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Influence of deformation on physical aging of polycarbonate

2. Volume recovery near ambient temperature

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Summary

Volume recovery of polycarbonate samples has been investigated by dilatometric and density measurements near ambient temperature. The volume changes with time have been measured either after heating above T_g and quenching, or after cold drawing at ambient temperature. Cold drawing drastically increases the volume recovery rate of polycarbonate, as compared with the rate observed after quenching. This is quite similar to the behavior previously reported on physical aging measured by dynamic mechanical tests (1). The observed decrease of specific volume after cold drawing can be explained by a densification effect due to molecular orientation.

Introduction

It is now widely accepted that the molecular mobility of amorphous polymers below the glass transition, T_g, can be related to the concept of free volume, v_f (2). Below T_g, the polymer glass is, in general, not in an equilibrium state. For example, it has been demonstrated that after a quench from the rubbery into the glassy state ("temperature jump") the specific volume, v, of the glass continues to decrease with time at constant temperature (3 - 5). Simultaneously, an increase of the relaxation times has been observed (3,5), directly indicating the decrease in mobility. These processes have been termed "volume recovery" (3) (or "volume relaxation") and "physical aging" (5). Another way to induce volume changes consists in the application of a sudden "pressure jump". In this case also, a continuous evolution of volume towards its equilibrium value, at constant pressure, has been found (4).

There exists a phenomenon where mobility plays a major role, namely yielding in glassy polymers, especially when they exhibit the "cold drawing" effect. Currently, there exist a variety of theories to explain the yield behavior, but none of them can satisfactorily predict all experimental observations (6,7). The main reason for this is the relative lack of detailed knowledge of the microscopic structure and motion in the glass.

It was decided to investigate the influence of cold drawing by volume recovery or physical aging due to the fact that the evolution of the molecular mobility can be characterized directly. In the first paper, concerning mechanical properties (1), an overview on the main parameters introduced by KOVACS (3) and STRUIK (5) to characterize the state of destabilization and the volume recovery of the glass has already been given. It is not the purpose of this work to discuss in detail the phenomenological theory developed by KOVACS and coworkers (8). Some expressions necessary to analyze the measurements will therefore only briefly be recalled.

Particularly, during an isothermal volume recovery experiment on a sample with an excess volume (for example after a quench), KOVACS has de-

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fined the volume departure, δ, with regard to the equilibrium value, v_∞, of specific volume as:

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

where $v(t_e)$ represents specific volume at time t_e elapsed since destabilization. The contraction isotherms of δ show a sigmoidal shape when plotted as a function of the logarithm of t_e. After an initial slow variation at short times t_e, δ shows a linear region with a constant decrease in function of log t_e. In this time interval, the isotherms may be characterized by their slope, $\tilde{\beta}$, defined as:

$$\tilde{\beta} = (d\delta\ /d\ \log\ t_e)_{min} \quad . \qquad (2)$$

Finally, at very long times, the sample gradually approaches equilibrium volume. A similar parameter, β ("volume relaxation rate"), has been utilized by STRUIK:

$$\beta = -(dv/d\ \log\ t_e)/v \quad , \qquad (2a)$$

which is practically equivalent to $\tilde{\beta}$.

To describe the isothermal variation of the mechanical properties during the aging process, STRUIK (5) has defined a shift rate, μ, as a function of the shift factor, a_δ, and t_e:

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

Furthermore, he has given an expression for the "volume sensitivity", S, connecting volume recovery and physical aging:

$$S = \mu\cdot\ln 10/\beta \quad . \qquad (4)$$

In this paper dilatometric measurements on quenched and cold drawn polycarbonate will be compared near ambient temperature. These volume recovery results will then be correlated with the dynamic mechanical experiments previously published (1). Finally, some surprising discrepancies between the volume recovery rate and specific volume, as measured after cold drawing, will be discussed.

Materials

Extruded sheets of bisphenol A polycarbonate (PC), 9.5 mm thick, manufactured by General Electric under the trade name Lexan 9034, were used in the experiments. The molecular characteristics, determined by gel permeation chromatography, were $\bar{M}_w = 32500$, $\bar{M}_w/\bar{M}_n = 2.86$.

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. As with the previously utilized Tuffak sheets (1), a very low residual birefringence, Δn, of about $2\cdot 10^{-4}$, was observed, probably resulting from the extrusion process.

The sheets were stored in the laboratory a few months before beginning the experiments. Test specimens were prepared from the sheets by cutting with a band-saw and finished by milling and grinding with abrasive paper. They were subsequently annealed at 120 °C for 40 hours in order to eliminate trace humidity and stored in a desiccator over silica gel.

Apparatus

Cold drawing of dumbbell-shaped samples (width 16.5 mm, length of the calibrated part: 70 mm) was performed with a Zwick mechanical tensile machine at constant cross-head speed, equivalent to a mean strain rate, $\dot{\epsilon}$, of about 10^{-3} s^{-1}. The extension ratio obtained was about 1.7 in all cases.

Volume recovery was measured with all-glass dilatometers, consisting of two parts: the sample chamber of about 10 cm^3 and the capillary of diameter 1 mm and length 200 mm. Approximate sample dimensions were: 54 X 12 X 9.5 mm^3 (quenched samples) or 55 X 13 X 7 mm^3 (cold drawn). After introducing the sample, both parts were joined together by spherical glass joints, sealed by silicon grease and fixed with a cyanoacrylate glue. The assembled dilatometer was then evacuated (to 0.5 Pa), filled with mercury and introduced in a water-filled thermostat at 27.5 ± 0.025 °C. The height of the mercury column was measured with a cathetometer with an accuracy of 0.02 mm, corresponding to a volume difference of 0.016 mm^3.

Density measurements were made with a density gradient column (9), filled with aqueous solutions of calcium nitrate. Its density, ρ, was calibrated with standard glass floats, at T = 23 °C. It ranged from 1.2098 to 1.1820 g/cm^3, with a sensitivity of $4.6 \cdot 10^{-5}$ g/cm^3 per mm. The accuracy was estimated at better than 10^{-4} g/cm . Samples for density measurements had a volume of about 40 mm^3.

Experimental method

Volume recovery experiments have been performed on PC samples either after quenching from the rubbery state, or after cold drawing at room temperature. In the first case, the previously weighed samples were heated for about 30 minutes at 165 °C to establish thermodynamic equilibrium. Next, they were quenched to room temperature and then introduced into the dilatometer. As the origin of the recovery time ($t_e = 0$), the beginning of the quench was chosen. In the second case, the tensile specimen was cold drawn at ambient temperature, which took about 20 minutes. The end of the cold drawing was chosen as $t_e = 0$. The sample for the recovery experiment was cut out and weighed from the central part of the deformed area.

Due to the fact that the experiments have been done at $T \ll T_g$, the above relations (1) and (2) could not be applied directly. Indeed, the initial volume, v_i, just after destabilization, and v_∞ could not be measured: the first volume, because about 15 to 30 minutes elapsed necessarily between the quench or the cold drawing and the first measurement; the equilibrium volume, because it would take geological times to reach volume equilibrium.

To circumvent these difficulties, the following method was used: From the variation of the mercury level, the variation of the macroscopic volume, V^*, of the sample was obtained:

$$(dV^*/d \log t_e)_T \; . \qquad (5)$$

Knowing the sample weight, W, the variation of the specific volume can be written:

$$(dv/d \log t_e)_T = (dV^*/d \log t_e)_T/W \; . \qquad (6)$$

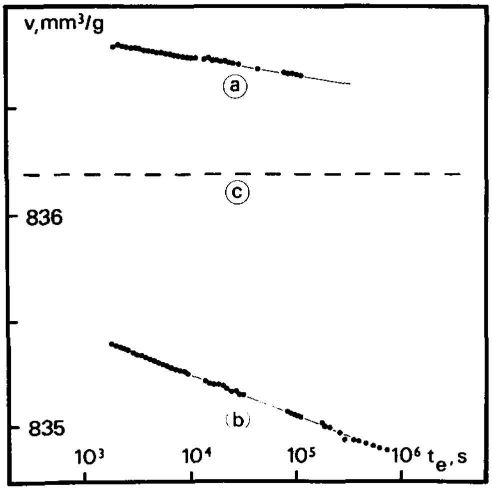

Fig. 1. Volume recovery curves for PC samples after the following treatments: (a) quench (#1), (b) cold drawing (#5), (c) annealing.

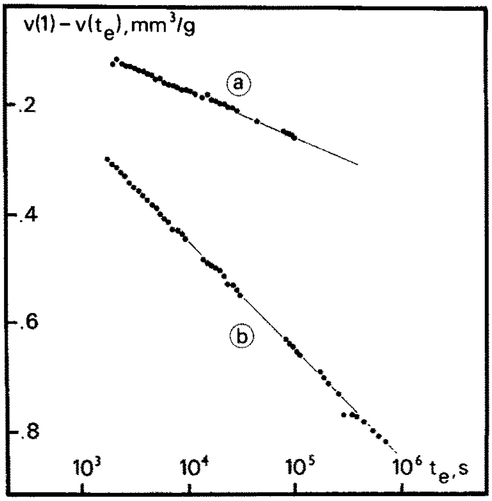

Fig.2. Experiments (a) and (b) from fig.1, replotted as volume changes $v(1)-v(t_e)$ versus aging time.

Then, it was sufficient to measure (with the density gradient column) the specific volume v_r of the sample after a time t_r = 30 minutes. After noting that the volume recovery has been found to be a linear function of log t_e, the change in specific volume is given by:

$$v(t_e) = v(1) + (dv/d \log t_e)_T \log t_e \ , \quad (7)$$

where v(1) represents the specific volume for t_e = 1 minute, with t_e expressed in minutes. By introducing the values for v_r, $(dv/d \log t_e)_T$ and log t_r in relation (7), the volume v(1) can then be calculated.

Results

The volume recovery curves for a quenched and a cold drawn sample are plotted in figure 1, together with the specific volume of the original well annealed PC (v_a = 836.2 mm³/g). In figure 2, $v(1) - v(t_e)$ for the same experiments is plotted, which allows a better comparison between the recovery rates. The experimental data for all samples are listed in table 1.

From the data, two findings are important. First, heating and quenching results in a specific volume increase, as expected, whereas after cold drawing the opposite happens. Secondly, despite this structural densification, the polymer shows isothermal volume contraction, i.e. it seems to go

Sample #	Treatment	Weight (g)	t_e max. (s)	v_r (mm³/g)	$\frac{-dv \cdot 10^2}{d \log t_e}$ (mm³/g)	v(1) (mm³/g)	$-\beta \cdot 10^4$
1	q.	6.740	112000	836.8	8.38	836.9	1.00
2	q.	6.321	93200	837.0	8.21	837.1	0.98
3	q.	6.173	38900	837.3	8.48	837.4	1.01
4	q.	6.139	80200	837.1	8.86	837.2	1.06
5	c.d.	5.337	708000	835.4	20.3	835.7	2.43
6	c.d.	5.545	516000	835.4	20.3	835.7	2.43

Table 1. Volume recovery data of PC samples (q. = quenched, c.d. = cold drawn). Specific volumes v_r were measured at 23 °C and corrected for 27.5 °C, using a thermal expansion coefficient, α, of $1.8 \cdot 10^{-4}$ K^{-1} (10).

further from its equilibrium state. Moreover, this recovery in the "wrong" direction is taking place with a recovery rate, which for the cold drawn samples is greatly enhanced with respect to the quenched ones.

Discussion

By heating the original PC to a temperature above T_g, all its structural memory is erased, after reaching thermodynamic equilibrium. At this temperature, its free volume fraction, $f = v_f/v_g$ (v_g is the specific volume at T_g), is higher than in the glassy state (2). When quenching the sample to 27.5 °C, an f greater than that corresponding to thermodynamic equilibrium at this temperature is frozen in, viz. its value at T_g, f_g. This results in a higher specific volume than in the original sample.

The value of f_g can be estimated with the W.L.F. equation, provided that $\Delta\alpha$, the difference between the coefficients of thermal expansion above and below T_g, is known (2):

$$f_g = c_2^g \cdot \Delta\alpha \,, \qquad (8)$$

where c_2^g represents the second constant of the W.L.F. equation. With data from publications (10) and (11) f_g was determined from relation (8), using for c_2^g its "universal" value 51.6. The results are summarized in table 2.

Now for simplicity, the thermal expansion coefficient α_o of the "occupied volume", v_o, is assumed equal to α_g (3). Then f remains constant ($= f_g$) immediately after the quench to $T < T_g$. If the time-dependent volume changes are due to a free volume decrease alone, then it has been shown (3) that

$$\delta(t_e) = (v(t_e) - v_\infty)/v_\infty = f(t_e) - f_\infty \,, \qquad (9)$$

where f_∞ represents the free volume fraction at equilibrium.

From the W.L.F. equation, one can deduce that when the equilibrium curve above T_g is extended to lower T values, it should intercept the occupied volume curve at a temperature $T_{g\infty}$, 51.6 °C below T_g. At this temperature, f_∞ is estimated to become zero. Consequently, due to the fact that the experiments have been carried out more than 100 °C below T_g, it follows from equation (9):

$$v_\infty = v(t_e)/(f(t_e) + 1) \,. \qquad (10)$$

When choosing $f(1) = f_g$ for $t_e = 1$ minute and introducing the appropriate values v(1) and f_g from table 1 and 2 in equation (10), it follows for the equilibrium volume of the quenched samples at 27.5 °C:

$$v_\infty = 820.3 \pm 0.6 \text{ mm}^3/\text{g} \,.$$

The volume relaxation rates can be compared with those determined by GREINER et al. (10) at higher temperatures ($T > 65$ °C). Furthermore, by combining results of the shift rate, μ, and volume sensitivity, S, obtained by STRUIK (12), one can also recalculate his β values. Fig.3 gives all these data together with our result at 27.5 °C. Obviously, the two curves behave similarly, falling off sharply below T_g. However, at lower temperatures there exists a marked difference in the numerical values, which are higher in experiments performed by GREINER et al. The data obtained by STRUIK remain constant below about 50 °C, showing a good agreement with our value for quenched PC. In the same figure the β value of the cold drawn PC is also plotted.

Reference	$\Delta\alpha \cdot 10^4$ (K^{-1})	v_g (mm^3/g)	f_g	T_g (°C)
HELLWEGE et al. (1962) (11)	3.90	857	0.020	141
GREINER et al. (1984) (10)	4.00	848	0.021	138

Table 2. Experimental parameters from references (10) and (11).

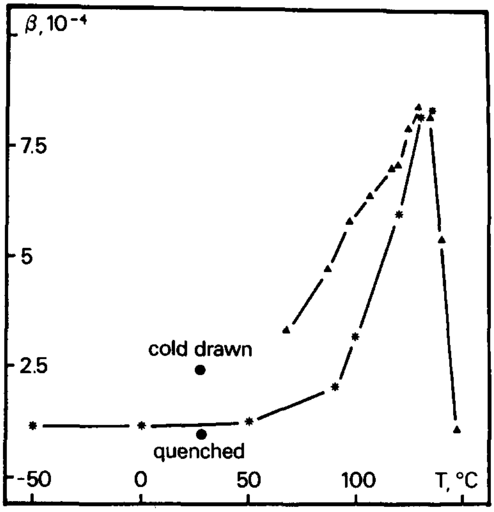

Fig.3. Relaxation rate, β, versus temperature: ✱ STRUIK (Makrolon 8032), ▲ GREINER et al. (Makrolon 3200), ● this work (Lexan 9034).

The volume decrease observed with the cold drawn samples was surprising, as an elastic tensile deformation normally increases the volume (for a Poisson ratio $\nu < 0.5$). Crystallization effects may be excluded because simple heating to 160°C for 30 minutes and quenching to room temperature results in the same volume as after a simple quench (melting temperature of crystallized PC: 221 °C (11)). Actually, such a densification has already been observed with PC and other amorphous polymers after yielding (13 - 16). As an explanation for this phenomenon, several authors proposed that chain orientation facilitates the dense packing of the molecules. That this should indeed be true, has been demonstrated by ROBERTSON in a paper concerning density in relation to polymer order (17). His calculations show that the degree of ordering may be related directly to the density.

In addition to this hypothesis, it is postulated that the volume decrease due to chain orientation affects only the occupied volume. It is assumed however, that v_f is increased by cold drawing. This assumption is supported by results of POWERS et al. (18) who observed a density decrease after strains up to about 3.5 %, followed by densification at higher ones. This behavior may be interpreted as due to continuous increase of v_f, masked by the orientation effects at high strains.

In order to have an estimation of the total v_f in cold drawn PC, the arguments of KOVACS (19) who has shown that the ratio $\delta_i / \tilde{\beta}$ increases as a function of $(\Delta\alpha / \tilde{\beta})(T_g - T)$ may be followed. In the absence of more precise information, it was assumed that $\Delta\alpha$ and T_g were not changed with respect to their values in undeformed PC, which means that the acceleration of the recovery (at the same T) would be uniquely due to free volume increase. This implies that δ_i ($\simeq \delta(1)$) is proportional to $\tilde{\beta}$, giving $\delta(1) = f(1) = 0.049 \pm 0.003$ for the cold drawn PC. Finally, by substituting the values obtained for v(1) and f(1) in equation (10), the equilibrium volume $v_\infty = 796.7 \pm 2.3$ mm^3/g is found (reported value for crystalline PC (20): $v_c = 760$ mm^3/g).

The value for the free volume fraction of the cold drawn PC seems rather high. It compares, however, quite well with the value f = 0.0444 obtained by MATSUOKA for PC yielded in tension at a strain rate of $8 \cdot 10^{-4}$ s^{-1} at 23°C, which he calculated with his model based on strain induced dilation (21).

Now, in order to compare our previously published mechanical measurements (1) with the dilatometric data, the volume sensitivity, S (eq.4), may be utilized. One finds

- after quenching: $S = (2.4 \pm 0.2) \cdot 10^4$,
- after cold drawing: $S = (2.2 \pm 0.2) \cdot 10^4$.

These values correspond almost exactly to STRUIK's data, viz. $S = 2.2 \cdot 10^4$, as deduced from (12).

Conclusion

It has been shown that in the cold drawn PC, despite the induced volume decrease, recovery proceeds not only by further densification, but also with an increased recovery rate. By comparing the mechanical and volume recovery experiments through the volume sensitivity, S, it appears that the previously determined (1) shift rate, μ, and the volume relaxation rate, β, increase proportionally. This indicates that with respect to the behavior after a quench, cold drawing has resulted in an enhancement of molecular mobility, and also of the free volume fraction. The contradiction between the latter conclusion and the observed densification after cold drawing can be explained by the influence of chain orientation.

Acknowledgments

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