Rejuvenation and physical ageing of a polycarbonate film subjected to finite tensile strains*

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Differential storage and loss tensile moduli, E' and E'', were determined intermittently at 10 Hz on specimens of an annealed polycarbonate film during stress relaxation at static tensile strains from 1.2 to 6.25% at 50°C. It was found that E' and $1/E''$ decrease when a static strain is applied but thereafter they increase progressively with time. These changes, which increase with the applied strain until it becomes 4%, are attributed primarily to a rejuvenation of a specimen (an increase in segmental mobility) followed by physical ageing (a progressive decrease in segmental mobility). Measurements at a static strain of 3% at six temperatures from 30°C to 130°C showed, among other things, that the rates of increase of E' and decrease of E'' are sensibly independent of temperature up to 110°C.

(Keywords: physical ageing; ageing reversal; differential dynamic moduli; glassy polymers; finite tensile strains; polycarbonate)

INTRODUCTION

It has been recognized[1] for a long time that isotropic amorphous polymers in the glassy state are seldom, if ever, in thermodynamic equilibrium, except occasionally when the temperature is not too far below the nominal temperature of the glass transition, T_g. Consequently, the mechanical and other physical properties depend on thermal and mechanical histories[2-4], thus complicating the characterization and understanding of such properties.

Figure 1 shows schematically how the specific volume of an amorphous polymer decreases when it is cooled continuously from an elevated temperature at which it is in thermodynamic equilibrium. If the cooling is interrupted at some temperature significantly below T_g (shown by arrow (a)), the volume now decreases continuously under isothermal conditions, tending at an ever decreasing rate toward the equilibrium volume, represented by the broken line. This volume contraction is accompanied by a progressive decrease in the free volume[1,2] and thus also in the mobility of short molecular segments[3,4]. From another viewpoint[5], the contraction rate is controlled by retardation times that increase with a reduction in volume.

A detailed study[2] of the time dependence of the storage and loss shear moduli of poly(vinyl acetate) during volume contraction at different temperatures has shown that the relaxation spectrum shifts rather uniformly with the degree of ageing (volume contraction), though some changes in its shape were noted. In recent years, as part of extensive studies of phenomena now commonly termed physical ageing, Struik[3,4] determined how the creep compliance and other mechanical properties depend on the ageing time after a specimen has been quenched from above to below T_g. Additional findings, including anomalies, have been discussed recently by McKenna and Kovacs[6], who investigated the effect of ageing time on stress relaxation and the accompanying normal force, both determined on poly(methyl methacrylate) at various torsional strains.

If we now consider an isotropic specimen that has been cooled from above to significantly below T_g and then aged until its volume is that exemplified by the bottom of arrow (b) in *Figure 1*. When this specimen is subjected to a finite strain in simple tension, then the segmental mobility increases initially and thus the relaxation times decrease. This means that the effects of physical ageing have been erased (at least partially)[4]. But thereafter, ageing begins again due to a progressive decrease in segmental mobility in the stretched specimen. Stated in another way, application of the tensile strain rejuvenates (or 'de-ages') the specimen partially, or even completely.

The decrease in relaxation times brought about by a simple tensile strain has been attributed[7] to the increase in volume, and thus in free volume, of the specimen. The fractional increase in volume equals $(1-2\nu)\varepsilon$, approximately, where ν and ε are the Poisson ratio and the tensile strain, respectively. However, it has been shown[4] that a finite torsional deformation rejuvenates an aged specimen by approximately the same amount as an equivalent tensile strain. To explain this phenomenon, Struik[4] postulated that molecular motions are activated by any type of finite deformation and give an increase in free volume. The volume change produced by a finite torsional deformation is a second-order effect and may be either positive or negative[8]. For several non-elastomeric polymers, it has been shown[9] recently that torsion (the length of a specimen being free to increase) effects a decrease in volume.

The present study of an annealed polycarbonate film was made to examine the rejuvenation given by the

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* This paper is dedicated to Dr Pierre Thirion on the occasion of this retirement.

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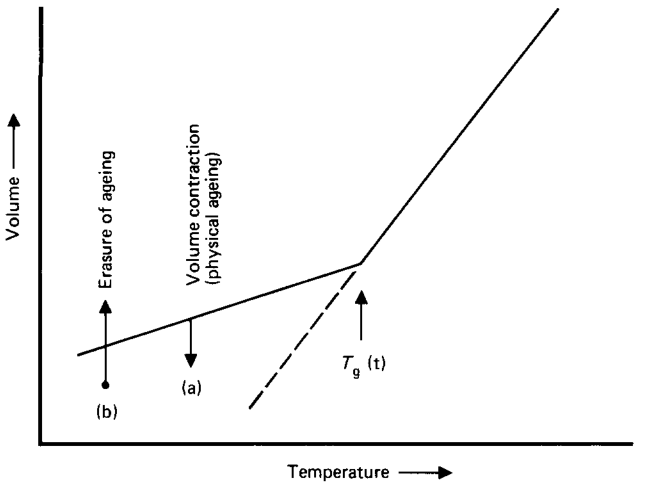

Figure 1 Arrow (a) represents the isothermal contraction of a specimen (physical ageing) that had been cooled rapidly from an equilibrium state above T_g. Arrow (b) indicates the volume increase produced by an applied tensile strain

stepwise application of finite tensile strains and also the physical ageing during stress relaxation. To monitor the changes in properties, the differential storage and loss tensile moduli (E' and E'') were determined intermittently at small amplitude of strain during the stress relaxation at constant strain. The advantages of this procedure are: (1) a measurement does not perturb a specimen significantly; and (2) an insignificant amount of ageing occurs during the brief period of time needed to make a measurement.

In a study[10] some years ago of a polycarbonate film, the dependence of E' and E'' at 110 Hz on the magnitude of the static tensile strain was determined over a wide temperature range, though only minor attention was given to the time dependence. The results were attributed to strain-activated relaxation processes. In addition, the effect of axial loads on the dynamic properties in torsion has been determined on several types of polyethylene[11,12] and on an unfilled and filled epoxy resin[13]. However, the possible role of physical ageing on the dynamic properties during creep was not considered.

EXPERIMENTAL

Polycarbonate film

A film of bisphenol-A polycarbonate about 76 μm thick (obtained from Rodyne Industries, Mt. Vernon, NY) was annealed by heating it at 155°C for one hour. It was then cooled continuously to 143°C during the subsequent half hour and to 138°C during the following hour. Thereafter, the average cooling rate was 0.26°C min^{-1} until the temperature reached 76°C. The density of the film at room temperature, obtained with an aqueous KI density-gradient column, was found to be 1.199 g cm^{-3}. This value agrees, within the probable experimental error, with those reported[14,15]. The M_w of the polycarbonate, obtained by low-angle laser light-scattering on solutions in methylene chloride, is 30 500[16]. Its glass-transition temperature presumably is close to 145°C. This value has been obtained[17] from the temperature dependence of the specific volume of a polycarbonate whose M_w was 40 000.

Apparatus

Measurements were made with a commercially available instrument, termed a Dynastat (Imass, Inc., Hingham, MA). Its main features have been described and illustrative data presented elsewhere[18–20]. Transient and dynamic viscoelastic quantities can be determined in tension, compression, or three-point bending under closed-loop servo-controlled conditions in either a load- or displacement-control mode. The temperature of a specimen can be controlled over a wide range of temperature to 0.1°C or less.

The present data were obtained on rectangular strips of the polycarbonate film whose width was typically 7 mm. After mounting a specimen in compression grips, the gauge length (distance between the grips) was typically between 25 and 26 mm. A fresh specimen was used for each experiment.

The complex dynamic modulus of each 'undeformed' specimen was determined by first applying a static tensile strain of about 0.2 or 0.3%. Thereafter, a sinusoidal strain whose amplitude was somewhat less than 0.1% was superposed on the static strain. From the sinusoidal voltages representing the resulting force and the applied displacement, the storage and loss moduli, E'_0 and E''_0, were computed by a microprocessor-based component. (Prior to making a measurement, the dimensions of the specimen and the compliance of the load cell and frame were entered in the 'scaling unit'.) The correction for inertia[20], needed with our instrument whenever the test frequency exceeds about 30 Hz, was not required because all measurements were made at 10 Hz.

To investigate rejuvenation and physical ageing, a tensile strain in the range 1.2 to 6.25% was first applied to a specimen in about 50 ms without overshoot. Periodically thereafter, E'_u and E''_u were measured, again at a strain amplitude less than 0.1%. The subscripts denote that these moduli were based on the dimensions of the undeformed specimen. To obtain moduli based on the dimensions of the stretched specimen, E'_u and E''_u were each multiplied by $\lambda^{1+2\nu}$ where $\lambda = (1+\varepsilon)$; Poisson's ratio ν was equated to 0.43[21]. The corrected values are denoted by E' and E''. In some instances, the relaxation of stress was determined during the period in which the dynamic moduli were measured intermittently.

RESULTS

Dynamic moduli and stress relaxation at 50°C

Figure 2 shows on doubly logarithmic coordinates the time dependence of E'/E'_0 at static strains from 1.2–6.25% ($E'_0 \cong 2000$ MPa). The four lowest lines are shifted down ward for clarity by the quantity A on the ordinate. It is seen that E' decreases when, or possibly shortly after, a static strain is applied, but thereafter it increases with time. Though the data were obtained only from about 10–3600 s, log E' was found in one experiment at a 3% strain to increase linearly with log t during a three-day period, t being the ageing time.

As *Figure 3* shows, E''/E''_0 increases when a static strain is applied, but thereafter it decreases. To display all data in a single figure, those at each strain have been shifted upward by the indicated value of A.

Values of log E'/E'_0 and log E''/E''_0 at 10 s, obtained from plots in *Figures 2* and *3*, are plotted against % strain in *Figure 4*. Curve B shows that E' decreases with the strain until the latter becomes about 4% and thereafter is sensibly independent of the strain. The horizontal segment of the curve corresponds to $E'/E'_0 = 0.776$, i.e., a 22%

decrease in E'. Curve A shows that E'' increases with the strain, again until it becomes about 4%. The horizontal portion of this curve corresponds to $E''/E''_0 = 3.25$, i.e., a 225% increase in E''.

The slope of each line in *Figure 2* was multiplied by (2.303×100) to obtain the rate of increase of E' expressed as a % per decade of time. Its strain dependence is shown in *Figure 5*. When the strain exceeds 4%, the rate is nearly 4.6% per decade of time, independent of the strain. Similarly, *Figure 6* shows that the decay rate of E'', obtained from the slopes of the lines in *Figure 3*, becomes

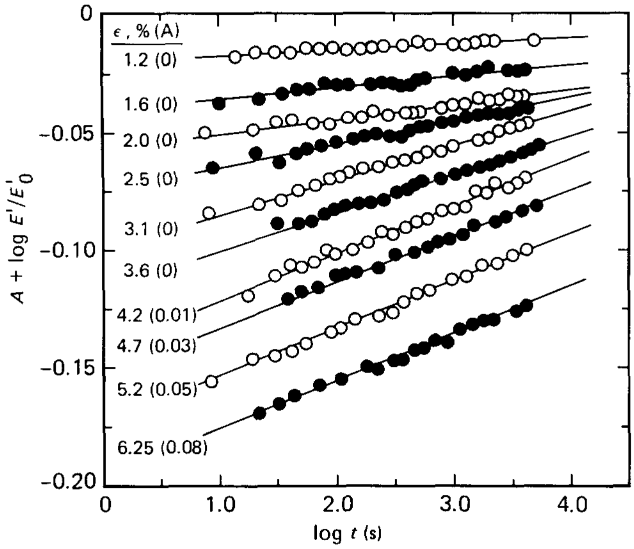

Figure 2 Time dependence of E'/E'_0 at 50°C evaluated at static tensile strains from 1.2 to 6.25%. E' and E'_0 are, respectively, the differential storage modulus and the storage modulus of the (essentially) underformed specimen, both determined in tension at 10 Hz. On the ordinate, 'A' serves to displace downward the four lowest lines for clarity

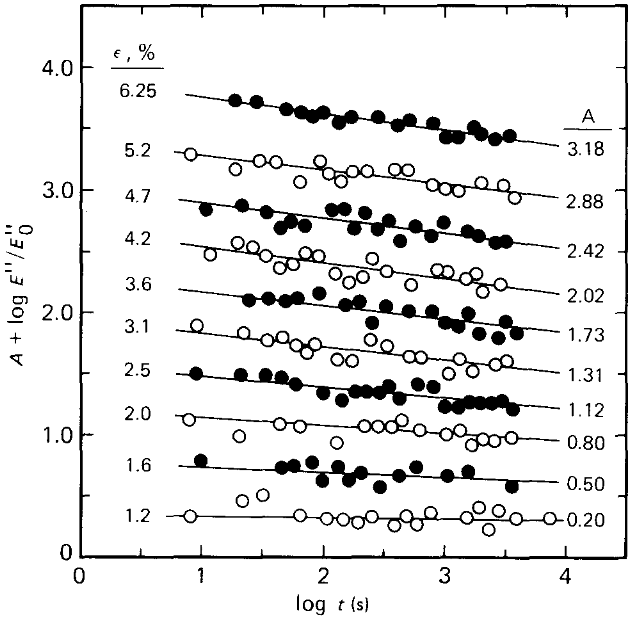

Figure 3 Time and strain dependence of the ratio of loss moduli, E''/E''_0. The experimental conditions are given beneath *Figure 2*

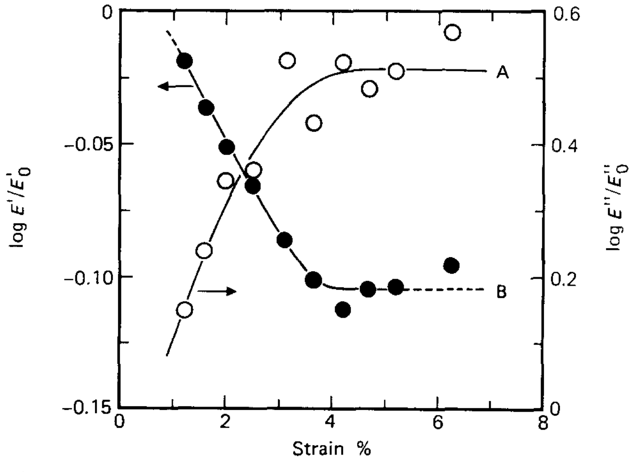

Figure 4 Strain dependence of log E'/E'_0: (●); and log E''/E''_0: (○); evaluated from the data in *Figures 2* and *3* at an elapsed time of 10 s

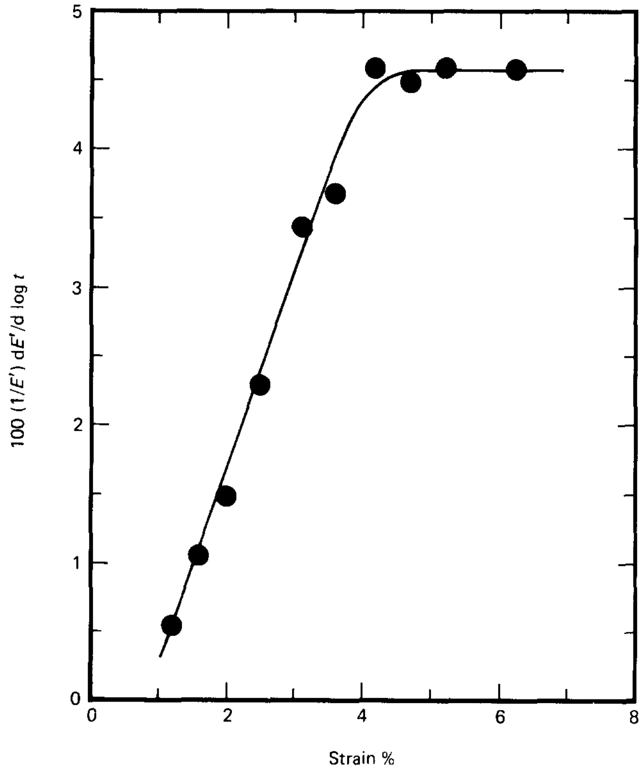

Figure 5 Strain dependence of the rate of increase of E', expressed as a % per decade of time, derived from the plots shown in *Figure 2*

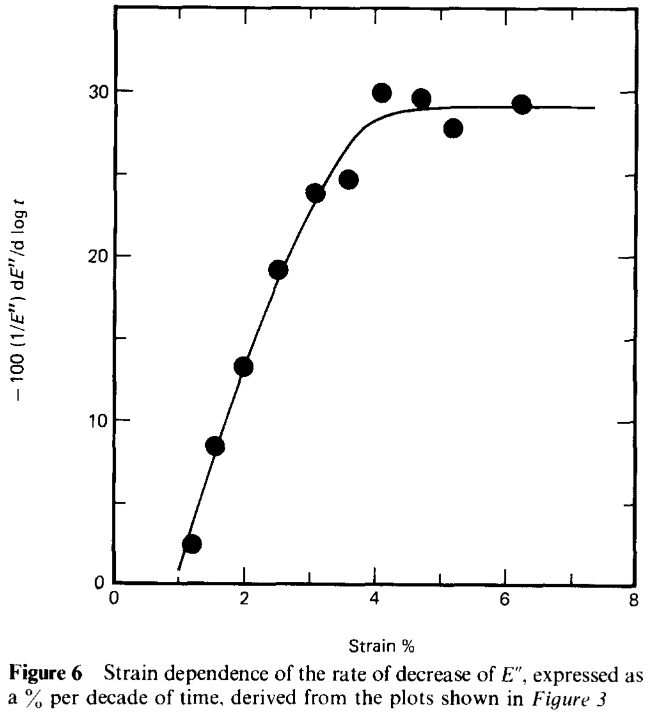

Figure 6 Strain dependence of the rate of decrease of E'', expressed as a % per decade of time, derived from the plots shown in *Figure 3*

constant when the strain exceeds 4%, its value there being nearly 30% per decade of time.

Stress relaxation was determined at a series of strains from 0.3–6.25%. *Figure 7* shows the time dependence of the non-linear stress-relaxation modulus $\sigma(t,\varepsilon)/\varepsilon$, where σ is the nominal stress. As expected for a tough glassy polymer, the modulus at a fixed time decreases with increasing strain and concomitantly the stress-relaxation rate increases.

To compare the rate of increase of E' with the decay rate of the stress at each strain, $\log E'$ was plotted against $\log \sigma$, each point representing data at the same value of time. Each plot gave an excellent straight line whose slope is $\partial \log E'/\partial \log \sigma$. The negative of this partial derivative, plotted against strain in *Figure 8*, attains a maximum at a strain of 3.5% and thereafter decreases for an unknown reason. At the maximum, $-\partial \log E'/\partial \log \sigma$ is about 0.9.

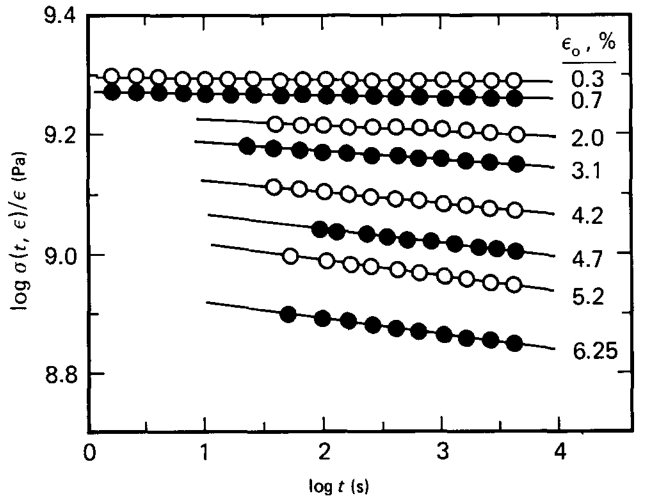

Figure 7 Time dependence of the non-linear stress-relaxation modulus at 50°C, determined at tensile strains from 0.3–6.25%

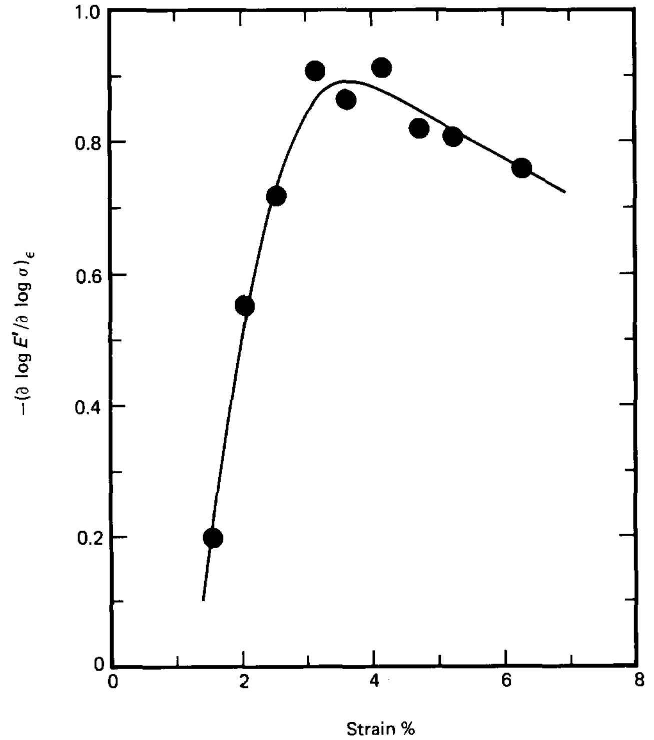

Figure 8 Strain dependence of the rate of increase of log E' divided by the rate of decrease of log σ (from stress relaxation) at 50°C. Data evaluated as explained in the text

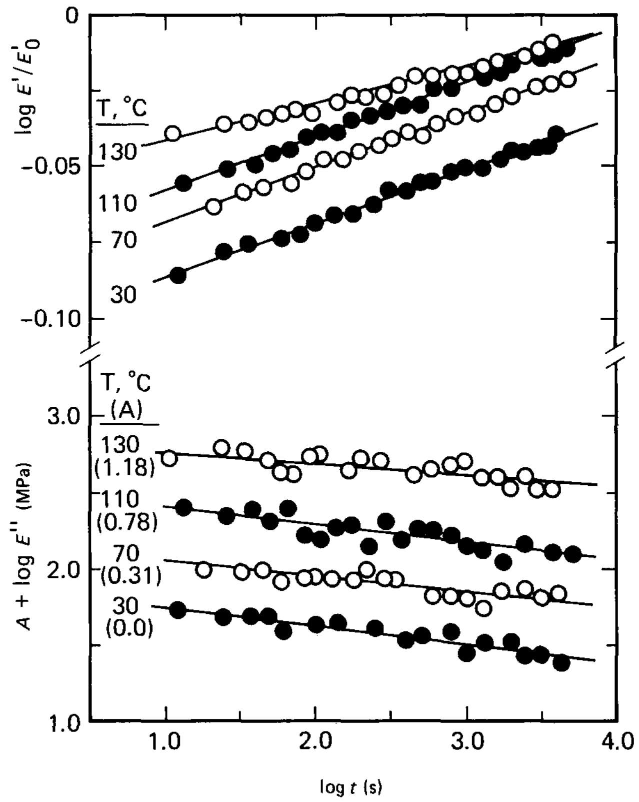

Figure 9 Time dependence of E'/E'_0 (upper panel) and E'' (lower panel) obtained at 10 Hz, at a static tensile strain of 3%, and at the indicated temperatures. On the ordinate of the lower panel, (A) serves to separate the lines for clarity

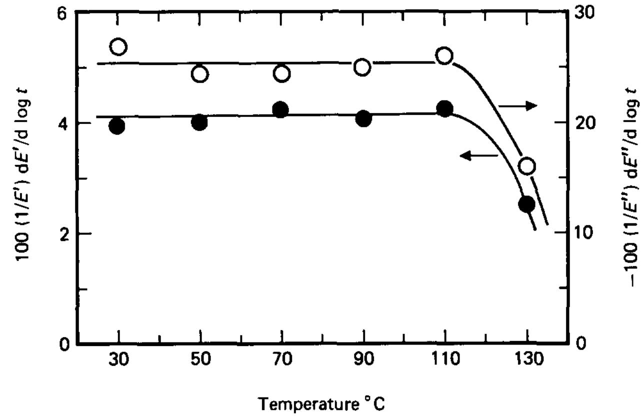

Figure 10 Temperature dependence of the rate of increase of E': (●); and the rate of decrease of E'': (○); both expressed as in *Figures 5* and *6*. Data derived from the plots shown in *Figure 9* and similar results at other temperatures

This means that the rate of increase of E' is only 10% less than the rate of stress relaxation. Because the increase in E' with time (*Figure 2*) results from a progressive decrease in segmental mobility, this change tends to reduce the rate of stress relaxation at each strain. Procedures have been developed[4] to predict creep curves over long periods of time during which creep and ageing occur simultaneously. The occurrence of ageing during stress-relaxation has also been discussed[4,22].

Temperature dependence

The upper and lower panels in *Figure 9* show the time dependence of E'/E'_0 and E'' at four temperatures when the static strain is 3%. The slopes of these plots and those at two other temperatures (not shown) yield the results in *Figure 10*. It is seen that the rate of increase of E' and the rate of decrease of E'' with time are essentially constant from 30°C–110°C. The lower rates at 130°C presumably result because this temperature is not far below T_g, which is 145°C as mentioned already.

Figure 11 shows that E'/E'_0 evaluated at 10 s increases with the temperature; concomitantly, E''/E''_0 decreases substantially. The latter data are somewhat unreliable and so are not shown.

Quenched and annealed specimens

A polycarbonate film was heated for 1 h at about 155°C and then quenched in ice–water. After 2 h and after 1 month, dynamic measurements were made at 50°C at a static strain of 3%. *Figure 12* shows the results as well as those obtained on the annealed film used in the other experiments. As shown, the rate of increase of E' is largest for the specimen tested one hour after it was quenched, though E'/E'_0 at 10 s is nearly the same for each specimen. *Figure 12* also indicates that a quenched specimen ages slowly at room temperature, causing its behaviour after one month to be nearly the same as that of the annealed film.

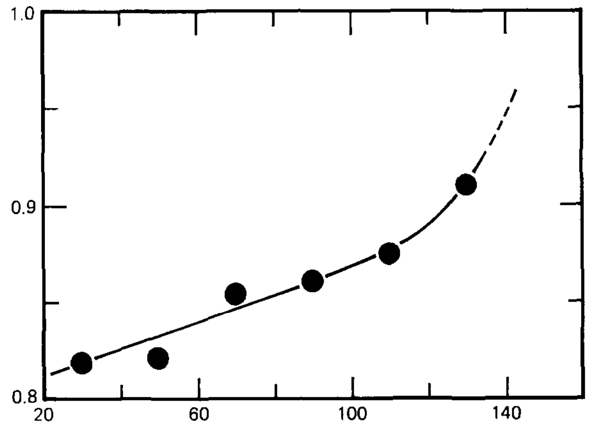

Figure 11 Temperature dependence of E'/E'_0 evaluated at an elapsed time of 10 s from the data in the upper panel of *Figure 9* and similar results at other temperatures

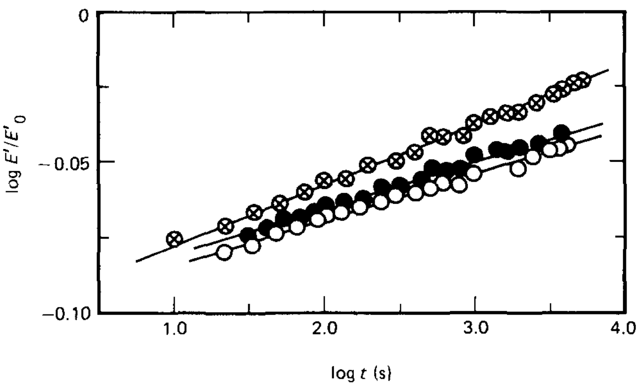

Figure 12 Effect of annealing on the time dependence of E'/E'_0 evaluated at 50°C, at 10 Hz, and at a static tensile strain of 3%. Top line is for a polycarbonate film 2 h after being quenched from above T_g; middle line is for the same material one month later; and bottom line is for the annealed polycarbonate used in all other experiments

DISCUSSION

Strain and time dependence of the dynamic moduli

A correlation of the strain and time dependence of E' and E'' can be attempted by assuming that these differential moduli are functions solely of some measure of the segmental mobility, M. In turn, M depends on the strain, ε, and ageing time, t. It then follows that

$$\mathrm{d}\log E' = \frac{\mathrm{d}\log E'}{\mathrm{d}M}\left[\left(\frac{\partial M}{\partial \log t}\right)_{\varepsilon}\mathrm{d}\log t + \left(\frac{\partial M}{\partial \varepsilon}\right)_{t}\mathrm{d}\varepsilon\right] \quad (1)$$

If E' is now held constant, the following relations for $(\partial \log t/\partial\varepsilon)_{E'}$ are obtained.

$$\left(\frac{\partial \log t}{\partial \varepsilon}\right)_{E'} = -\frac{\partial M/\partial\varepsilon)_t}{(\partial M/\partial \log t)_{\varepsilon}} = -\frac{(\partial \log E'/\partial\varepsilon)_t}{(\partial \log E'/\partial \log t)_{\varepsilon}} \quad (2)$$

The derivative $(\partial \log t/\partial\varepsilon)_{E''}$ can be defined similarly. Provided that E' and E'' are in fact functions only of M, it follows that

$$\left(\frac{\partial \log t}{\partial \varepsilon}\right)_{E'} = \left(\frac{\partial \log t}{\partial \varepsilon}\right)_{E''} \quad (3)$$

From the data at 50°C, shown in *Figures 2–6*, the derivatives in equations (3) were evaluated at $t = 10$ s and at five strains. As shown in *Table 1*, the two derivatives are equal only approximately. The derivative at constant E' exceeds that at constant E'' by some 10–30%. It thus appears that the assumption made is not precisely true.

Temperature effects

As *Figure 10* shows, the time dependence of E' and E'' is temperature-independent from 30°C–110°C when the static strain is 3%, and presumably at other strains also. This finding is rather similar to the reported[2] time dependence of G' and log tan δ for poly(vinyl acetate), obtained during volume contraction at several temperatures down to about 13°C below the nominal T_g. Also, the time dependence of the creep compliance of poly(vinyl chloride), measured during a short period on specimens 2 h after they had been quenched from above T_g to different test temperatures, is essentially constant from 20°C–50°C (see Figure 103 in ref. 4). On the other hand, as mentioned earlier, temperature has a significant effect on E'/E'_0 and E''/E''_0, each evaluated 10 s after the application of a strain of 3%.

When a glassy specimen that has been aged at a low temperature is heated rapidly to a temperature below its nominal T_g, its specific volume can change with time, under isothermal conditions, in a manner that depends on the thermal history of the specimen. Typically, the volume first increases slowly and under certain conditions passes through a maximum and thereafter decreases. (Such phenomena are termed 'memory effects'.) The question thus arises whether the data in *Figures 9* and *10* depend somewhat on the time required to heat a specimen to a test temperature and the time before a strain is applied.

Table 1 Derivatives evaluated at 50°C and an elapsed time of 10 s

100ε	$(\partial \log t/\partial\varepsilon)_{E'}$	$(\partial \log t/\partial\varepsilon)_{E''}$	Ratio
1.2	1400	1280	1.1
1.6	700	540	1.3
2.0	450	340	1.3
2.5	320	250	1.3
3.1	240	200	1.2

Typically, this total time was no longer than 1 h. It is believed that this thermal treatment had little or no effect on the data for the following reasons. (1) The original polycarbonate film was well annealed, and the test temperatures, except 130°C, were substantially below T_g. A consideration of these facts in the light of published data that illustrate the memory exhibited by polystyrene[23] suggests that any time-dependent change in volume during an hour or so should be very small at the various test temperatures, possibly excluding 130°C. (2) No evidence was obtained that E'_0 at a particular temperature depends on the thermal history in an experiment, though no detailed study was made.

Properties at small tensile strains

Some unpublished results indicate that the true gauge length of a specimen is possibly 4 or 5 mm longer than the initial distance between the grips, which was about 25 mm. If such is indeed true, then each of the reported static strains should be multiplied by a factor of about 5/6. Even if the strains shown on the abscissas of *Figures 4–6* are thus reduced, the plotted quantities still appear to extrapolate to zero at some non-zero strain. Therefore, probably little or no rejuvenation occurs unless the applied tensile strain exceeds some critical value.

The constancy of the quantities shown in *Figures 4–6* at strains above 4% suggests that such applied strains give the same increase in segmental mobility. Hence, a plastic deformation probably occurs or begins to occur.

Final comments

The present data are considered to reflect primarily an increase in segmental mobility (rejuvenation) when a finite tensile strain is applied to a specimen and thereafter a progressive decrease in segmental mobility (physical ageing). Nevertheless, any analysis beyond such qualitative considerations must be based on a recognition of the complex nature of the experiments performed. In particular, the response to an applied tensile strain depends on both shear and bulk (dilational) processes, and when the applied strain is relatively large, as in the present study, both processes are non-linear viscoelastic. Thus, owing to the non-linear behaviour in tension, a ratio such as E'/E'_0 is undoubtedly not an ideal measure of rejuvenation. In regard to bulk processes, it may be recalled that a treatment[5] of isotropic changes in volume in the absence of surface forces requires, in general, a distribution of retardation times, each being dependent on the instantaneous 'structure' of the glass. However, because rejuvenation results from the application of finite deformations in torsion as well as in tension (see Introduction), it may be concluded that bulk processes are not primarily responsible for an increase in segmental mobility. Furthermore, experiments similar to those discussed in this paper have been made recently[24] in simple compression. The results are similar to those in tension, though minor differences were observed.

Another type of experiment has been made to probe the effect of strain and time on the properties of a glassy polymer. Specifically, it has been shown[25,26] that the permeability and effective diffusivity of several gases in a glassy film increase substantially when the film is subjected to a constant tensile strain but thereafter these transport coefficients decrease progressively with time. Although gas transport in a glassy polymer is a somewhat complex process[27], it is apparent that the thermal motions of molecular segments have a significant effect, most directly on gas diffusivity. Thus, these results and those from the mechanical experiments discussed herein reflect, though in different ways, the rejuvenation produced by the stepwise application of a tensile strain and the physical ageing thereafter.

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