

Residual Stresses and Birefringences in Large, Quenched Samples

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Synopsis

As large polymer samples are quenched rapidly, residual stresses (and birefringence) are frozen into the final part due to the different thermal/contraction histories of the surface and center portions. The present work on polystyrene, a continuation of earlier studies, deals with the effects of sample size and initial temperature; these results are treated with the general theory of Lee, Rogers, and Woo. Finally, data for two other amorphous polymers, poly(methyl methacrylate) and polycarbonate, are presented; in these cases the simpler theory of Aggarwala and Saibel is used. The theories help explain the relative behavior of the three materials and are qualitatively useful. However, the complexity of the rheo-optical response precludes doing a completely rigorous treatment.

INTRODUCTION

As large parts are shaped and solidified, the nonhomogeneous cooling history produces what are often called *residual stresses*, accompanied by residual birefringences. The term *thermal stresses* is also sometimes used, but we prefer to reserve that term for cases where the temperature gradient is present at the moment of consideration (such as in the tubes of a heat exchanger). In contrast, residual stresses are the result of *prior* temperature gradients, the sample being at a uniform temperature (usually room temperature) when it is being studied. The birefringences being considered here are not due to the prior (flow-induced) orientation of the molecules, although this effect could also be present, but rather to the residual stress mechanism itself. The physical picture has to do with the nonuniform history of the volume contraction and the anisotropic stresses thereby produced. When the surface contracts, the center is still hot and the stresses produced there relax; however, when the center solidifies also, the entire sample is now acting in an elastic manner. The net result of this complex process is a sample with the surface under compression and the center under tension. In the case of inorganic glasses the compressive stresses can be quite significant, this being the mechanism for producing tempered glass.¹ The effects are much less striking in polymers, however, because the samples will show internal cracks—or shatter immediately—under severe quenching conditions.² Nonetheless, residual stresses are surely present, even if accidentally, in all rapidly cooled molded or extruded parts. This is not

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necessarily detrimental and may increase the impact strength or change the nature of the failure mechanism.³

The thrust of the present study, which builds on the earlier work of Wust and Bogue⁴ on polystyrene, is to observe and to quantify residual birefringences as a function of thermal history for several materials. Residual stresses are quite difficult to measure directly, even in simple shapes, whereas residual birefringences can be readily measured by sectioning the sample (see Fig. 1) and the technique is also applicable to complex parts. The prior paper⁴ reviews the literature on both methods. The difficulty with birefringence, of course, is that the rheoptical behavior must be known in great detail, a requirement that is only partially met.

In the present work we turn to the effects of sample size and initial temperature on the birefringence profiles. And also we extend to two additional amorphous polymers, giving us finally data on three materials: polystyrene (PS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC). The theoretical treatment will be described in the next section.

THEORY

Although we measured residual birefringences, the theory is cast in terms of residual stresses, and we therefore present the basic equations in that form. The most general treatment is that of Lee, Rogers, and Woo (LRW),⁵ who imagine a slab similar to that shown in Figure 1 but of infinite extent in the 2- and 3-directions. One must imagine a solidification of the extremities, however, because there must be a mechanism for averaging out the stresses there (and in fact elsewhere along the 2- and 3-directions). That is,

$$\int_{-b}^b \sigma(x_1, t) dx_1 = 0 \quad (1)$$

where $\sigma = \sigma_{22} = \sigma_{33}$. With various assumptions, this "squeezing stress" (σ) is given by

$$\sigma(x_1, t) = \int_0^t 2G(t-t') \frac{\partial}{\partial t'} [\epsilon_2(t') - \epsilon_1(x_1, t')] dt' \quad (2)$$

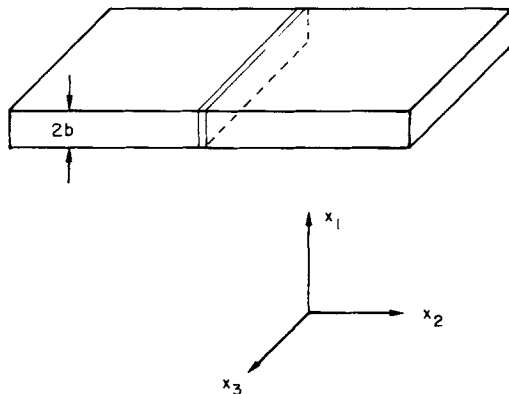


Fig. 1. Schematic diagram of the slab used in the residual birefringence measurements.

where t is time, $G(t-t')$ is a relaxation modulus, and $\epsilon_2 = \epsilon_{22}(t) = \epsilon_{33}(t)$ and $\epsilon_1 = \epsilon_{11}(x_1, t)$ are linear strains. The trace of stress σ_{kk} is presumed to be instantaneously related to the volume change (ϵ_{kk}) and the temperature change (i.e., an instantaneous PVT relation is assumed), cast in terms of a compressibility factor and a thermal coefficient of expansion. By using such relations LRW recast eq. (2) in the form

$$\sigma(x_1, t) = 3 \int_0^t R(t-t') \frac{\partial}{\partial t'} [\epsilon_2(t') - \alpha T(x_1, t')] dt' \quad (3)$$

where $R(t-t')$ is an auxiliary modulus function related to $G(t-t')$ through an integral equation, but is not qualitatively different in shape than $G(t-t')$. As implied by Wang et al.⁶ and shown in some detail by Wust,² this general theory can be reduced to the simpler theory of Aggarwala and Saibel⁷ by imagining rheological behavior in which G is zero above some critical temperature (T_g) and a large constant below it (i.e., the material either has no memory at all or complete memory). After a number of steps eq. (3) reduces to

$$\sigma(x_1, t) = \int_{\bar{t}(z)}^t 6\beta \left\{ \frac{1}{b-\bar{z}(t)} \int_{\bar{z}(t)}^b \frac{\partial}{\partial t'} [\alpha T(x_1', t')] dx_1' - \frac{\partial}{\partial t'} [\alpha T(x_1, t')] \right\} dt' \quad (4)$$

where $\bar{t}(z)$ is the time at which a particular position z passes through T_g , $\bar{z}(t)$ is the position of the solidification line at any time t , α is the thermal coefficient of expansion, and 6β is an elastic modulus related to Young's modulus.⁴ Equation (3) is the theory of Aggarwala and Saibel⁷ as used by Wust and Bogue.⁴ For predicting birefringence the function $R(t-t')$ in eq. (3) and the modulus 6β in eq. (4) must be replaced by the strain optical coefficient C_ϵ , either a constant or a function of temperature (and thus of time). In the work with the LRW theory de la Vega replaced $R(t-t')$ by the assumed form

$$S(t-t') = C_\epsilon(t') \exp \left\{ -\frac{1}{\tau_0} \int_{t'}^t \exp[K(T-T_R)] dt'' \right\} \quad (5)$$

where τ_0 is a characteristic relaxation time (at a reference temperature T_R), K is a linearized shift factor, and $C_\epsilon(t')$ is short-hand for $C_\epsilon[T(t')]$, which becomes a constant, $C_\epsilon(T_e)$, for $T < T_e$. The temperature T_e is defined below. Using the WLF equation for mechanical response, de la Vega estimated K to be $0.3126^\circ\text{C}^{-1}$, but in the case of the optical response this is better described as an adjustable parameter. Equation (5) is an arbitrary assumption, among several that were considered in the thesis.⁸ Note that while eq. (1) requires a balance of the negative and positive portions of the stress profile, no such requirement is imposed on the birefringence (unless, of course, a constant value of C_ϵ is used).

A conceptual difficulty in the Wust-Bogue work, which continues also into the present work, is that one must use an optical coefficient with a sign which is characteristic of the rubbery state (negative in the case of

PS) and with a magnitude characteristic of the near- T_g region. In one sense this seems reasonable inasmuch as the molecular "action" must be frozen out shortly after passing through T_g . This is consistent with experimental work to be discussed later, in which we sectioned some of the final samples, thereby relieving the residual stresses in them. This removal of the residual stresses did not affect the residual birefringences, which indicates rather clearly that the birefringences must have been frozen-in during an earlier part of the cooling history. But in another sense the need to use a coefficient near T_g is not reasonable: a significant amount of the strain rearrangement occurs after the center has frozen (dropped below T_g), but before the entire sample has come to thermal equilibrium. To obtain reasonable predictions one must continue to use near- T_g coefficients in this latter portion also. Wust and Bogue rationalized that fact by calling on a concept from volume aging studies, via the so-called "effective temperature" T_e as defined by Rusch.⁹ T_e is the temperature the material would hypothetically have if its actual (possibly nonequilibrium) free volume were to be calculated by equilibrium equations. Because a rapidly cooled glass is necessarily not in volume equilibrium, T_e will be substantially above the actual temperature T and is in fact only somewhat lower than the usual value for T_g . Following Rusch, T_e appears in the form of a WLF equation, both above and below the glass transition, as follows:

$$\log a_{T,V} = \frac{-C_1(T_e - T_R)}{C_2 + T_e - T_R} \quad (6)$$

where T_R is a reference temperature and $a_{T,V}$ is a generalized shift factor. More details and numerical values are given in Wust and Bogue.⁴ For whatever the physical reason the theory, as it is presently formulated, forces one to use strain optical coefficients in the near- T_g region if one is to obtain satisfactory predictions.

EXPERIMENTAL

Three amorphous polymers were studied: polystyrene (PS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC). The PS was Shell TC 3-30, which has been used extensively in prior work.⁴⁻¹⁰ Its molecular parameters are $M_w = 2.83 \times 10^5$ and $M_w/M_n = 4.6$. Slablike samples were compression-molded with a hydraulic press, as described by Wust.² The PMMA was provided in sheet form in two thicknesses ($\frac{1}{4}$ and $\frac{1}{8}$ in.) by the Rohm and Haas Co., (Knoxville, TN). The material was unoriented and not crosslinked and carries the designation Plexiglas UVAIL. The PC was also supplied in sheet form, in the same two thicknesses, by the Rohm and Haas Co. (Bristol, PA) and is designated as Tuffak. Approximate values of T_g for the three materials, taken from the literature, are about 100°C (PS), 104–110°C (PMMA), and 145–156°C (PC).¹¹

Two samples sizes were used: $1 \times 2 \times \frac{1}{4}$ in. and $1 \times 2 \times \frac{1}{8}$ in. The PS samples were essentially stress-free (as determined by birefringence) after removal from the slowly cooled mold. The as-received PMMA and PC samples had considerable initial birefringence and were annealed (at 100°C for PMMA and 130°C for PC) and cooled slowly back to room temperature. The procedure was repeated twice, which essentially eliminated residual effects

from the PMMA but not entirely from the PC; however, the residual birefringence in PC was small compared with that ultimately induced by the ice water quench and was neglected. All of the work on PS was done by de la Vega⁸ and all of that on PMMA and PC by Lee.¹¹

The samples were heated in a laboratory oven to the initial temperature (either 120 or 160°C for PS and PMMA; and 160, 170, or 180°C for PC). They were held there for approximately 30 min, removed by tongs, and plunged into an ice water bath. In the case of PS at 160°C, de la Vega found considerable distortion of the shape during the heating and developed a method for framing the samples along the edges. He first tried aluminum frames but later settled on epoxy-molded frames since the latter more nearly approximate the contraction behavior of PS. In the case of PMMA and PC, Lee observed shape distortion at high temperatures but not at the temperatures finally used and therefore did not use the framing technique.

The quenched samples were sectioned as shown in Figure 1, the cutting being done on a Gillings-Hamco thin-sectioning machine and the surfaces polished with decreasingly smaller abrasive materials. By using different thicknesses Wust was able to choose a thickness (4.3 mm) for which no effect of the polishing or of stress relief in the 2-direction could be detected. Finally birefringence profiles across the thin (or 1) dimension were made by placing the sample in an optical line containing a light source, microscope, and Babinet compensator. Complete details of the cutting optical techniques are given by Wust^{2,4} and de la Vega.⁸

An ice water quench was used in all of the experiments. An important aspect of the analysis has to do with the temperature distribution within the sample during the quench. This was considered in detail by Wust, who embedded thermocouples at various positions in a ¼ in. thick sample. The results were treated with transient heat transfer theory for finite slabs, with the Biot number being essentially infinite for the ice water quench. In dealing with other materials and other thicknesses, an infinite Biot number was again assumed, but an appropriate adjustment for the differing thermal diffusivities of the three materials was introduced.¹¹ For qualitative reasoning it is often useful to have an idea of the cooling rate in real time. From Wust's experiments on a ¼ in. PS slab starting at 130°C: the centerline temperature dropped to 95°C after 30 s and to 50°C after 60 s. The ⅛ in. samples can be expected to cool to the corresponding temperatures in one-fourth of the times noted.

As a check on the character of the residual birefringences, Lee cut apart several of the sectioned samples of PMMA along their centerlines, thereby relieving the stresses there.¹¹ The birefringences were unchanged by this cutting, showing that the stress state in the final sample does not have a significant effect on the final birefringences. This result, while not definitive, indicates that the birefringence is frozen-in early in the cooling history and not at the end of it.

DETAILED STUDIES ON POLYSTYRENE

In the new work on PS,⁸ the effects of sample thickness and of initial temperature (T_0) were studied, as shown in Figures 2 and 3. As one might suppose, there are larger birefringences in the thicker sample, because the

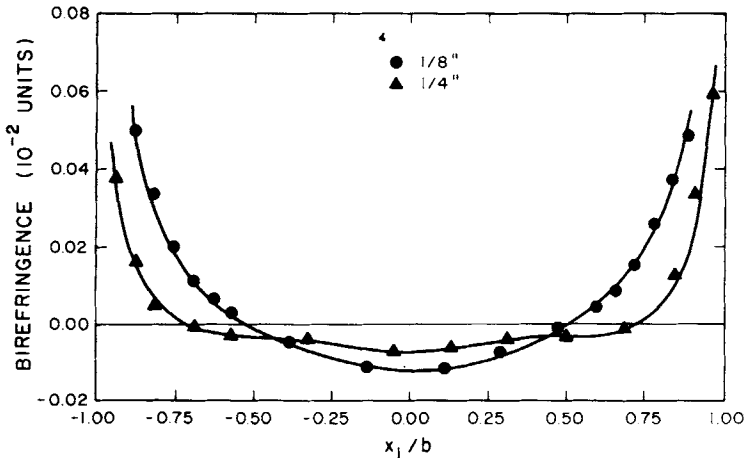


Fig. 2. Effect of thickness on the birefringence profiles (PS, $T_0 = 120^\circ\text{C}$): (●) $\frac{1}{8}$ in.; (▲) $\frac{1}{4}$ in.

thermal gradients persist longer. A general observation is that many of the profiles are not "balanced" (in the sense of the negative and positive portions being equal), as were those of Wust and Bogue. Starting from a high temperature (160°C) produces a very large degree of unbalance.

In an attempt to explain results such as these, de la Vega⁸ undertook to use the optical form of both eq. (5) (with variable C_e) and the general LRW theory [eq. (3)]. In comparative studies he explored the effect of (1) changing the effective T_g , since T_g is known to increase at high cooling rates¹⁰; (2) using an effective temperature T_e [see eq. (6)] for calculating C_e ; (3) allowing the thermal coefficient of expansion (α) to be a function of temperature; and (4) introducing a relaxation time for the birefringence as shown in eq. (5). The temperature-dependent strain optical coefficient, $C_e(T_e)$, was taken from the prior work.⁴

All of the variables studied affected the results but in particular cases

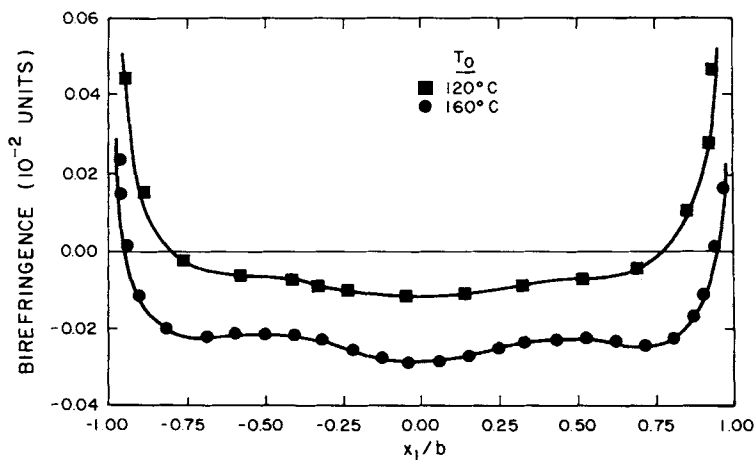


Fig. 3. Effect of initial temperature T_0 on the birefringence profiles (PS, $b = \frac{1}{4}$ in.): (■) 120°C ; (●) 160°C .

(3) and (4) had significant effects on both the magnitude and the shape of the profiles. The computer program is very time-consuming due to the multiple integrations and to the need to use extremely small time and spatial steps near the beginning of the quench. Discontinuities near the surface were a continuing difficulty and can never be entirely eliminated due to the discontinuous temperature change at the surface itself. After a number of runs it was concluded, however, that all of the trends shown in Figures 2 and 3 could be predicted, although by no means uniquely. There are a large number of adjustable parameters. The apparent (or rate-dependent) T_g (app), the effective temperature T_e , and the expansion coefficient α (if constant) are known to within reasonable limits; but τ_0 and K are adjustable. If we introduce $\alpha(T)$, then further adjustable parameters occur. It would require an extensive independent study to establish all of the parameters *a priori*. Also recall that the LRW theory, despite its generality, does not allow for time-dependent volume changes, and these need also to be included.

A good (but arbitrary) theoretical fit to the data of Figure 3 is shown in Figure 4. For this choice of parameters the theory correctly predicts the essential feature—namely, that a high initial temperature give rise to an unbalanced profile. We show Figure 5, however, to demonstrate that a very different choice for τ_0 , if coupled with a temperature dependent function $\alpha(T)$, gives a prediction similar to that of the previous figure (for $T_0 = 120^\circ\text{C}$).

STUDIES ON PMMA AND POLYCARBONATE

For any analysis of residual birefringence one must have independent data for the stress (or strain) optical coefficient. Considerable data for PS are available (see Wust and Bogue⁴). There are some literature data for PMMA, as reported by Tsvetkov and Verkhovina,¹² but apparently none for PC. We therefore undertook measurements of the stress optical coefficient for these two latter materials. The technique was essentially the same

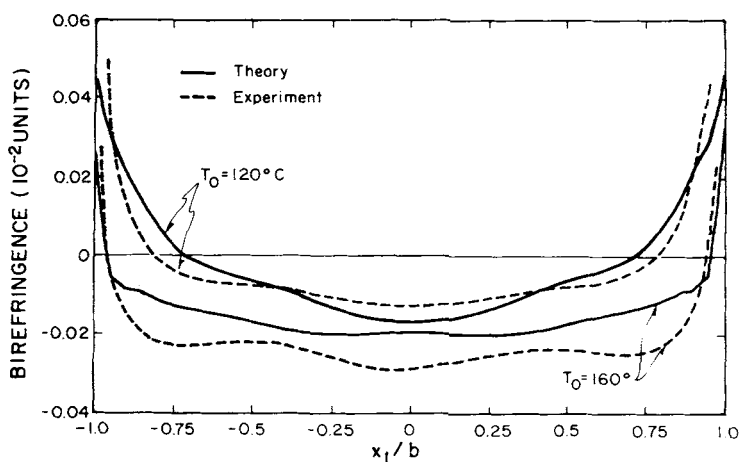


Fig. 4. Good but non-unique fit of theory (—) to experimental (---) profiles [PS; $T_0 = 120^\circ\text{C}$ ($T_e = 92.8^\circ\text{C}$); $T_0 = 160^\circ\text{C}$ ($T_e = 91.5^\circ\text{C}$); $T_g(\text{app}) = 100^\circ\text{C}$; $C_e = f(T_e)$; $\alpha = 2.1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$; $\tau_0 = 1 \text{ s}$].

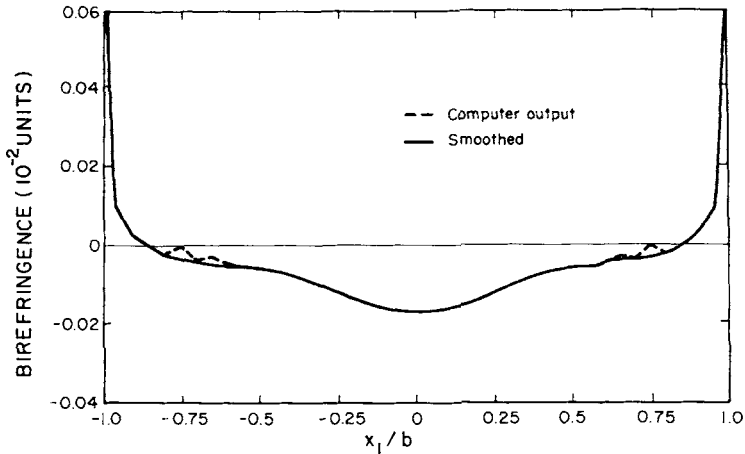


Fig. 5. Theoretical prediction using temperature-dependent coefficient of volume expansion [PS, $T_0 = 120^\circ\text{C}$, $T_e = 93.4^\circ\text{C}$, $T_g(\text{app}) = 103^\circ\text{C}$, $C_e = f(T_e)$, $\alpha = f(T)$, $\tau_0 = 300$ s]: (---) computer output; (—) smoothed.

as that used earlier,⁴ with the samples of PMMA and PC being slabs taken from the materials used in the residual experiments. Wust and Bogue reported significant time effects in the birefringent response of PS, but decided on a short-time (10–15 s) coefficient as the appropriate one for rapidly cooled samples. The applied tensile stress was increased incrementally, and the birefringence read in approximately 10–20 s. The results are reported in Figures 6 and 7 in units of Brewsters, where $1 \text{ Br} = 10^{-13} \text{ cm}^2/\text{dyn}$.

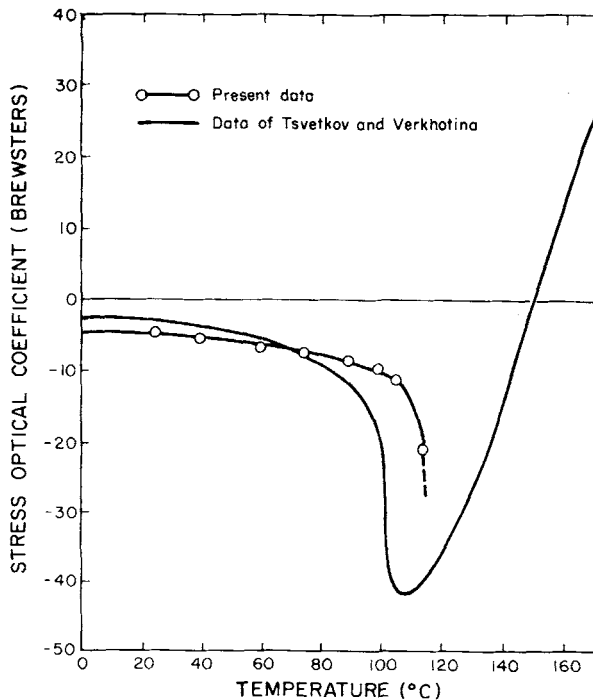


Fig. 6. Stress optical coefficient for poly(methyl methacrylate): (○—○) present data; (—) data of Tsvetkov and Verkhotina.

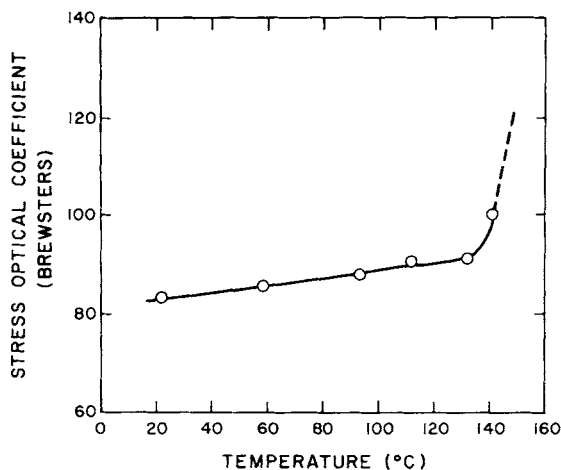


Fig. 7. Stress optical coefficient for polycarbonate (present data).

We are in qualitative, but not quantitative, agreement with Tsvetkov and Verkhotina¹² for PMMA. We tend to attribute the difference to rate (time) effects, which are quite significant in the near- T_g range; Tsvetkov and Verkhotina made their measurements after some minutes, compared to seconds in our work. With regard to the data for PC we note only that the sign is always positive, showing, however, a sharp increase in magnitude near T_g (about 145°C). The dotted line is an arbitrary extrapolation, to provide a rough estimate of the coefficient just above T_g .

In the residual effects analysis one needs the strain optical coefficient (C_ϵ), which can be obtained by multiplying the stress optical coefficient by Young's modulus. Modulus data for PMMA were taken from Takahashi et al.,¹³ and similar data for PC were taken from Snell and Etre.¹⁴ Shear moduli were converted to Young's moduli by multiplying by 2.7 in the glassy state and by 3.0 near T_g . The calculated values for C_ϵ are shown in Table I.

In the residual experiments slabs of both materials were heated, quenched, and sectioned for measurement of the birefringence. The results are shown in Figures 8–10. At 160°C the PMMA curves are similar in shape and sign to those of PS, except the magnitudes are considerably smaller. The PC profiles are inverted in sign compared with the other two, as one would expect from the different sign of the optical coefficients for this material. The effect of sample thickness is relatively minor, but there is a striking effect of initial temperature (T_0) in the case of PMMA; the curve at 120°C changes sign only near the midpoint and is distinctly unlike the corresponding curve for PS, which has a more or less parabolic and balanced shape at this temperature. This difference is not easily explained. At high temperatures the stress optical coefficient for PS goes to a very large negative number whereas that for PMMA goes to a small negative number and then reverts to a positive value (see the data of Tsvetkov and Verkhotina in Fig. 6). However, our theoretical studies with PS seem to indicate that optical behavior at temperatures 40–50°C above T_g is of little or no importance because the material is relaxing quickly there. Thus we are inclined to disregard the positive values in Figure 6 at temperatures above

TABLE I
 Optical Coefficients for PMMA and PC^a

| T (°C) | PMMA | | | PC | | |
|--------|--|--|--------|--|--|-------|
| | C_σ (10^{-13} cm ² /dyn) | E (10^{10} dyn/cm ²) | C_t | C_σ (10^{-13} cm ² /dyn) | E (10^{10} dyn/cm ²) | C_t |
| 40 | -5.8 | 4.0 | -0.02 | — | — | — |
| 80 | -6.0 | 1.1 | -0.007 | 87 | 2.1 | 0.2 |
| 100 | -9.0 | 0.6 | -0.005 | — | — | — |
| 115 | -22.0 | 0.15 | -0.003 | 90 | 2.1 | 0.2 |
| 145 | — | — | — | 101 | 2.0 | 0.2 |
| 150 | — | — | — | ≈120 | 0.9 | ≈0.1 |

^a Stress optical coefficients (C_σ) measured in the present work; Young's moduli (E) obtained from the literature (Ref. 13 for PMMA, Ref. 14 for PC); strain optical coefficients (C_t) calculated from $C_t = EC_\sigma$.

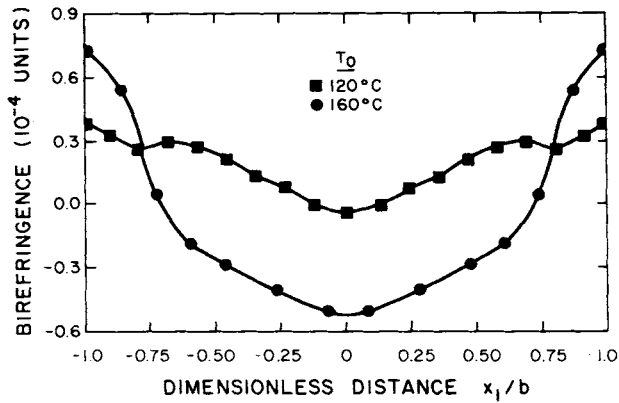


Fig. 8. Effect of initial temperature (T_0) on the birefringence profiles (PMMA, $b = 1/8$ in.): (■) 120°C ; (●) 160°C .

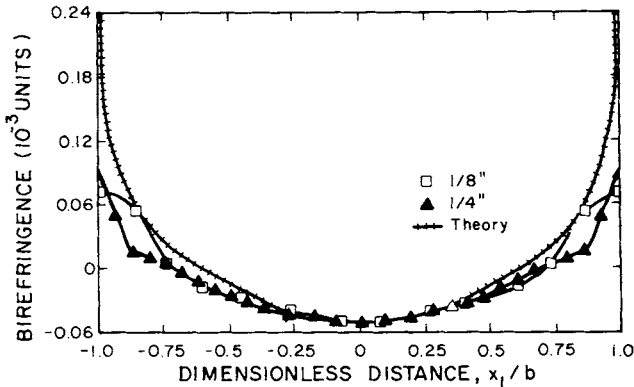


Fig. 9. Fit of simplified theory (+++) to birefringence profiles [PMMA, $b = 1/8$ in. (□) or $1/4$ in. (▲), $T_0 = 160^\circ\text{C}$].

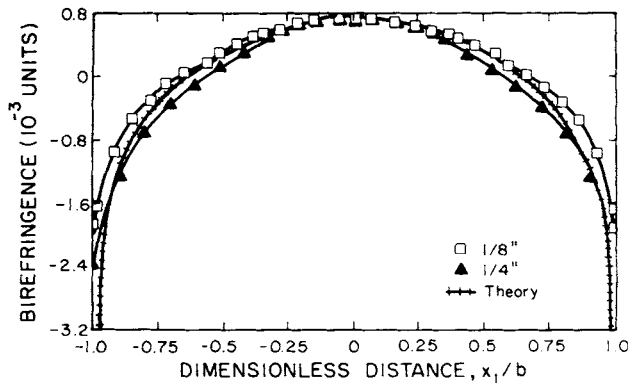


Fig. 10. Fit of simplified theory (+++) to birefringence profiles [PC, $b = 1/8$ in. (□) or $1/4$ in. (▲), $T_0 = 180^\circ\text{C}$].

about 150°F. During a quench the center is either under no stress or a small compressive stress initially and passes to a tensile stress in the final stages of cooling. The dynamic response of PMMA must favor the compressive part of this history more strongly than it does for PS, inasmuch as the always-negative optical coefficients will convert compressive histories to a positive birefringence.

Since a complete analysis with the LRW theory is beyond carrying out, as noted in the previous section on PS, we turned to the simpler theory of Aggarwala and Saibel as shown in eq. (4). In the manner of Wust and Bogue, we selected a single (constant) strain coefficient for each material to force a fit of theory to the data. Such a procedure necessarily leads to balanced profiles and so one can only hope for a reasonable fit at the higher initial temperatures. The actual values of C_ϵ chosen for the fits were -0.0029 for PMMA (which corresponds to about 115°C on the $C_\epsilon-T$ curve) and $+0.047$ for PC (which corresponds to a temperature a few degrees above 150°C); from the prior work, the C_ϵ value for PS was -0.012 (which corresponds to about 94°C). In short, in all cases if one chooses a strain optical coefficient in the neighborhood of T_g , both the magnitudes and the signs can be predicted. (The coefficient cannot be selected *a priori*, however, because the $C_\epsilon-T$ function is changing rapidly in this regime and is extremely sensitive to the placement of the modulus curve on the temperature scale.) This was the idea put forth by Wust and Bogue as an empirical finding. However, the facts that the change of sign (in the case of PC) and the much smaller magnitudes (in the case of PMMA) are properly predicted lends credibility to the concept.

CONCLUSIONS

If large samples are rapidly quenched (into ice water), one sees finally a profile of residual birefringences across the small dimension, which are a measure of the residual stresses there. In general the curves show high (absolute) birefringences at the surface and low ones in the center, as one expects from our knowledge of residual stresses. However, the details of the birefringent profiles are quite complex and one sometimes sees "balanced" shapes (equal positive and negative portions) but often not. While the thickness of the samples has some effect, the initial temperature of the hot slab is a more prominent variable. High initial temperatures lead to highly skewed (unbalanced) profiles in the case of PS but to reasonably balanced ones in the case of PMMA and PC. The reasons for these differences are not understood, although it appears to be due to the complicated dynamic response near T_g , and the cooling rates there, and not to the rheoptical behavior at the high initial temperatures.

Some theoretical understanding of the PS profiles was obtained by using the general theory of Lee, Rogers, and Woo,⁵ in which one introduces a relaxation function for the birefringence. By an arbitrary adjustment of parameters, the variously shaped profiles for PS could be fit. A fully rigorous treatment is impossible, however, because of the great complexity of the problem: the sample is nonhomogeneous in temperature, stress, strain and density (and finally birefringence); and one must know in detail the time-temperature functions for the volume response and the rheoptical response, ranging from a temperature well above T_g to one well below it.

Many of the results could be fit, however, with the simpler theory of Aggarwala and Saibel,⁷ in which one presumes a discontinuous change from a melt to a solid as the material passes through T_g . As an empirical assumption we take the strain optical coefficient (C_ϵ) to be constant during the quench. The C_ϵ values found by fitting are reasonable, however, in a comparative sense. If one considers the C_ϵ vs. T function for each material in the neighborhood of its T_g , the fitting parameter C_ϵ shows the right magnitude and the right sign for all of the materials studied (PS, PMMA, and PC).

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