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Influence of Deformation on the Physical Ageing of Polycarbonate

1. Mechanical Properties Near Ambient Temperature

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Summary

Physical aging behavior of polycarbonate samples has been studied by dynamic mechanical torsion tests near ambient temperature in the range of 0.01 to 100 rad/s. Aging effects have been measured either after heating above T_g and quenching, or after cold drawing at ambient temperature, or after a combination of both. On the quenched samples our results are consistent with findings of STRUIK (1) obtained by creep tests, i.e. an aging rate, μ, of about 1. On the other hand, on the cold drawn samples μ was found to be about 2.3 when determined from storage modulus data, and about 1.5 from loss modulus, indicating an acceleration effect on the molecular mobility in PC.

Introduction

On the molecular level, the mechanism by which amorphous polymers deform plastically below their glass transition temperature, T_g, is still not well known. Currently, none of the various theories proposed can account for all aspects observed experimentally (2,3).

When yielding under tension, some polymers exhibit very large macroscopic deformations known as 'necking' or 'cold drawing'. However, the observed molecular relaxations are of low amplitude and have long retardation times, τ. This apparently contradictory behavior raises the question of the origin of molecular mobility which is necessary for plastic deformation of these polymers.

In order to observe the variations of molecular mobility, it is convenient to measure isothermally the physical aging behavior which is intimately related to the structural recovery of the glass. In fact, a glass is not in thermodynamic equilibrium; for this reason, its structure will evolve with time towards the equilibrium state. KOVACS (4) and STRUIK (1) have postulated that the time-dependent evolution of specific volume and mechanical properties of a quenched polymeric glass result from the diminishing molecular mobility or the decreasing free volume, v_f.

In order to characterize the amount of instability of the glassy state, KOVACS has chosen the volume departure, δ, with regard to the equilibrium value, v_f, of specific volume:

$$\delta = (v(t_e)-v_\infty)/v_\infty \, , \qquad (1)$$

where $v(t_e)$ represents the specific volume at time t_e elapsed since destabilization.

Concerning the retardation spectrum of the polymer glass, physical aging results in a shift of the whole spectrum along a logarithmic time scale towards longer retardation times. This occurs without an appreciable change in the shape of the spectrum. This behavior can be described (5), in terms of temperature, T, and volume departure, δ, by:

$$\tau_i(T,\delta) = \tau_{i,r}\, a_T \cdot a_\delta \ , \qquad (2)$$

where the subscript i refers to the i-th retardation mechanism and the subscript r to a fixed reference temperature, T_r. The parameter a_T refers to temperature dependence of τ_i (at fixed δ), and a_δ its structure dependence (at fixed T).

Experimentally, the parameter a_δ may be determined by measuring the isothermal variation of mechanical properties during physical aging. In fact, the retardation spectrum (obtained by creep, stress relaxation or dynamic measurements) shifts along a logarithmic time scale of τ_i, with log a_δ as the shift factor.

STRUIK has shown (1) that (in temperature range $T_\beta < T < T_g$) there exists a double logarithmic shift rate, μ, defined as:

$$\mu = -(d \log a_\delta / d \log t_e)_T \ , \qquad (3)$$

which remains constant over large time intervals, i.e. as long as equilibrium has not been reached. He also has shown that a non-equilibrium state may be induced in an amorphous polymer by deformation. According to him however, the shift rate, μ, should never exceed a value of about unity.

According to KOVACS (5), measurement of isothermal volume evolution represents a convenient means to characterize structural non-equilibrium. He has shown that the contraction isotherms of δ exhibit a sigmoidal shape when plotted as a function of the logarithm of aging time, t_e, with slope, $\bar{\beta}$, at the inflection point:

$$\bar{\beta} = (d\delta \ / \ d \log t_e)_{min} \ . \qquad (4)$$

In making experiments at a temperature $T << T_g$, the equilibrium volume may never actually be attained: equilibrium time, t_∞, increases roughly exponentially with $(T_g - T)$. Therefore, it becomes impossible to determine δ and the slope $\bar{\beta}$. However, one may describe volume recovery by taking, instead of v_∞, a reference volume, v_r, measured after a reference aging time, t_r. For the so obtained contraction isotherms, we may then define, by analogy to equation (4), a slope β at the inflexion point:

$$\beta = (dv \ / \ d \log t_e)/v_r \ . \qquad (5)$$

In this context, we were interested in studying the influence of structural destabilization of polycarbonate (PC) by various thermal and mechanical treatments on its physical aging behavior.

In this, the first part, we will consider dynamic mechanical measurements near ambient temperature after cold drawing as compared to quenching. In a forthcoming paper, we will deal with volume recovery measurements after the same treatments.

Materials

Extruded sheets of bisphenol A polycarbonate, 2 mm thick, manufactured by Rohm & Haas under the trade name Tuffak, were used in the experiments. The molecular characteristics, determined by gel permeation chromatography were: $\bar{M}_w = 26500$, $\bar{M}_w/\bar{M}_n = 2.33$. A glass transition temperature of 140 °C was measured by differential scanning calorimetry with a Perkin Elmer DSC-1B, using a heating rate of 16 °C per minute.

On measuring the birefringence, Δn, of the sheets with a Leitz polarizing microscope and a Berek compensator we found values of about $2 \cdot 10^{-4}$. This birefringence probably resulted from the extrusion process and was not eliminated by heating above T_g. Nevertheless, compared to the calculated birefringence ($\Delta n = 0.2$) for totally oriented amorphous PC (6), this value indicated very low orientation and could be neglected.

Test specimens were prepared by cutting with a band-saw and finished by milling. Due to the fact that PC absorbs some water, we annealed some test specimens at 120 °C for two days. In the quenching experiments, these samples showed no change in aging behavior with respect to unannealed ones. Accordingly, subsequent experiments on quenched and also on cold drawn samples have been performed without prior annealing.

Apparatus

The cold drawing was performed with a Zwick mechanical tensile machine at constant cross-head speed. Dumbbell-shaped specimens (calibrated dimensions: length 80 mm, width 20 mm) were deformed with mean strain rates, $\dot{\varepsilon}$, of 0.02 or 0.06 s^{-1} respectively. Extension ratios of 1.7 were obtained in all experiments.

Rectangular samples for subsequent torsion tests were cut out of the central part of the cold drawn area. The dynamic shear moduli $G'(\omega)$ and $G''(\omega)$ were measured in forced torsional oscillation using the Rheometrics RMS-605 mechanical spectrometer. This equipment allows measurements in the angular frequency, ω, range of 0.01 to 100 rad/s. During aging tests, the sample temperature was maintained constant (stability ±1 °C) in an oven by forced air convection. The overall experimental error was estimated to be about 1 percent on G' but up to 12 percent on G'', due to the very small values of loss angle observed.

For the dynamic tests, sample dimensions were: length 65 to 69 mm, width 10 to 12 mm, thickness 2 mm (quenched samples) or 1.3 to 1.4 mm (cold drawn). Tests were performed at shear strains of 0.5 percent, in the linear deformation range. The measurement time, t_m, for one mechanical spectrum depends both on frequency range and number of discrete measurements. Using 5 data points per frequency decade and a maximum frequency of 100 rad/s, time intervals t_m are as follows:

ω_{min} (rad/s)	0.01	0.1	1
t_m (s)	2100	380	180

In the experiments with thermal treatment, annealing was performed at T_o = 160 °C in the RMS sample chamber for at least 30 minutes. After quenching to the aging temperature T_1, thermal equilibrium was reached a few minutes later.

The birefringence of the cold drawn samples was measured by first cutting a wedge off the end of each sample and then, on the polarizing microscope between crossed polarizers, by counting fringe order (= destructive interference) in this wedge under yellow Na light illumination (7).

During experiments on cold drawn samples, small dimensional recovery as a function of aging time, i.e. decrease of length and increase of width and thickness, was observed. As it was impossible to measure these variations directly during aging tests in the RMS spectrometer, we tried to evaluate the length decrease on other cold drawn samples. The induced systematic overestimation of G' values for increasing aging times should have resulted in shift rate values several percentage points too high. We are currently investigating more exactly the influence of recovery on μ.

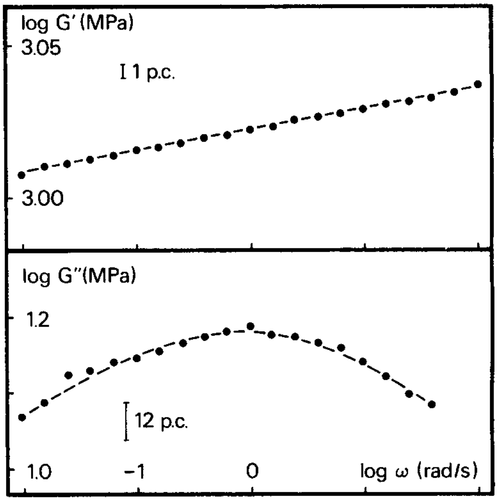

Fig.1 - Dynamic mechanical spectra of original PC (#1); above: storage modulus , below: loss modulus.

Experimental method

We used a method similar to the one utilized by STRUIK (1). The principal difference consisted in replacement of creep tests by dynamic measurements. We defined the aging time, t_e, of each sample as the time elapsed after modification of its thermodynamic state, either by quenching from above T_g or by deformation at room temperature.

The effect of physical aging on mechanical properties was measured by recording dynamic spectra $G'(\omega)$ and $G''(\omega)$ at increasing t_e. In order to be sure that the influence of the aging process was negligible during the measurement of each spectrum, measurement times, t_m, were $\leq 0.1\ t_e$. Also, we used the middle of the time interval t_m as the value of t_e.

The dynamic mechanical spectra recorded at increasing t_e were superposed, taking the curve after the longest aging time as a reference. It appeared that almost perfect superposition could be obtained by simple horizontal shift along the logarithmic frequency scale. From the corresponding shift factors, log a_δ, the shift rate, μ, was then calculated.

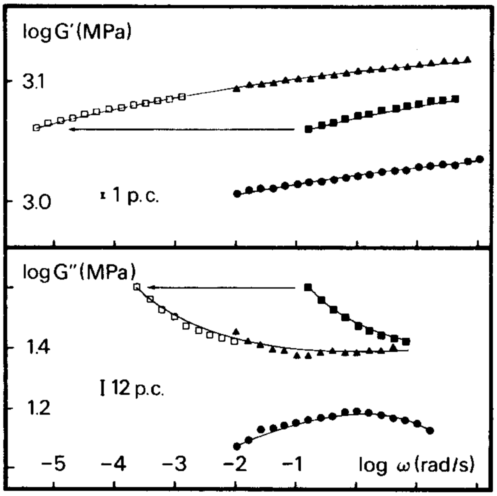

Fig.2 - Evolution of dynamic mechanical spectra of quenched PC (#3) during aging; above: storage modulus, below: loss modulus (■ : $t = 2170$ s; ▲ : $t = 76300$ s; ● : original PC).

Results

Measurements were made near room temperature. Five types of tests were performed, differing in the thermal or mechanical treatment prior to aging experiments (Table 1):

(a) No thermal or mechanical treatment, T_1 = 28 °C;

(b) Heating to T_0 = 160 °C, quenching to T_1 = 25 or 30 °C;

(c) Cold drawing at T_0 = 20 °C, heating to T_1 = 28 or 29 °C;

(d) Heating to T_0 = 160 °C, quenching and cold drawing at T_0' = 20 °C, heating to T_1 = 28 °C;

(e) Cold drawing at T_0 = 20 °C, heating to T_0' = 160 °C, then quenching to T_1 = 28 °C.

Sample #	Type	T_1(°C)	$\dot{\varepsilon}$ (s^{-1})	$\Delta n \cdot 10^2$	t_e max (s)	μ(G')	μ(G'')
1	a	28	-	-	88000	-	-
2	b	30	-	-	176000	1.1	n.m.
3	b	25	-	-	76300	1.0	0.9
4	c	28	0.06	n.m.	30000	2.1	1.4
5	c	28	0.06	2.8	240000	2.4	1.6
6	c	29	0.02	3.2	252000	2.5	n.m.
7	d	28	0.02	3.1	73800	2.6	1.7
8	e	28	0.06	n.m.	64000	0.9	n.m.

Table 1. Experimental results (n.m. = not measured).

(a) When testing sample #1 without any destabilizating treatment, we observed no change in mechanical properties during the test. This behavior was expected since its total 'real' aging time exceeded 1 year. Its dynamic spectra are shown in Fig.1.

(b) After quenching from T > T_g, the first measurement (t_e = about 30 minutes) showed a decrease of G'(ω) and an increase of G''(ω) as compared to sample #1. Both spectra have evolved with aging time, approaching those of type (a) (Fig.2). After calculating the shift factors, shift rates μ(G') and μ(G'') were determined (Fig.3). Whereas the magnitude of μ(G') = 1.1 (#2) viz. 1.0 (#3) agrees well with STRUIK's value from creep (1), the shift rate μ(G'') = 0.9 appears to be somewhat low. However, due to the

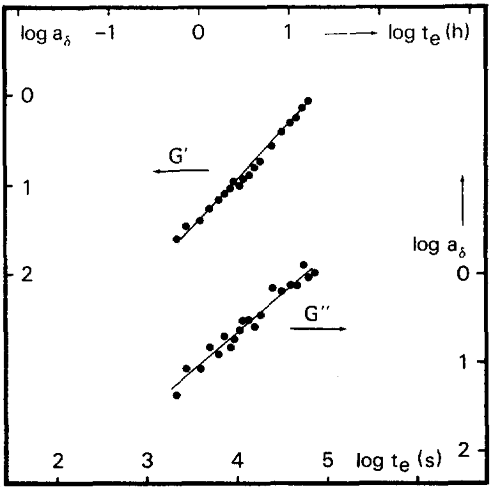

Fig.3 - Shift factors, log a_δ, determined from storage (left) and loss modulus (right) spectra of quenched PC (#3) versus log t_e.

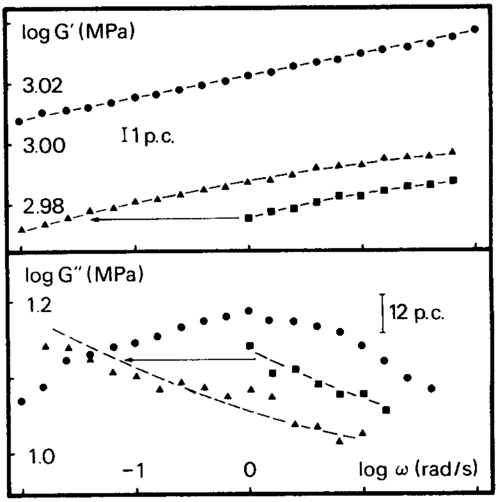

Fig.4 - Evolution of dynamic mechanical spectra of cold drawn PC (#5) versus log t_e; above: storage modulus , below: loss modulus (■ : t = 4130 s; ▲ : t = 240000 s; ● : original PC).

great experimental uncertainty of loss moduli (cf.Fig.2), shift factors and the deduced shift rate should be less reliable.

(c) Cold drawing of an amorphous polymer results in orientation of molecular chains, producing mechanical anisotropy and optical birefringence. The resulting symmetry is transverse isotropy, with the draw axis as symmetry axis (8). When making torsion tests on an oriented polymer with twist axis parallel to the draw direction, its shear modulus is higher than in the isotropic state. In cold drawn PC, HENNIG (9) found an increase of about 15 percent, which is of the same order as our results (samples #4 to #6). We also measured an increase of loss moduli as compared to sample #1. During aging $G'(\omega)$ was increasing and $G''(\omega)$ was decreasing: they evolved therefore in the same direction as type (b) samples, but appreciably faster (Fig.4). Therefore, their shift rates were much higher: $\mu(G') = 2.1$ to 2.5 and $\mu(G'') = 1.4$ to 1.6 (Fig.5).

(d) When cold drawing a sample immediately after quenching from $T > T_g$, we observed the same aging behavior as for samples (c) after cold

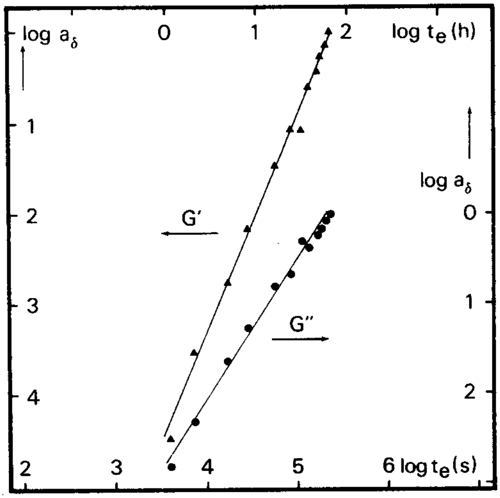

Fig.5 - Shift factors, log a_δ, determined from storage (left) and loss modulus (right) spectra of cold drawn PC (#5) versus log t_e.

drawing alone, with approximately the same shift rates: $\mu(G') = 2.6$ and $\mu(G'') = 1.7$.

(e) However, by inverting the order of cold drawing and quenching of experiment (d), the aging behavior is similar to that observed after a simple quench from $T > T_g$ (type b): $\mu(G') = 0.9$.

Discussion

If one compares the aging rates of quenched samples (b) and cold drawn ones (c), it seems obvious that high plastic deformation drastically increases molecular mobility. Whereas our values of shift rates for quenched PC agree well with STRUIKS'S values measured by creep (1), the greatly enhanced values for cold drawn PC seem to contradict his conclusions relating to the influence of cold drawing on aging. Indeed, he found that cold drawing of PVC reactivated aging and had the same effect as a quench from $T > T_g$, with shift rate of about unity. Moreover, our results are also in conflict with his general assumption of a limiting value of about 1 for μ.

To be sure of our measurements reliability, we have to justify that the shift rate increase did not result from orientation relaxation. Such a relaxation, though, should diminish storage modulus down to the value of non-oriented PC, quite the contrary of the observed behavior (Fig.6). Therefore, it seems that the higher shift rate after cold drawing is effectively due to an acceleration effect on the kinetics of mobility decrease.

The two experiments combining quenching and cold drawing are interesting in two ways. First, STRUIK had already shown (1) that aging is thermoreversible, i.e. heating the sample above T_g erases its memory. Experiment (e) shows that this erasing effect is also observed on cold drawn samples: After heating above T_g and quenching, this sample exhibited normal aging behavior like that which follows a simple quench. Secondly, experiment (d) has demonstrated that the severe plastic deformation produced by cold drawing has masked the aging effect of the preceding heat treatment.

Finally, we have to discuss our finding that shift rates derived from loss modulus data are systematically lower than those from storage modulus: by about 10 percent after quenching and by about 35 percent after cold drawing. Conversely, when using shift factors deduced from $G'(\omega)$ data, no satisfactory superposition of $G''(\omega)$ data could be achieved.

These observations are reminiscent of work published by KOVAVCS and

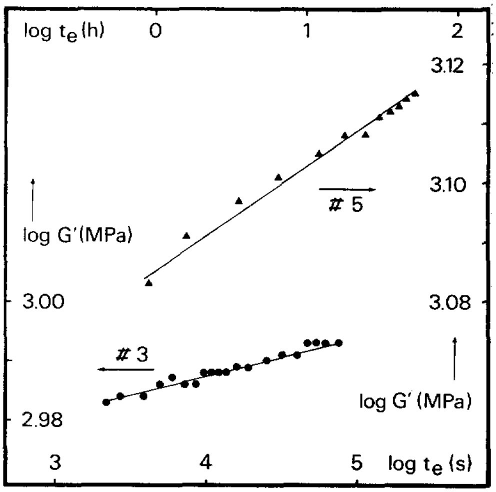

Fig.6 - Evolution of storage modulus at ω = 10 rad/s for quenched (#3) and for cold drawn (#5) samples during physical aging.

coworkers on poly(vinylacetate) (10). When measuring time dependence of G' and tg δ during isothermal experiments, they obtained different shift factors. They concluded that this indicated a slight change in shape of the relaxation spectrum associated with change of free volume. It is not excluded that our findings on PC result from the same phenomenon, meaning that the concept of thermorheological simplicity (11) is not fully satisfied.

To further understand these findings, volume recovery experiments after the same treatments have been performed. They will be published in the near future, with a comparison of both types of measurements.

Acknowledgments

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References

1. L.C.E.Struik,"Physical Aging in Amorphous Polymers and Other Materials," Elsevier Amsterdam (1978).
2. P.Bowden, in "The Physics of Glassy Polymers," ed. by R.N.Haward, Applied Science Publishers London, 279 (1973).
3. R.N.Haward, in "The Physics of Glassy Polymers," ed. by R.N.Haward, Applied Science Publishers London, 340 (1973).
4. A.J.Kovacs, Fortschr. Hochpolym. Forsch. 3, 394 (1963).
5. A.J.Kovacs, Ann.N.Y.Acad.Sci. 371, 38 (1981).
6. B.v.Falkai, G.Spilgies and H.J.Biangardi, Angew.Makromol.Chem. 108, 41 (1982).
7. R.D.Andrews, J.Appl.Phys. 25, 1223 (1954).
8. S.G.Lekhnitskii, "Theory of Elasticity of an Anisotropic Elastic Body," Holden-Day San Francisco, 24 (1963).
9. J.Hennig, Kunststoffe 57, 385 (1967).
10. A.J.Kovacs, R.A.Stratton and J.D.Ferry, J.Phys.Chem. 67, 152 (1963).
11. R.M.Christensen, "Theory of Viscoelasticity," Academic Press New York, 96 (1971).

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