms of the series—zero and square of the deformation amplitude gave satisfactory results. We had also made an attempt to calculate the value $|G^*|$ by the same approach, but because of the more appreciable nonlinear behavior of the system used in our study, even the terms of fourth power series of deformation amplitude are insufficient to describe the nonlinear effects. Therefore, this approach was discarded and the sensitivity of the epoxy system to deformation amplitude was studied by investigation of the relation between the values of the moduli in the linear and nonlinear range. Figure 8 shows temperature dependence of the critical deformation amplitude γ_0^{cr} and of the ratio $K = |G^*|_l/|G^*|_n$ at different frequencies of loading, where $|G^*|_l$ and $|G^*|_n$ are values of $|G^*|$ in the linear ($\gamma_0 \to 0$) and nonlinear ($\gamma_0 = 0.03$) ranges, respectively. Functions $\gamma_0^{cr}(T)$ and $K(T)$ pass through minimum and maximum, respectively. The minimum value of the function $\gamma_0^{cr}(T)$ decreases and the maximum of $K(T)$ grows with the increase of loading frequency. It should be noticed that the values of γ_0^{cr} in the range of the minimum of the function $\gamma_0^{cr}(T)$ are very small; for example, the minimum value of γ_0^{cr} at a frequency of 40 Hz is less than one thousandth. The temperatures of the minima and maxima in Figure 8 increase with the frequency increase, similar to the case in which the dependences $|G^*|$ vs. T in the linear range of the polymer were studied as a function of the increase of frequency (see Figure 2). It seems reasonable to define the temperature corresponding to the minimum and maximum on Figure 8 as the glass transition temperature T_g of polymers. Data obtained by use of dynamic measurements at small amplitudes shows that this temperature corresponds to the maxima of the loss modulus G'' of the tangent mechanical loss angle. It is well known that the value T_g in this case depends also on the loading frequency. Evidently, in the glass

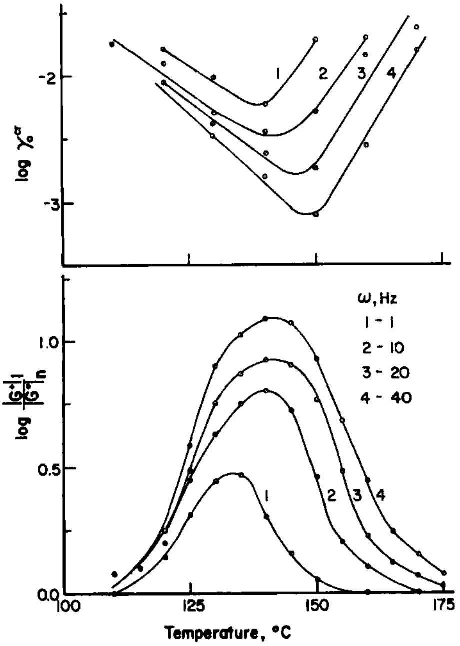

FIGURE 8 Temperature dependences of the critical deformation amplitude and of modulae ratio at different frequencies.

transition region relaxation processes exist, which depend on the contribution of two types of structural motions: a segmental motion in the same polymeric chain and a motion of separate chains of the polymer. A cyclic deformation in the glass transition point affects both relaxation processes and because of that, minimum and maximum appear on the curves of $\gamma_0^{cr}(T)$ and $K(T)$ described above. Evidence that the maximum was due to glass transition temperature of the polymer may be found in the work of Davis and Macosko,[21] in which uncrosslinked polymers were subjected to dynamic

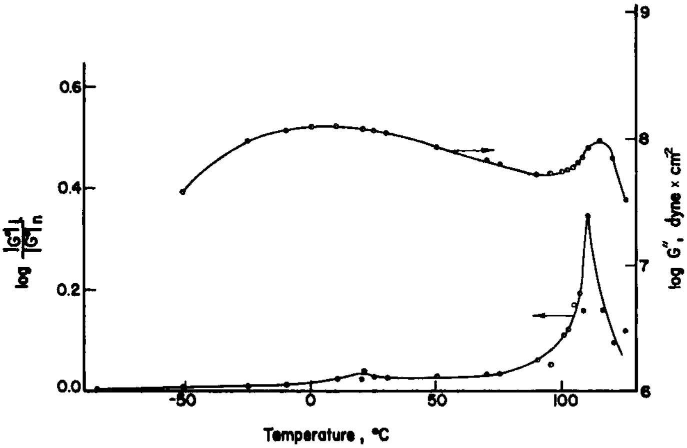

FIGURE 9 Temperature dependences of the loss modulus in the range of linear behavior and of modulae ratio at frequency 1 Hz for PMMA (data from work[21]).

strains with large amplitudes over an extensive temperature range. The results of this work on PMMA were elaborated in the way suggested above and they are shown in Figure 9. Not as in the original study by Davis and Macosko, we assumed that the index of sensitivity of the material to cyclic deformation can be expressed by the relation $K = |G^*|_l/|G^*|_n$, where $|G^*|_n$ was the value of complex modulus in the nonlinear range at $\gamma_0 = 0.02$. The pronounced maximum of the function $K(T)$ was observed at the temperature corresponding to the maximum of the loss modulus in the linear range. This fact can be seen as a proof that the minimum and maximum of functions $\gamma_0^{cr}(T)$ and $K(T)$ correspond to the glass transition temperature. The results mentioned above agree with the following facts: the maxima in nonlinearity in creep experiments[28] and in loss modulus[22] occur for PC at its glass transition temperature and γ-peak, respectively; maximum frequency sensitivity of the fatigue crack propagation at the β-peak of the polymer.[29]

The fact that the maximum in the function $K(T)$ appears at the glass transition temperature provides a method to measure the value of T_g of polymers. The measurement of T_g consists of two stages: first, determination of the temperature dependence of the modulus $|G^*|$ at two markedly different deformation amplitudes at the same loading frequency and second, determination of the position of the maximum on the curve which describes the modulus ratio versus temperature. When rigid dynamometric devices are used the definition of phase angles between stress and deformation is not necessary. Application of this method presents a certain advantage because the resolution increases with the increase in frequency of the applied strain. The value of the maximum of the function $K(T)$ increases, but at small amplitudes the maximum of the function $\tan \delta(T)$ decreases with increasing frequency. Because, as mentioned before, the effect of amplitude on the polymer in the transition zone seems to be of thixotropic nature and is recoverable, all the measurements can be produced on one sample if the resting time of the sample between experiments is long enough. While executing these measurements, small deformation amplitudes should be applied during the heating cycles and large ones when the sample is cooled down.

Reduction of transition temperature

It was mentioned before, that while frequency increased at small deformation amplitudes, a shift of transition zone occurred towards higher temperature (Figure 2). Results of Figure 6 show that at large amplitudes, the transition zone shifted in towards lower temperatures. This shift grows with the increase of the value γ_0. It is interesting to consider the dependence of transition temperature upon frequency for different values of deformation amplitudes (Figure 10). The transition temperature T_t was determined by the point of intersection of the straight lines which can be drawn on the curve describing the dependence of $|G^*|$ versus T (Figure 7) through the glassy region and through the transition zone. It can be seen from Figure 10 that with the

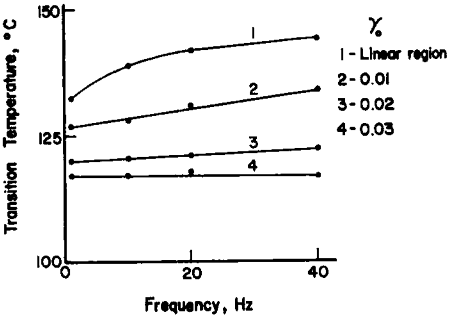

FIGURE 10 Frequency dependence of the transition temperature at different deformation amplitudes.

increase of deformation, the frequency dependence of T_t decreases and finally vanishes. Considering this fact, it seems to us that the magnitude of deformation influences the frequency dependence of the transition temperature from glassy to rubbery state, similarly to the effect known for transition from rubbery to fluid state.[15] The largest reducing effect of T_t was found to be approximately 28°C at the frequency of 40 Hz and at a deformation amplitude of 0.03. The phenomenon of material softening due to cyclic deformation with large amplitudes, which seems to correspond to the lowering of the glass transition temperature in polymers, subjected to steady stresses[30] and those with residual stresses,[31] has to be considered when they are used in components subjected to dynamic loadings.

CONCLUSION

This work seems to be the first investigation of viscoelastic behavior of a crosslinked polymer at large deformation amplitudes in the transition zone from glassy to rubbery state. The value of the modulus $|G^*|$ of crosslinked polymers is sensitive to cyclic deformation amplitudes particularly at the glass transition temperatures. In the transition zone, a process leading to an equilibrium state characteristic for the frequency and the amplitude of loading can be observed. This process was detected by determination of dynamic properties of the polymer until the equilibrium value at a given amplitude and frequency of loading was reached. The duration of the transition process is exponentially related to the reciprocal value of temperature and extends from tens of minutes to a few seconds.

There is a possibility to define the glass transition temperature while applying cyclic deformations, by measurement of the temperature dependence of the relation between the equilibrium values of moduli $|G^*|$ at two markedly different amplitudes. In this experiment, the glass transition temperature is determined by a peak in the above relation and there is no necessity to measure the phase angle between deformation and stress.

Cyclic deformation imposed on the crosslinked polymer cause truncation of its glassy region. The effect becomes more pronounced with increase of deformation amplitudes. The transition temperature from the glassy state to the transition zone ceases to depend upon frequency when large loading amplitudes are used contrary to the well known situation in which the transition temperature increases with the increasing frequency of application of small amplitude stresses.

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