Anisotropic hygroelastic behaviour of oriented poly (methyl methacrylate)

D. Cohn and G. Marom
Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University, Jerusalem, Israel

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A series of samples of oriented poly(methyl methacrylate) was prepared by drawing at a range of temperatures above T_g to a constant extension ratio. The birefringence was used as a measure of orientation. The specimens were immersed in water at 21°C and the coefficients of hygroelasticity were calculated from the dimensional change and weight gain data. Two coefficients, namely the longitudinal and the transverse, were measured for each sample. The longitudinal coefficients of hygroelasticity exhibit a linear decrease and the transverse exhibit an increase as the birefringence increases from zero. The results are analogous to those obtained for thermoelasticity (Wilson, J. D. and Treloar, L. R. G. *J. Phys. (D)* 1972, 5, 1614).

INTRODUCTION

Molecular orientation in polymers results in anisotropic mechanical and physical properties, and a number of studies have been concerned with various aspects of this phenomenon. A few specific examples for PMMA are the effect of orientation on the modulus[1], the strength and fracture surface energy[2,3] and the thermal expansivity[4]. Since the latter properly is analogous to hygroelasticity, let us elaborate on the findings by Wilson and Treloar[4] in their work on anisotropic thermal expansivity of oriented Perspex. Their results obtained with drawn specimens having birefringence values in the range 0–14.4 x 10^{-4}, showed that the longitudinal thermal expansion coefficient decreases while the transverse one increases with increasing orientation. The dependence on the birefringence was linear in both cases. It was also concluded that the birefringence bore specific relation to molecular orientation, and could be used in quantitive relations expressing the expansivities.

A previous study concerning the coefficient of hygroelasticity pointed out the analogy between hygroelasticity and thermoelasticity, and suggested how it could be used for the prediciton of a polymer lifetime under particular swelling conditions[5]. Another work which laid the foundation for the present research showed that in highly anisotropic materials, i.e., unidirectional glass-reinforced composites, the hygroelastic behaviour is also anisotropic, as manifested by the difference between axial and transverse coefficients[6].

In the present paper we present a detailed account of the hygroelastic behaviour of oriented PMMA at 21°C. We focus our attention on the effect of orientation on the rate of water take-up, and especially on the coefficient of hygroelasticity. We also examine the effect of the specimen thickness on the values of the coefficient.

EXPERIMENTAL

Preparation of specimens

Specimens of length 15.0 and width 3.0 cm were cut from PMMA sheets of thicknesses in the range 1.2–2.3 mm. Orientation was achieved by a drawing procedure carried out in a hot chamber of an Instron machine. The free length between the clamps was 10 cm before drawing and 20 cm after, resulting in an overall extension ratio of 2. The extent of orientation was varied by changing the drawing temperature in the range 110°–160°C and the drawn specimens were quenched in the extended state by cool water. A constant rate of extension of 50 cm/min was observed. (It has been shown before that for given extension ratio and rate of extension the birefringence decreases with increasing temperature[3].) In order to be able to observe the uniformity of the drawing process in any region of the specimen a grid of lines forming 0.5 x 0.5 cm^2 squares was marked on the surface prior to drawing.

Three 4.3 x 1.5 cm^2 specimens for hygroelasticity experiments were cut with a milling machine from the oriented plates. The long dimension of each specimen was parallel to the drawing direction. The birefringence (Δn) of each specimen was determined with quartz red I compensator; the error in the birefringence measurement was about ±0.5 x 10^{-4}. No birefringence difference was observed between specimens cut of the same drawn plate.

Measurements of hygroelasticity

The coefficient of hygroelasticity was defined before[5] by

$$\mu = \frac{\Delta L/L_0}{\Delta V^*/V_0} \qquad (1)$$

where $\Delta L/L_0$ is the relative length change, V_0 is the original specimen volume, and ΔV^* is the volume occupied outside the polymer by the diffused liquid weighing ΔW. It should be noted that ΔV^* is usually greater than the actual volume change of the material, ΔV. Thus $\Delta V^* = \Delta V + \delta$, where δ accounts for the volume of the liquid molecules which occupy the free volume of the polymer without causing any volume increase, and for the different density of the liquid within the polymer.

Specimens for hygroelasticity measurements were immersed in distilled water, and taken out periodically for

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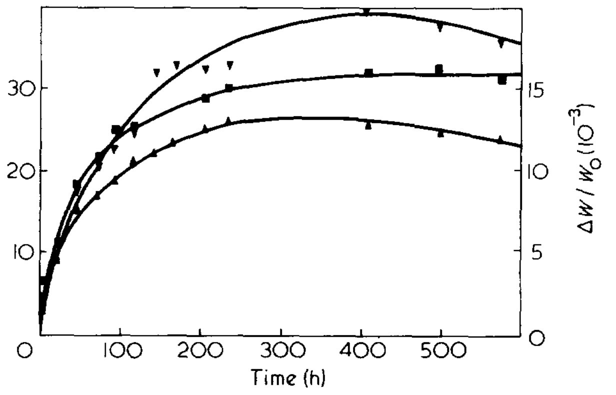

Figure 1 Plots of longitudinal (▲) and transverse (▼) dimensional changes and of the relative weight change (■) as functions of the swelling period. ($\Delta n = 7.7 \times 10^{-4}$)

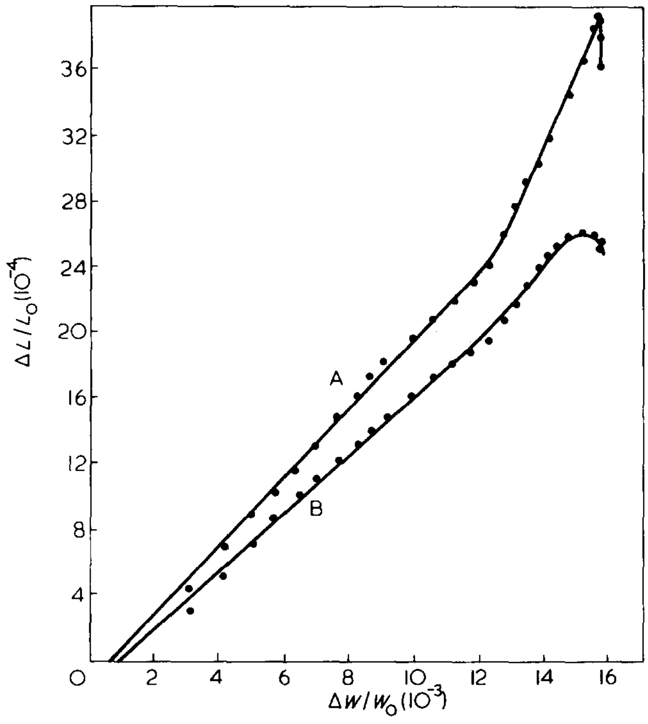

Figure 2 Plots of $\Delta L/L_0$ *versus* $\Delta W/W_0$ for the data of *Figure 1*. A, transverse; B, longitudinal

weighing and dilation measurements. ΔL was measured by placing each specimen in a stainless steel fixture attached to a dial gauge capable of measuring to half a micron. The maximum temperature variation allowed during ΔL measurements was ±0.5°C, and this resulted in ΔL changes of less than about ±1 μm (as determined by the difference between the coefficients of thermal expansion of the stainless steel frame and the various specimens, according to reference 4). At least 3 specimens were used for each birefringence.

The dimensional changes due to water absorption were measured for each specimen in both longitudinal (orientation direction) and transverse directions. The corresponding coefficients of hygroelasticity, denoted by μ^L and μ^T respectively, were worked out from these dimensional change data. *Figures 1* and *2* demonstrate how the experimental data were processed to result in the μ values. The demonstration is carried out for specimens of $\Delta n = 7.7 \times 10^{-4}$. *Figure 1* presents plots of the longitudinal and the transverse relative dimensional changes and of the relative weight change *versus* the water immersion period. The data in *Figure 1* were used to produce plots of $\Delta L/L_0$ *versus* $\Delta W/W_0$ for the longitudinal and the transverse cases. For reasons discussed later μ was worked out from the initial linear part of the curve by multiplying the slope by the water to polymer density ratio. No significant effect of orientation on polymer density was traced, and the average polymer density value taken was 1.175 g/cm^3.

RESULTS AND DISCUSSION

Effect of plate thickness

The thickness of the sheet is known to affect the transport behaviour of a liquid in it, and to determine the limit whereby a sheet is thin enough to result approximately in one-dimensional penetration. For transport of methanol in PMMA[7] for example, an ideal Case II transport in a 1 mm thick sheet becomes anomalous in a 3 mm thick sheet, and a typical 'step' concentration profile in the first shows a gradient in the latter.

It was, therefore, important to examine whether the thickness of the hygroelasticity specimens (in the range 1.0–1.8 mm) affected the values of μ. This was checked for both unoriented and oriented specimens, and some of the results are presented in *Table 1* and *Figure 3*. *Figure 3* presents plots of $\Delta W/W_0$ *versus* immersion time for unoriented specimens of different thicknesses. It is seen that at any instant the thicker the specimen is the lower the $\Delta W/W_0$ value it exhibits. However, it is important to note that this behaviour is controlled in the first 100–120 h by the different W_0 values (resulting from the different thicknesses), while ΔW itself exhibits similar values regardless of the specimen thickness. This suggests that the penetration during the first period is controlled by the specimen surface area.

Table 1 Effect of sheet thickness on μ

Δn	Thickness (cm)	Surface area (cm^2)	Surface area/volume (cm^{-1})	μ^L	μ^T
0	0.180	15.4	12.9	0.16	0.16
0	0.152	15.1	14.8	0.17	0.17
0	0.122	14.7	18.4	0.16	0.16
7.1	0.150	15.1	15.1	0.15	0.19
7.1	0.120	14.7	18.4	0.14	0.19
7.7	0.130	14.8	17.1	0.15	0.21
7.7	0.110	14.6	20.0	0.15	0.20

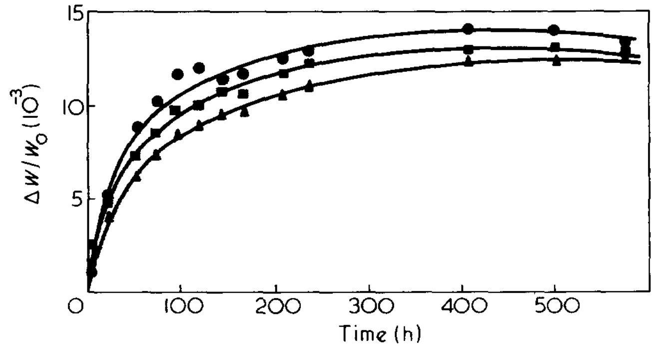

Figure 3 Effect of plate thickness on rate of water take-up increase: 1.22 mm (●), 1.52 mm (■), 1.80 mm (▲), ($\Delta n = 0$)

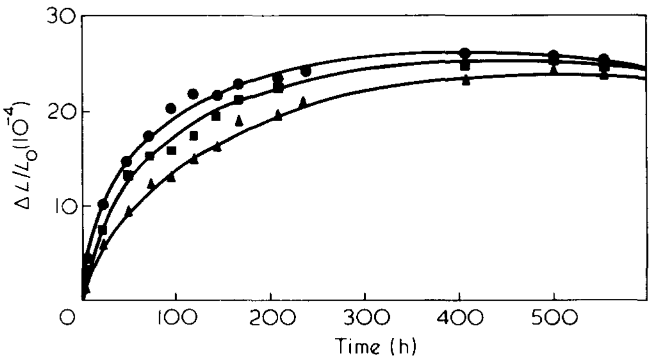

Figure 4 Effect of plate thickness on rate of dimensional change: 1.22 mm (●), 1.52 mm (■), 1.80 mm (▲); (Δn = 0)

Table 1 shows that this parameter is insignificantly affected by the thickness variation.

The values of μ in *Table 1* exhibit independence of the thickness within the limits of the experimental error. This is an important observation which reflects the fact that the dimensional change due to swelling is a direct function of the relative water take-up irrespective of the thickness in the examined range. Thus, it is thought that water penetration in the present experiments may be justifiably regarded as a one-dimensional phenomenon, and the thickness effect is negligible.

Anisotropy of coefficients of hygroelasticity

Let us examine the prominent features of *Figures 1* and *2*. *Figure 1* indicates that after about 300 h the weight gain reaches a constant value. At that point the equilibrium swelling concentration is probably attained. The expansion results reach a maximum after 250 h in the longitudinal case and after 400 h in the transverse. This trend was exhibited by all the oriented specimens; the period of time required for the maximum to appear decreased as the orientation increased. In contrast to the oriented specimens the unoriented did not exhibit a maximum in $\Delta L/L_0$ even after 600 h, as shown in *Figure 4*. In *Figure 2* we see that $\Delta L/L_0$ as a function of $\Delta W/W_0$ exhibits the following trend: at first it is linear, then in the vicinity of $\Delta W/W_0 = 13 \times 10^{-3}$ the slope starts to increase until a sharp maximum, corresponding to that in the $\Delta L/L_0$ data, is reached. It is thought that the behaviour described in the preceding paragraph is a result of a relaxation process which takes place within the swollen drawn specimens. A recent paper[8] indicated that the shrinkage stress associated with the relaxation of PMMA of Δn about 10×10^{-4} was between 5–8 MPa. This stress developed when the oriented sample, constrained to a constant length, was heated to a temperature just above T_g. It is reasonable to assume that swelling, although occurring at a temperature much below T_g results in a similar, but much smaller, relaxation effect. The relaxation caused by swelling initially results in higher expansion as $\Delta W/W_0$ increases; these higher expansions are manifested by the increased slopes of the curves of $\Delta L/L_0$ *versus* $\Delta W/W_0$. Later as the swelling proceeds the relaxation induces shrinkage, and $\Delta L/L_0$ starts to decrease; hence, the observed maximum. It should be noted that birefringence measurements with either swollen or dry specimens did not exhibit any changes due to the proposed relaxation process. However it is maintained that relaxation of swollen drawn PMMA does occur, although its effect on the birefringence is small, and is below the limits of birefringence detection by the method employed in this work.

In view of the above reasoning the value of μ was calculated from the slope of the initial linear part (until $\Delta W/W_0 \sim 13 \times 10^{-3}$) of the $\Delta L/L_0$ *versus* $\Delta W/W_0$ curve.

Figure 5 presents the results of μ^L and μ^T as a function of the birefringence. The longitudinal coefficient of hygroelasticity exhibits a linear decrease as a function of the birefringence. A statistical treatment of the data produces a high negative correlation which is significantly different than zero at the 5% level of significance. The transverse coefficients generally increase with Δn, yet the linear correlation is significantly different from zero at the 10% level only. This was probably caused by the fact that the oriented specimens were narrow (length to width ratio of 3), yielding a relatively higher error in transverse $\Delta L/L_0$. The effect of orientation on hygroelasticity is similar to that on thermoelasticity shown by Wilson and Treloar[4], and it is therefore proposed that $\mu^L - \mu^T$ represents a measure of the anisotropy of hygroelasticity.

The above results can be discussed in terms of the analogy between thermoelasticity and hygroelasticity. The two phenomena depend on the intermolecular forces, while the length of the interatomic bonds is independent of either the temperature or the volume of the diffused water, respectively. Orientation of a polymer gradually results in a situation whereby the behaviour in the longitudinal direction is controlled more and more by the interatomic bonds; concomitantly, the intermolecular forces become more effective in the transverse direction. Thus, as the degree of orientation increases the axial thermal expansion and swelling decrease, and the transverse properties increase.

Effect of orientation on rate of water take-up

Figure 6 contains plots of $\Delta W/W_0$ *versus* immersion period for specimens of equal thicknesses and different orientations. It is seen that orientation has no significant effect on the rate of water take-up. This is unlike the analogue case of unidirectional fibre-reinforced composites, where the diffusion into the fibres and the matrix are different. It is therefore clear that the anisotropic behaviour of μ derives from the effect of orientation on $\Delta L/L_0$, as seen in *Figure 7* which compares longitudinal $\Delta L/L_0$ curves for different orientations.

CONCLUSIONS

The present study is concluded as follows.

(1) Hygroelastic behaviour of oriented poly(methyl methacrylate) is anisotropic

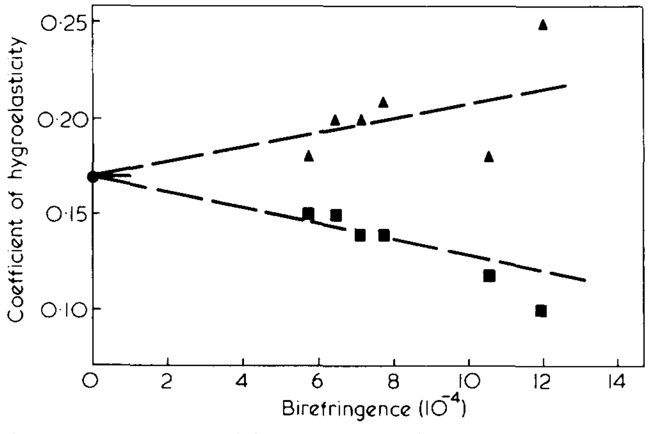

Figure 5 Longitudinal (■) and transverse (▲) coefficients of hygroelasticity as functions of the birefringence

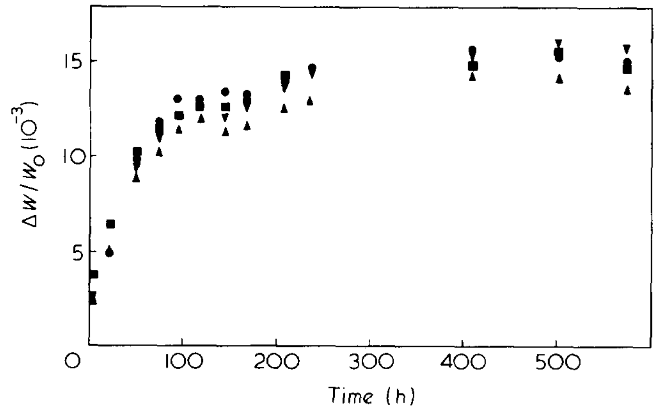

Figure 6 Effect of orientation on rate of water take-up: $\Delta n = 0$ (▲), $\Delta n = 7.1 \times 10^{-4}$ (▼), $\Delta n = 10.5 \times 10^{-4}$ (●), $\Delta n = 11.9 \times 10^{-4}$ (■)

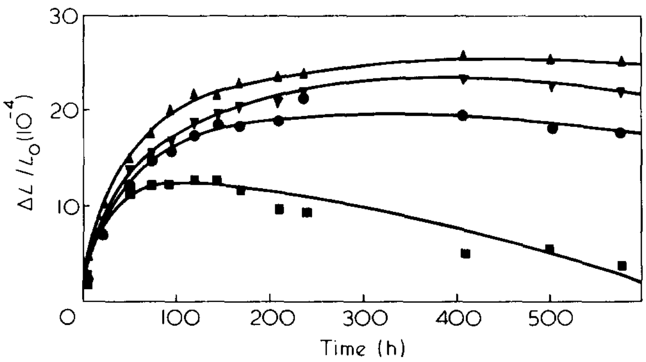

Figure 7 Effect of orientation on longitudinal $\Delta L/L_0$: $\Delta n = 0$ (▲); $\Delta n = 7.1 \times 10^{-4}$ (▲), $\Delta n = 10.5 \times 10^{-4}$ (●), $\Delta n = 11.9 \times 10^{-4}$ (■)

(2) The longitudinal coefficient of hygroelasticity decreases while the transverse increases with the orientation; in both cases a linear dependence on birefringence is exhibited.

(3) The results are in complete analogy with those of anisotropic thermal expansivity of oriented poly(methyl methacrylate).

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