Physical ageing of stretched specimens of a polycarbonate film and its temperature dependence

B. Haidar* and T. L. Smith†
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, USA

(Received 19 June 1989; revised 14 September 1989; accepted 20 October 1989)

Well annealed specimens of polycarbonate film were first subjected rapidly to a static elongation of 2.6% at 13 temperatures from −110 to 110°C. During stress relaxation at each temperature, the static strain was modulated with a sinusoidal tensile strain of small amplitude ($\leqslant 0.1\%$), usually from 0.4 to 25 Hz, to determine the (differential) storage modulus E'. Such measurements were repeated intermittently at values of the elapsed (ageing) time t_e during periods of several hours or more. During such periods, E' increased continuously, a reflection of physical ageing, a hardening process. Initially, the storage modulus E'_0 was significantly higher than after the static elongation was applied; the latter produces de-ageing, a softening process. From the data, the ageing rate $\mathrm{d}\log E'/\mathrm{d}\log t_e$ was evaluated and found to be independent of frequency and t_e. The ageing rate showed a minimum at about 30°C, a pronounced maximum at −40°C and then became almost zero at −110°C. Also discussed is the temperature dependence of $\mathrm{d}\log E'/\mathrm{d}\log f$, where f is the frequency, and the effect at two temperatures of different values of the static elongation on both the ageing rate and the frequency dependence of E'. From all data, the ageing-rate parameter μ was also evaluated and discussed.

(Keywords: physical ageing; de-ageing; elongated polycarbonate; differential storage modulus; temperature and frequency dependence)

INTRODUCTION

An amorphous polymer in the glassy state is seldom in thermodynamic equilibrium, and so its physical properties depend on the thermal and mechanical histories. Specimens cooled rapidly from the rubbery to the glassy state have been used in studies, under isothermal conditions, of the time dependence of the specific volume[1] and the storage and loss moduli in shear[2]. Following these early studies, Struik[3,4] studied extensively the dependence of the creep compliance and other physical properties on the time after a specimen had been quenched from above to below T_g and termed the observed phenomenon 'physical ageing'. This type of ageing results from a progressive decrease in the mobility of short molecular segments.

After the extensive investigations by Struik[3], other studies of the ageing of specimens cooled from the rubbery to the glassy state have included those made by measuring intermittently stress relaxation in torsion and the associated normal force[5] and the creep compliance in shear[6,7].

In the characterization and application of a glassy polymer, it is invariably subjected to mechanical deformations. Thus, it is of value to know the initial effect of an applied deformation on the segmental mobility, hence the physical properties, and also how the mobility changes with the elapsed (ageing) time t_e. In a study of a polycarbonate film[8], specimens were subjected to static extensions greater than 1%. During the subsequent stress relaxation of each specimen, the static extension was modulated intermittently with a sinusoidal tensile strain, whose amplitude was 0.1% or less, at 10 Hz to obtain the storage and loss moduli E' and E'' as functions of t_e. Application of the static deformation caused E' to become less than that for the undeformed specimen, but thereafter to increase slowly and continuously with time. This behaviour shows that the segmental mobility increased at first, a reflection of a de-ageing or softening process; then the mobility increased slowly, a reflection of physical ageing, which is a hardening process. As these experiments were made in extension (simple tension), the observed phenomena might be attributed to changes in the volume, or free volume, if no other information were available to negate this view.

In a later study[9], cylindrical specimens of polycarbonate were subjected to a series of static strains in both simple compression (uniaxial stress) and extension. Then each static strain was modulated with a sinusoidal strain of small amplitude at 1 Hz. In each experiment, E' was found to decrease at first and then to increase slowly with time. As simple compression gives a decrease in volume, the results cannot be explained in terms of free volume as usually defined. Actually, the amount of de-ageing, or softening, was greater in extension than in simple compression. It was concluded[9] that de-ageing results primarily from the shear component of the applied static strain and that the volume changes either increase or decrease the amount of de-ageing, depending on whether the applied static deformation increases or decreases the volume. This conclusion is the same as the criterion for the yielding of glassy polymers[10,11].

---

* Permanent address: CNRS, Mulhouse, France

† To whom correspondence should be addressed

0032-3861/90/101904-05

The primary purpose of the present study was to determine the ageing rate of specimens subjected to a static extension of 2.6% over a wide range of temperatures. Other ancillary properties investigated included the frequency dependence of E' at different values of t_e during the ageing of the statically deformed specimen at each temperature.

EXPERIMENTAL

The polycarbonate film (Lexan, from General Electric Co.) was annealed for 1 h at 160°C, then cooled slowly to 120°C and annealed for one month at this temperature. The film was 0.13 mm thick.

Measurements were made with a Dynastat (Imass Inc., Hingham, MA). This apparatus is discussed elsewhere along with illustrative data[12–14]. Specimens 7 mm wide were mounted in the Dynastat between compression grips 25 mm apart. After a selected temperature was reached, which was controlled to 0.1°C or less, the specimen was subjected to a tensile strain of 0.2 or 0.3%, and the storage modulus E'_0 of this slightly deformed specimen was measured at frequencies from 0.4 to 25 Hz.

Next, the specimen was stretched 0.77 mm and maintained at this deformation throughout the experiment. After an elapsed time somewhat greater than 100 s, the specimen was modulated intermittently with a sinusoidal tensile strain whose amplitude was 0.1% or less, as illustrated schematically in *Figure 1*, to determine the storage modulus (differential) E'. Initially, E' was determined at frequencies from 4 to 25 Hz, but not at lower frequencies because some ageing would have occurred during the time required to make such measurements. When t_e became 600 s and greater, E' was determined at frequencies from 0.4 to 25 Hz. Such measurements were made at 13 temperatures from -110 to 110°C.

As mentioned above, the length of an undeformed specimen between the grips was 25 mm. When such a specimen is stretched ΔL (mm), the strain is not $\Delta L/25$ because it is not uniform near the grips. Two determinations of the end correction, by a method similar to that described elsewhere[15], showed it to be 4.3 ± 0.07 mm, and so the effective gauge length is about 29 mm, assumed for expediency to be independent of temperature. In this study, ΔL was always 0.77 mm, and so the tensile strain was about 0.026, or 2.6%.

As in previous studies[8,9,16], values of E' were not equated to those measured directly but were obtained from the relation:

$$E' = E'_u(1+\varepsilon)^{2\nu+1}$$

where E'_u is that determined directly, based on the original dimensions of a specimen, ε is the static (constant) strain and ν is Poisson's ratio equated to 0.43[17]. Because all static strains used in this study are small compared to unity, the above equation is approximated closely by:

$$E' = E'_u[1+(2\nu+1)\varepsilon]$$

All values of E' reported in this paper are based on the dimensions of each specimen when statically deformed.

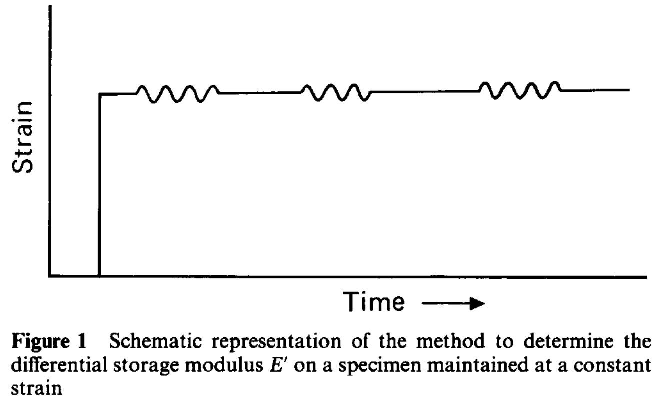

Figure 1 Schematic representation of the method to determine the differential storage modulus E' on a specimen maintained at a constant strain

RESULTS AND DISCUSSION

Evaluation of ageing rates

Figure 2 shows on doubly logarithmic coordinates the frequency dependence of E'_0 and also E' at elapsed times from 180 to 8090 s, the data being at -30°C and E' measured on the specimen at an extension of 2.6%. Results from similar experiments at 50°C are shown in *Figure 3*.

To obtain the quantitative measure of the ageing rate that we find most useful, values of $\log E'$ at 5 Hz were read from the lines in *Figures 2* and *3* and plotted against $\log t_e$, as shown in *Figures 4* and *5*. These plots give straight lines whose slopes are the ageing rates at -30 and 50°C, respectively. Because the lines at the different values of t_e in *Figures 2* and *3* are parallel, the slopes of the lines in *Figures 4* and *5* are independent of the frequency, at least from 0.4 to 25 Hz. At all temperatures from -110 to 110°C, the ageing rate $\mathrm{d}\log E'/\mathrm{d}\log t_e$ was found to be independent of the values of frequency and t_e covered in our experiments.

The curve defined by the full circles in *Figure 6* represents the dependence of the ageing rate on temperature. As shown, the ageing rate passes through a minimum at about 30°C, through a pronounced maximum at about -40°C and becomes almost zero at -110°C. The open circles show the temperature dependence of the frequency dependence of E' expressed as $\mathrm{d}\log E'/\mathrm{d}\log f$. This quantity is small and nearly constant from 110°C down to about 20°C. Then it increases rapidly and presumably passes through a maximum at about -110°C, though the maximum was not found because temperatures below -110°C could not be reached with the thermostat on the Dynastat, which is cooled with liquid nitrogen.

For annealed polycarbonate, there is no dispersion (transition) between T_g ($\simeq 145$°C) and that observed at 1 Hz at about -100°C. This fact accounts for the low frequency dependence of E' at temperatures above 20°C, as shown in *Figure 6*, and for the presumed maximum in the frequency dependence of E' at about -110°C. We can propose no explanation for the pronounced maximum in the ageing rate at -40°C, though it occurs near the temperature at which the frequency dependence of E' exhibits an inflection point. As already mentioned, the ageing rate is independent of frequency.

Another measure of the ageing rate is μ, introduced by Struik[3], which can be evaluated by shifting the lowest three lines in *Figure 2*, for example, to the left until they superimpose with the line at $t_e = 8090$ s. The shift distances, $\log a$, are plotted against $\log t_e$ in *Figure 7*. (The reference state at which $a=1$ is the ageing time 8090 s.) The slope of the line, 1.13, equals μ. In Struik's studies[3], it was commonly necessary to make small vertical shifts to effect superposition of creep-compliance

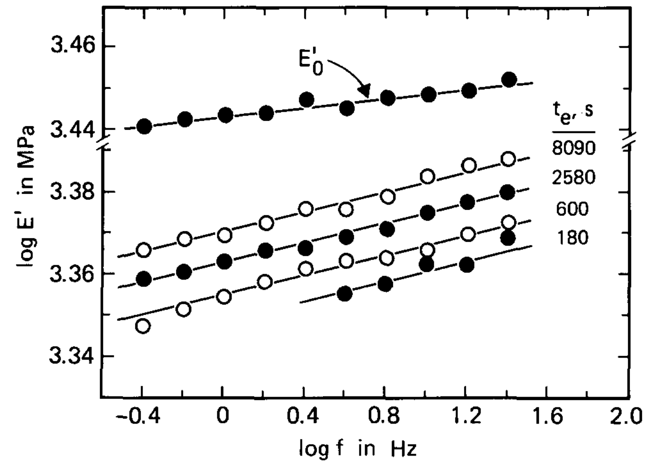

Figure 2 Doubly logarithmic plots showing the frequency dependence of E' at four values of the elapsed (ageing) time t_e, after a 2.6% elongation was applied to the specimen at −30°C. The uppermost line shows E'_0 determined before the specimen was deformed

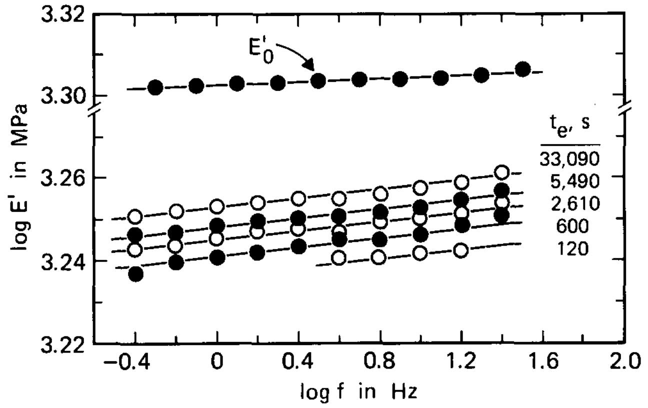

Figure 3 Plots similar to those in *Figure 2*, except that the data were determined at 50°C

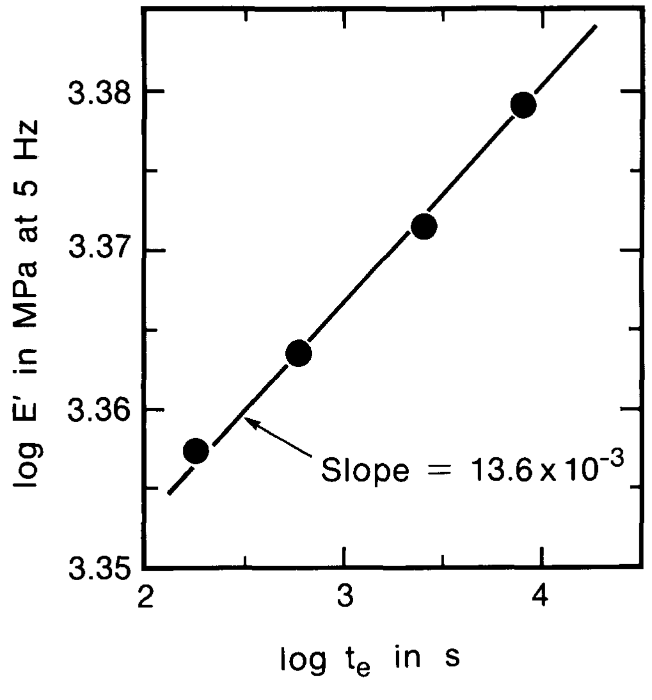

Figure 4 Crossplot of data at 5 Hz from *Figure 2*; the slope of the line is the ageing rate at −30°C

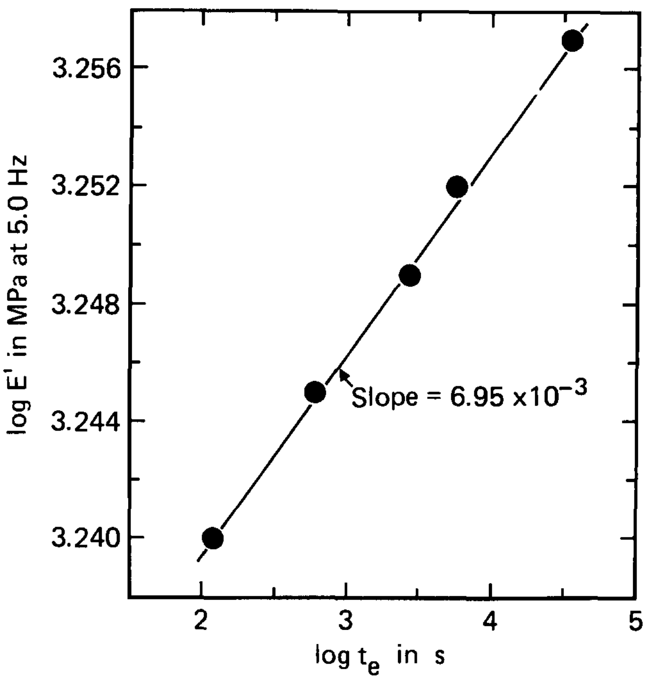

Figure 5 A plot similar to that shown in *Figure 4*, except that the data, obtained from *Figure 3*, are at 50°C

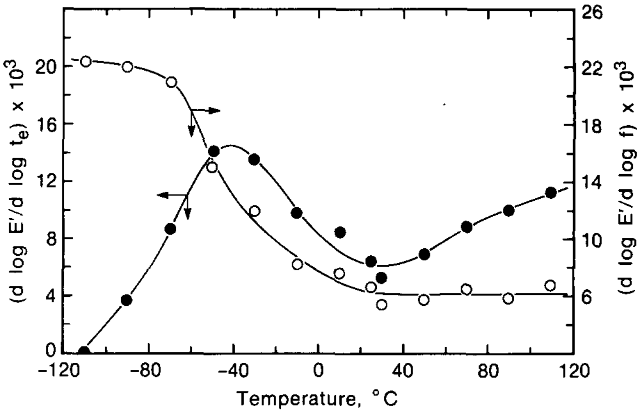

Figure 6 Temperature dependence of the ageing rate d log E'/d log t_e and also the frequency dependence of E' expressed as d log E'/d log f

data obtained at different values of t_e. In treating the present data, it is not possible to determine whether vertical shifts are needed. From our data, μ can also be evaluated from the equation:

$$\mu = \frac{(\partial \log E'/\partial \log t_e)_f}{(\partial \log E'/\partial \log f)_{t_e}} \qquad (1)$$

Figure 8 shows μ plotted against the temperature. Below 30°C, the curve is rather similar to that obtained for the ageing of polycarbonate in the undeformed state (see figure 15 in ref. 3), but at temperatures above 30°C it is dissimilar in that μ increases continuously with the temperature.

For the ageing of undeformed specimens quenched from the rubbery to the glassy state, an analysis has shown that μ should not exceed unity[3]. This prediction is supported by certain experimental data[3], though it has not always been possible to evaluate μ because, in such instances, the set of time- or frequency-dependent data[2,5] obtained on quenched specimens at small deformations during physical ageing could not be superimposed

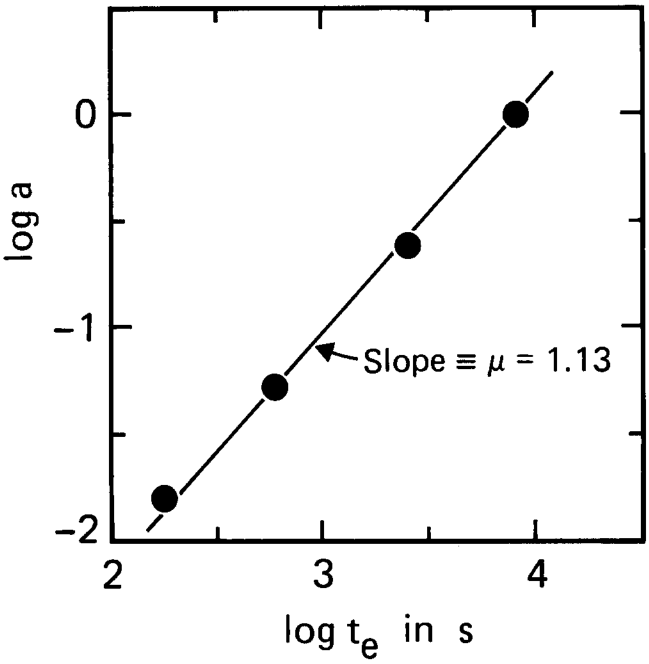

Figure 7 Dependence of the shift factor log a on the logarithm of the elapsed time t_e; the slope equals the ageing-rate parameter μ. Log a was obtained from shifting the lowest three lines in *Figure 2* left-wards to superimpose with data at $t_e = 8090$ s

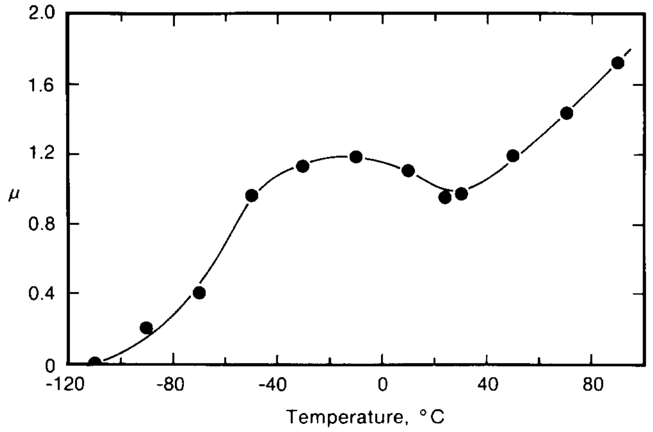

Figure 8 Temperature dependence of μ, obtained from the slopes of plots like those in *Figure 7* or from equation (1)

entirely. The increase of μ with temperature above 30°C (*Figure 8*) reflects the progressive increase in the ageing rate, which at and above T_g becomes too rapid to observe by ordinary experimental techniques. Also, the ageing of deformed specimens is different and undoubtedly more complex than that for isotropic specimens.

Figure 9 shows the temperature dependence of E'/E'_0 evaluated at 10 Hz and 200 s after the static strain of 2.6% was applied. The ratio E'/E'_0 at any temperature increases with a reduction of the frequency and the ageing time at which this ratio is evaluated, as can be deduced from *Figures 2* and *3*.

Behaviour at different static tensile strains

Experiments similar to those discussed in the preceding section were made at different static strains but only at 50 and 90°C. The ageing rates d log E'/d log t_e are shown in *Figure 10*. In light of *Figure 6*, the observed temperature dependence is as expected, and also the strain dependence is similar to that reported previously[8,9].

Figure 11 shows how the frequency dependence of E', expressed as in *Figure 6*, depends on the strain. It is temperature-independent at 50 and 90°C, in agreement with *Figure 6*. *Figure 12* shows values of μ derived from the data in *Figures 10* and *11* by use of equation (1).

SUMMARY REMARKS

The present study is the most extensive to date of the de-ageing (increase in the mobility of short molecular segments) that occurs when a static elongation is applied rapidly to a glassy specimen and, in particular, of the subsequent physical ageing (progressive decrease in the segmental mobility) of the deformed specimen. Such investigations are of importance because the data commonly provide a qualitative explanation of some of the complex mechanical properties exhibited by glassy polymers when subjected to finite deformations, as illustrated elsewhere[18].

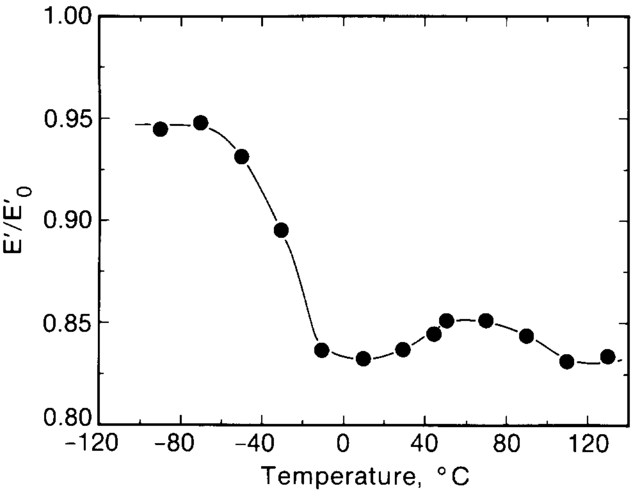

Figure 9 Temperature dependence of E'/E'_0 obtained from data at 10 Hz and 200 s after the strain of 2.6% was applied to the specimens

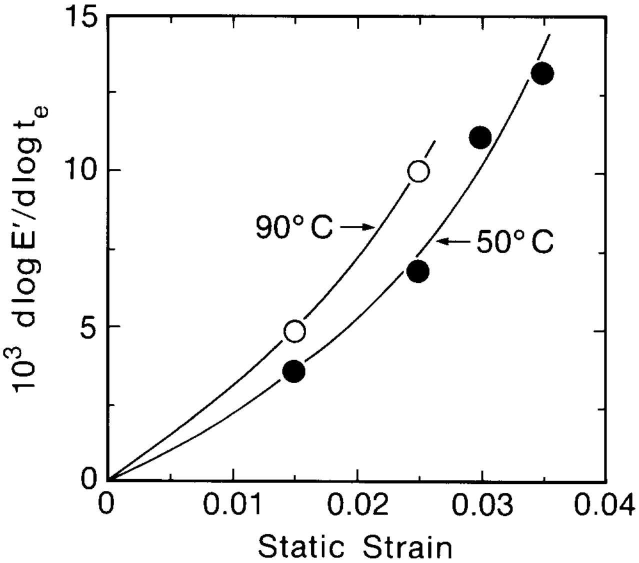

Figure 10 Dependence of the ageing rate on the static strain at 50 and 90°C

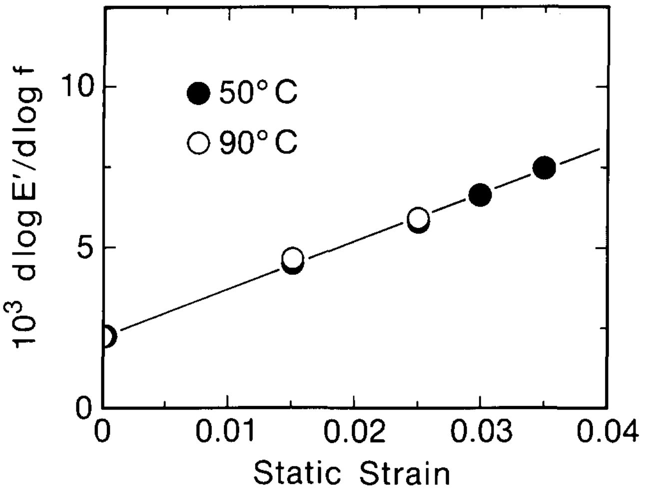

Figure 11 Dependence of d log E'/d log f on the static strain at 50 and 90°C

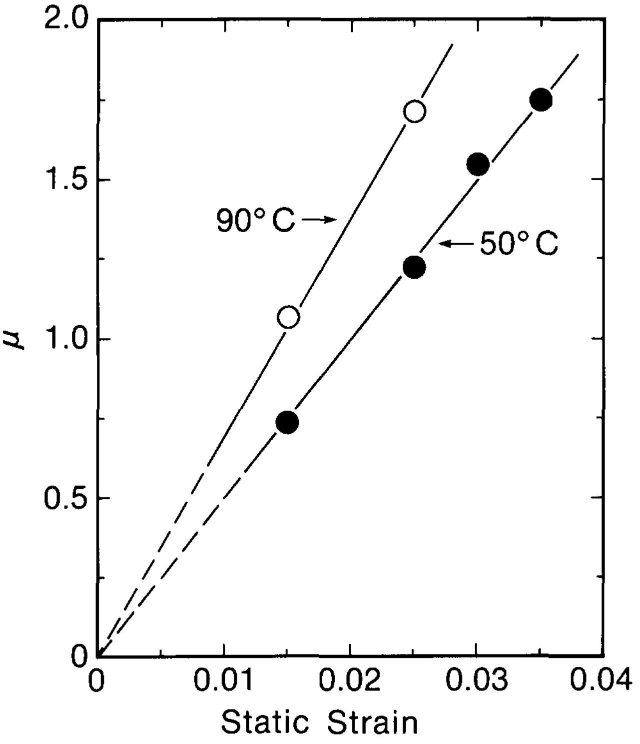

Figure 12 Dependence of μ on the static strain at 50 and 90°C; μ was evaluated from the data in *Figures 10* and *11* by use of equation (1)

In this study, well annealed specimens of a polycarbonate film (Lexan) were subjected rapidly to a constant elongation of 2.6% at 13 temperatures from −110 to 110°C. Then, on each specimen, E' was determined at a small amplitude at frequencies from 0.4 to 25 Hz, usually. Such modulations were repeated intermittently during an elapsed (ageing) time t_e from a few hours up to 9 h, the maximum value being dependent, in part, on the ageing rate and thus on the temperature. From the data, the ageing rate d log E'/d log t_e was evaluated and found to be independent of the elapsed time and the frequency over the ranges covered. With a reduction in temperature from 110°C, the ageing rate decreased first, then passed through a minimum at about 30°C, next reached a pronounced maximum at −40°C and finally decreased to almost zero at −110°C. This behaviour is one example that shows clearly that physical ageing of deformed specimens can occur at many temperatures below T_g.

The frequency dependence of E' determined on the statically deformed specimens, expressed as d log E'/ d log f where f is the frequency, was almost constant from 110°C down to about 20°C, and then it increased to a relatively high value at −110°C. At still lower temperatures, it must decrease to a very small value, though we were unable to make measurements at temperatures below −110°C. This unusual phenomenon occurs because well annealed specimens of polycarbonate show no dispersion (transition) below T_g until at about −100°C at 1 Hz.

REFERENCES

1 Kovacs, A. J. *Adv. Polym. Sci.* 1963, **3**, 394
2 Kovacs, A. J., Stratton, R. A. and Ferry, J. D. *J. Phys. Chem.* 1963, **67**, 152
3 Struik, L. C. E. in 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
4 Struik, L. C. E. *Polym. Eng. Sci.* 1977, **17**, 165
5 McKenna, G. B. and Kovacs, A. J. *Polym. Eng. Sci.* 1984, **24**, 1138
6 Plazek, D. J., Nagi, K. L. and Rendell, R. W. *Polym. Eng. Sci.* 1984, **24**, 1138
7 Schwarzl, F. R., Link, G., Greiner, R. and Zahradnik, F. *Prog. Colloid Polym. Sci.* 1985, **71**, 180
8 Ricco, T. and Smith, T. L. *Polymer* 1985, **26**, 1979
9 Smith, T. L., Levita, G. and Moonan, W. K. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 875
10 Whitney, W. and Andrews, R. D. *J. Polym. Sci.* (*C*) 1967, **16**, 2981
11 Ward, I. M. 'Mechanical Properties of Solid Polymers', Wiley-Interscience, New York, 1971
12 Sternstein, S. S. in 'Advances in Chemistry Series', No. 203 (Ed. C. D. Craver), American Chemical Society, Washington, DC, 1983, pp. 123–47
13 Yang, P., Carlsson, L. and Sternstein, S. S. *Polym. Compos.* 1983, **4**, 104
14 Smith, T. L. and Opermann, W. Technical Papers of 39th Annu. Tech. Conf., Soc. Plastic Eng., 1981, Vol. 27, p. 163
15 Read, B. E. and Dean, G. D. 'The Determination of the Dynamic Properties of Polymers and Composites', Wiley, New York, 1978, p. 36
16 Ricco, T. and Smith, T. L. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 513
17 Yee, A. F. *Am. Chem. Soc. Polym. Prepr.* 1981, **22**(2), 285
18 Smith, T. L. and Haidar, B. in 'Proc. Xth Int. Congr. Rheol.', Sydney, Australia, August 1988, Vol. 2, p. 282