The Influence of Thermal History on Internal Stress Distributions in Sheets of PMMA and Polycarbonate

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Synopsis

The through-thickness birefringent patterns ($n_x - n_z$) of PMMA and polycarbonate (PC) are measured as a function of thickness, cooling rate, and annealing time. A method is demonstrated for separating the elastic stress from the residual birefringence. The residual birefringence is explained as the residual orientation induced when cooling through the glass transition. The shape of the elastic (tempering) stress distribution is apparently independent of the cooling rate and annealing time, the choice of polymer, and the sheet thickness. The magnitude of the tempering stress is dependent on cooling rate but nearly independent of choice of polymer and sheet thickness. The decays of both the tempering stress and the residual orientation are measured as a function of annealing time at 120°C for polycarbonate. The measured birefringence decays only slightly; however, the elastic tempering stress reverts, on annealing, to permanent (anelastic) orientational strain. The tempering stress at the sheet surface is not an adequate criterion for defining toughness in polycarbonate.

INTRODUCTION

The effect of cooling rate and subsequent annealing on the internal stress distribution in inorganic glass have been studied intensively over the years.[1-3] This work has been necessary because of the stringent requirements of producing a tough but economical glass from inexpensive starting materials. However, owing to the high cost of polymer resins and processing equipment and the lower temperatures involved in polymer processing, the emphasis in polymer studies has been on higher machine throughput and dimensional stability than on optimizing the internal stress pattern in cast, injection-molded, and extruded sheets. This gap in our information has been filled partially by recent studies by Broutman[4] on internal stresses in plastic sheets. His conclusions oppose those who invoke structural relaxation to explain polymer embrittlement. We present here our experimental results on the resultant internal stress distribution in PMMA and polycarbonate sheets subjected to various thermal treatments.

EXPERIMENTAL

Material Characterization

The two polymers under investigation are PMMA and PC. The PMMA is ICI cast Perspex sheet, with less than 0.1% initiator. From GPC measurements[5] $\overline{M}_w$ is 1.5×10^6 (g/mole), and $\overline{M}_n$ is 0.5×10^6. The PC is extruded high-viscosity Makrolon sheet (3200) with no UV stabilizers and 1% additives. The $\overline{M}_w$ is about 2×10^4 (g/mole), based on previous studies.[6]

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Thermal Treatment

Sheets of both PMMA and PC were first dried, then heated to 40°C above their glass transitions, and then quenched into different media. Some of the sheets were cooled into either still air at 20°C (simulating cooling after extrusion) or water at 20°C. Sheets were also cooled conductively between copper platens and heated to different temperatures to simulate cooling during injection molding and thermoforming.

Cooling rates were measured for PMMA using an implanted thermocouple at the sheet midplane for both convective (air or water at 20°C) and conductive (copper) quenching. The results for the copper quench ($T = -145$°C) are plotted in Figure 1 against a reduced time axis. The line is the calculated (error function) cooling curve, fitted for a ratio of surface conductance/bulk conductivity (h/k) of 10. Knowledge of the thermal conductivity for the polymer (which we assume to be approximately constant) thus gives a value for the surface conductance of 2.0 J/m² sec °C. The assumption that this value also applies to the conditions of the water quench is justified by the similar internal stress distributions in the two types of quenching. The surface conductance for air cooling is only 0.15 J/m² sec °C. Knowledge of the surface conductance is useful because it enables cooling curves to be calculated for any initial temperatures, sample thickness and geometry, and quenching method and temperature. Once the surface conductance has been measured and the heat capacity and thermal conductivity are determined, cooling curves for the sample surface can be determined, using the series solution for the cooling of a slab, where $x = \pm l$, as shown in Figure 1. Also, these
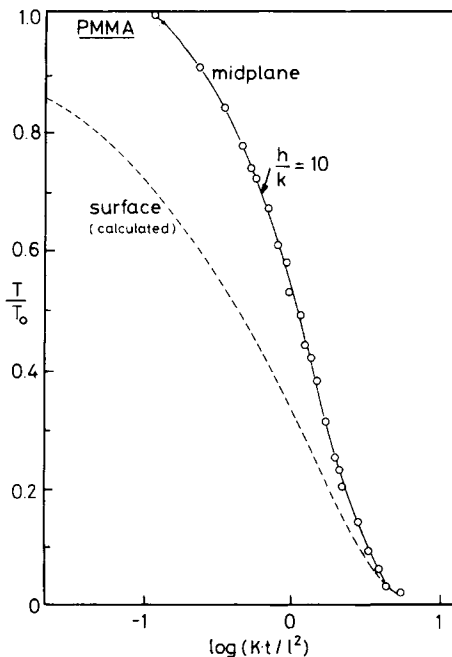

Fig. 1. Measured cooling rate for 2-mm PMMA sheets cooled from +145°C onto copper platens at −145°C, plotted in reduced parameters. The data points are fitted with the calculated error function curve for a ratio of surface conductance (h)/bulk conductivity (k) of 10. For the reduced ordinate, l is sheet thickness (in cm) and $K = k/C_p\,\rho$.

thermal parameters can be used, along with the volumetric expansivity, to model the generation of internal stresses during cooling for different quench media once the relaxational behavior in the glass transition is defined.

Using Birefringence to Determine Internal Stress Distributions

Measurement of birefringence is a convenient method for determining the through-thickness internal stress distribution in polymer sheets. However, a major drawback is that molecular orientation induced by flow of the polymer during cooling also induces birefringence that is not directly related to the internal stress state. In this section we outline a method developed to separate these two contributions. This separation is necessary if birefringence is to be used to determine internal stress distributions.

Sections were removed from the central portion of the sheet as shown in Figure 2. The birefringence $(n_x - n_z)$ varied as a function of Z (depth in the sheet); it was measured in monochromatic (sodium) light using crossed polaroids and a traveling microscope. A white light source and Berek compensator were used to locate the zero-order fringe and to determine the sign of the birefringence. The plot of the birefringence against distance from sheet surface (schematized in Fig. 2 and shown in Figs. 4 and 6) does not have equal areas above and below
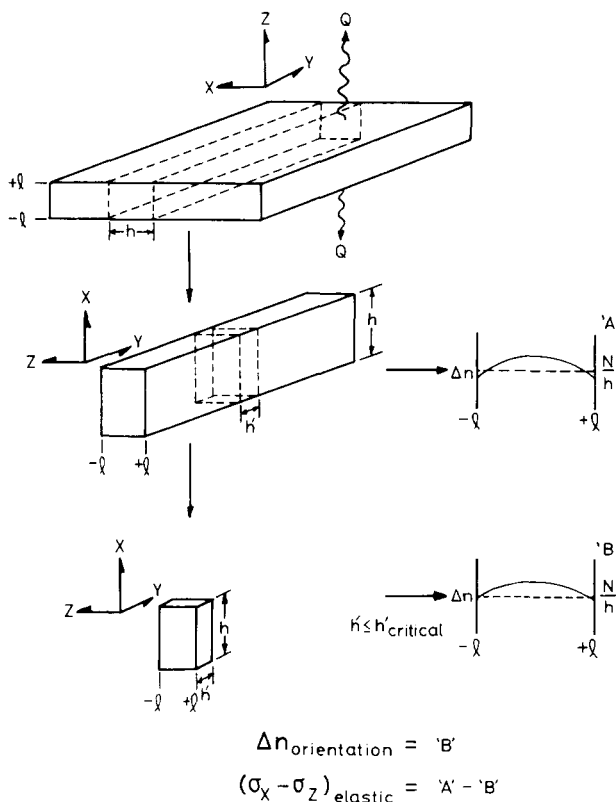

$$\Delta n_{orientation} = \text{`B'}$$

$$(\sigma_x - \sigma_z)_{elastic} = \text{`A'} - \text{`B'}$$

Fig. 2. Schematic outline of the method used to separate the elastic stresses ('A' − 'B') and residual birefringence due to molecular orientation ('B') from the as measured birefringence pattern ('A'). The optic axis is in the x direction for both 'A' and 'B', and N/h is the fringe order.
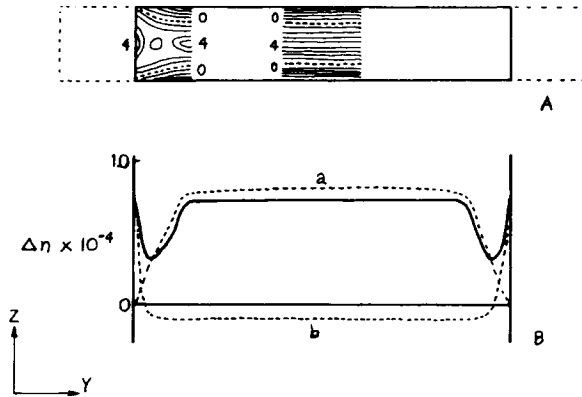
Fig. 3. (A) Sketch showing fringe pattern association with end effects. The extent of the sheet as quenched is indicated by the dotted ends which were removed prior to optical examination. (B) Plot of birefringence along midplane of specimen (——) with estimates of the contributions due to σ_y (- - -a) and σ_z (- - -b).

the zero-order fringe line. This inequality is in contrast to results from inorganic glasses and indicates that the birefringence in polymers is due not only to the internal stress distribution in the plane of the sheet, which must integrate to zero, but also to either a nonzero stress (σ_z) perpendicular to the plane of the sheet, or molecular orientation, or both.

Both the z-direction and x-direction tempering stresses can be relieved by cutting a slice thin enough to remove the bulk constraints imposed by the sheet. The samples were sliced using both a slicing wheel and a fret saw; the latter was the preferred method. The critical thickness ($h'_{critical}$ in Fig. 2) to relieve the elastic internal stresses is 1 mm; slices thinner than 1 mm did not further shift the fringe patterns. Furthermore, cutting the 1-mm slices in half along the mid-plane of the original sheet, an operation which would certainly relieve the internal stress if any remained, again had very little effect on the fringe patterns. Thus, confident that σ_y and σ_z have been relieved, the resultant fringe pattern, as schematized in 'B' of Figure 2, can be substracted from the initial pattern 'A.' This difference, shown for PMMA in Figure 5, yields a pattern in the shape of a parabola, which integrates to zero, suggesting that σ_z is small in relation to σ_x.

We have attempted to estimate the magnitude of σ_z by observing the fringe patterns close to the edges of a trimmed specimen which had been cooled from 150°C on copper platens at 20°C. The fringe pattern is represented in Figure 3(A), while Figure 3(B) shows a plot of the birefringence along the midplane, together with an estimate of the components of σ_y and σ_z. At the edges σ_y is zero, and hence the contribution to birefringence is due to σ_z (compressive). It appears from the pattern that σ_z becomes negative within about 2 mm of the edge surfaces; and, therefore, with a specimen area of 1500 mm^2, the compressive load in the z direction near to the specimen edges will be balanced by a tensile load over what is the greater central area. Hence, the tensile σ_z will be around $300/(1500 - 300) = 0.25$ of the average σ_z at the edges. For the PMMA specimens in this example, the average value for σ_z remote from the edges is approximately 1.75 MN/m^2. The measured value of tensile σ_y on the midplane (the peak value of Fig. 5 for the 20°C copper quench) should thus be refined by
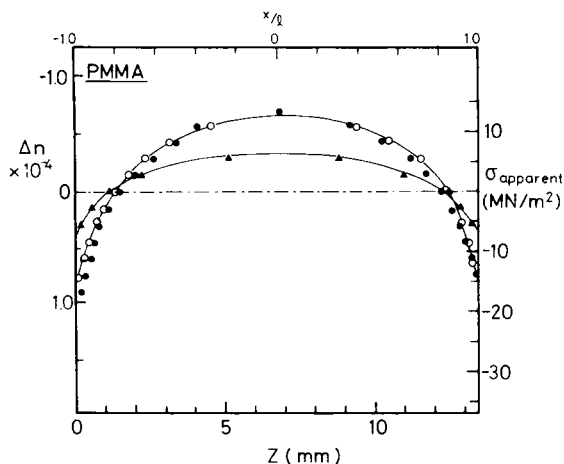
Fig. 4. As-measured birefrigence pattern for $\frac{1}{2}$-in. PMMA sheets cooled from 150°C as follows: (●) water quench at 20°C; (○) copper platens at 20°C; (▲) air at 20°C. The apparent stress is calculated by applying a stress optical coefficient of 1.8×10^{11} Brewsters. $(1 \text{MN/m}^2 = 145 \text{ psi})$.

increasing by around 13%. As the correction will be less on planes nearer to the planar surfaces, it will have a correspondingly smaller effect on the ability of the pattern (e.g., Fig. 5) to integrate to zero. While noting the existence of a tensile stress σ_z over the central area of the midplane, we have treated it as a correction which could be applied if a precision measure of the internal stress is required. We have, however, chosen to neglect it in the discussion which follows.

This technique of separating the elastic internal stresses and the residual orientation allows us to follow both the elastic stress relaxation and the orientational relaxation of glasses when they are cooled and subsequently annealed.

COOLING RATE EFFECTS

The as-measured birefringence pattern for quenched 12-mm Perspex sheet is shown in Figure 4. The area does not integrate to zero, so this pattern cannot reflect just the $x-y$ plane elastic stress, as discussed above. The apparent elastic stress has been calculated using the stress birefringence coefficient of 1.8×10^{11} Brewsters. The measured birefringence distribution for water-quenched and copper (20°C)-quenched sheets is nearly identical, allowing us to conclude that the surface conductance (h) is about the same for both water and copper quenching.

The elastic internal stress and residual orientation were separated using the method outlined in Figure 2. This separation is shown in Figure 5 for three different thicknesses of Perspex sheets, quenched into water from 150°C.

Figure 5 shows that the residual orientation, expressed as birefringence, is tensile in the midplane of the sheet and slightly compressive at the surfaces. This shape of the residual orientation distribution is independent of sample thickness.

The source of the residual molecular orientation in the core of the sheet, which is in the same direction as the core tensile stress, is seen to be plastic flow of the core material in response to the internal stress generated during cooling through the glass transition. The flow must occur in the transition region because the
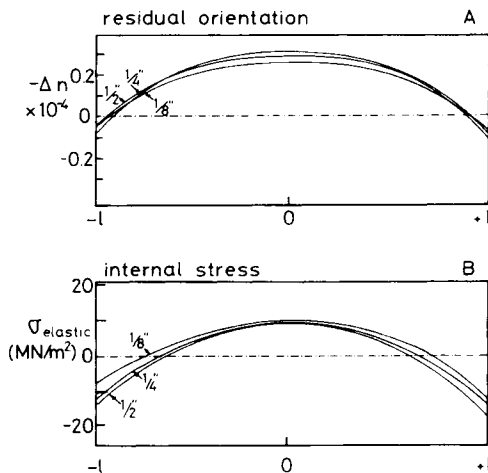
Fig. 5. Residual birefringence (A) and internal stress distribution (B), separated from the data of Fig. 4 for $1/2$-in. PMMA sheets, and from further data on $1/4$-in. and $1/8$-in. sheets. The quench is water at 20°C for these results. The separation was effected using the method outlined in Fig. 2.

elastic internal stresses are not large enough to induce plastic flow in the glass. The plastic strain optical coefficients (SOC) are very sensitive to temperature in the glass transition region. Using SOC values for PMMA of $-2.5 \times 10^{-4}/100\%$ at 125°C and $-5 \times 10^{-4}/100\%$ at 100°C,[7] the calculated plastic strains due to the elastic stresses are about 10% at 125°C and 5% at 100°C.

Figure 5B shows a small effect of thickness on the apparent elastic stress, which may be attributed to the small z-component tempering stress, which should approach zero as the sheet thickness approaches zero. The elastic (tempering) stress approaches $3 MN/m^2$ (tensile) in the midplane and $-14 MN/m^2$ (compressive) at the surface, which is about 20% of the yield stress for PMMA at room temperature.

The as-measured birefringence pattern for 4-mm polycarbonate sheets is shown in Figure 6. Again, the birefringence patterns in sheets quenched in either water or copper at 20°C are nearly identical, as was observed for PMMA. This time, however, the positive and negative areas nearly balance to zero, implying a very small contribution of residual orientation to the overall birefringence pattern in rapidly quenched polycarbonate. The sheets that were quenched onto copper platens at 120°C (simulating thermoforming and similar to injection-molding conditions) and the sheets cooled in air at 20°C show the same imbalance as was observed in PMMA, so the residual orientation must be contributing to the birefringence pattern in the slowly cooled sheets.

For the rapidly quenched 4-mm sheets, the as-measured birefringence pattern is almost completely due to the elastic internal stresses, and the separation technique of Figure 2 does not noticeably alter the parabolic curves in Figure 6. The internal stresses are greater for PC than for PMMA, which may be related to the faster cooling rate through the glass transition for PC ($T_g = 150$°C) than for PMMA ($T_g = 110$°C) when the quenching medium is at 20°C.

The elastic stress pattern was separated from the total birefringence pattern for a set of 2-mm PC sheets quenched onto copper platens at different temperatures; these results are shown in Figure 7. Again, the difference in the shape
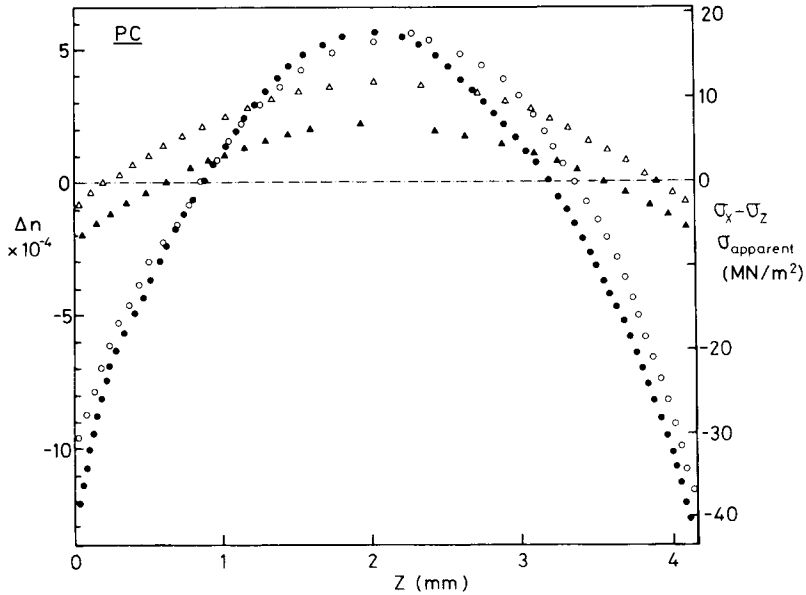
Fig. 6. As-measured birefringence pattern for 4-mm polycarbonate sheet, quenched from 180°C into different cooling media: (●) water at 20°C; (O) copper platens at 20°C; (△) copper platens at 120°C; (▲) air at 20°C. The apparent stress was calculated by applying a stress optical coefficient of 1.3×10^{10} Brewsters.

and magnitude of the stress distribution are virtually independent of sheet thickness. Also, the effect of platen temperature strongly influences the induced elastic stresses when the platen temperature is varied in the region of 100°C (the recommended mold temperature for injection molding and thermoforming PC). Manufacturers (e.g., General Electric[8] and Bayer[9] emphasize the sensitivity of the dimensional stability and toughness in molded PC parts to the mold temperature. Finally, it is worth noting that the location of zero elastic stress (in
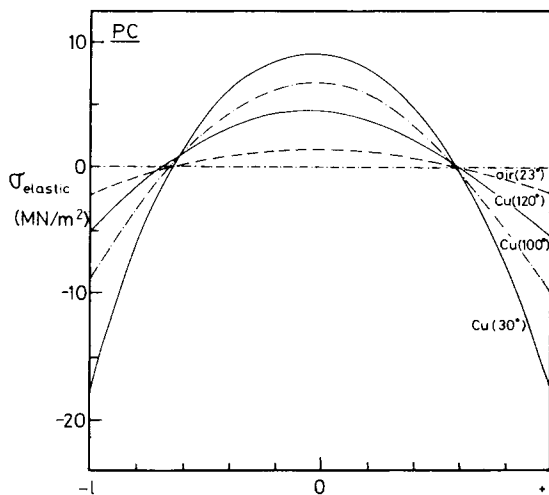

Fig. 7. Separated elastic internal stress distribution for 2-mm polycarbonate sheets both quenched from 180°C onto copper platens at the temperatures indicated, and air cooled.

reduced parameters) is independent of sample thickness, cooling medium, and choice of polymer (in terms of PMMA and PC), suggesting that simple continuum models of tempering stress generation should be applicable to cooling of polymer sheets.

The residual orientation component of the birefringence, as separated from the overall birefringence in Figure 6 for the 4-mm sheets of PC, is shown in Figure 8. The rapidly quenched samples have negligible residual orientation, and the copper (120°C)-quenched sheets show the greatest residual orientation. The residual orientation might be slightly compressive at the surface (as in PMMA sheets), but the small magnitude of the strain makes it difficult to quantify the strain state at the surfaces.

Annealing Effects

Upon the advice of manufacturers,[8] molders and end-users often anneal polycarbonate at 120°C after forming to improve dimensional stability and to avoid craze initiation. The effect of the anneal is typically monitored by following the variation of the birefringence pattern with annealing time. Therefore, we have applied our separation method (Fig. 2) to annealed PC sheets, to determine how both the elastic stress and the residual orientation components of the total birefringence relax upon annealing.

Sheets of 4-mm PC were quenched into water at 20°C, then annealed at 120°C. The change of the total birefringence pattern during annealing is shown in Figure 9. Polycarbonate is embrittled by an anneal longer than 1 hr at 120°C.[10,11] However, the birefringence pattern is not removed by such an anneal; rather, it only decays slightly. The separation technique was applied to these annealed sheets, and the separated elastic stress component is shown in Figure 10. The elastic stress has indeed relaxed at annealing times less than 10 hr at 120°C: the elastic stress apparently decays in parallel with the increase in brittleness. After the relaxation to a compressive surface stress of about 2MN/m², no further decay is observed from 10 to 100 hr of annealing.

An unexpected effect was observed when the birefringence owing to residual orientation was separated. This is shown in Figure 11. Although the initially unannealed sheet showed negligible orientation, the annealed sheets display a large strain component, which, being compressive at the surfaces, must have come from the initially elastic stresses relaxing on annealing into plastic strain. Remember that these sheets are 4 mm thick, thick enough so that a plane strain
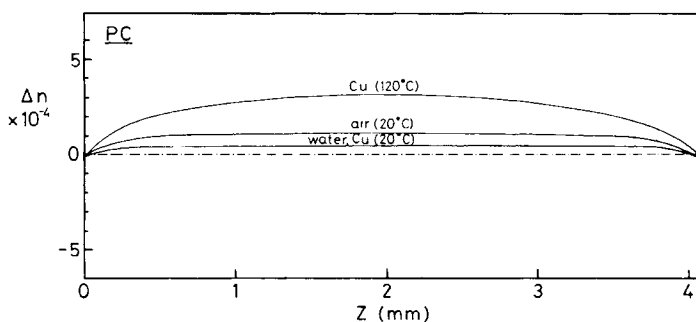

Fig. 8. Residual birefringence for 4-mm polycarbonate sheet separated from the data in Fig. 6.
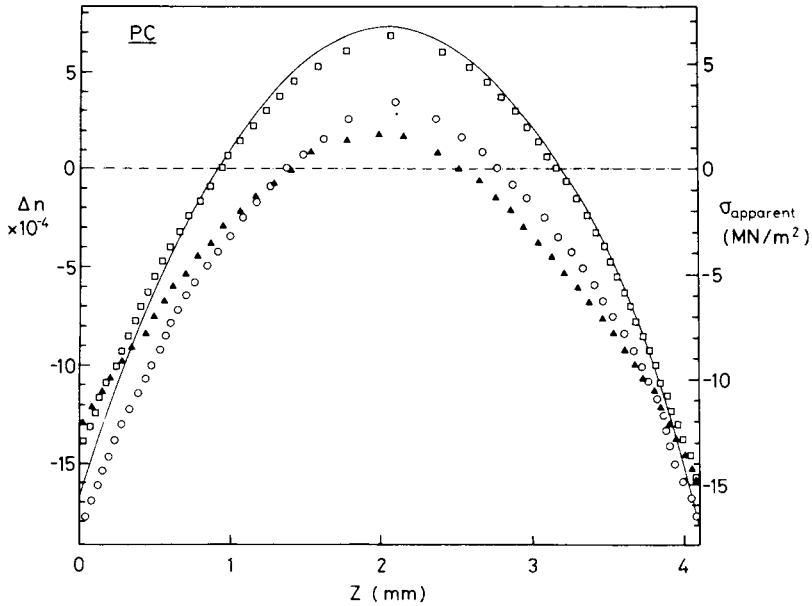
Fig. 9. Effect of annealing time on the overall birefrigence distribution in 4-mm polycarbonate sheets quenched into water at 20°C from 180°C and then annealed at 120°C as follows: (——) unannealed; (O) 10 hr; (□) 25 hr; (▲) 100 hr.

state exists, and that bulk constraints could restrict the method of elastic stress relaxation on annealing.

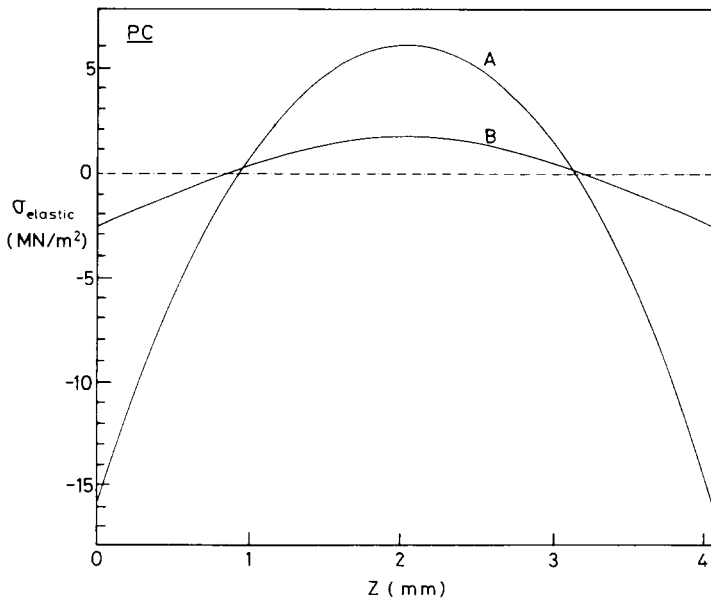This effect also suggests an explanation of the observation (Fig. 8) that the

Fig. 10. Separated elastic stress components for the 4-mm polycarbonate sheets of Fig. 8. Curve (A) is the unannealed sheet, and curve (B) is for specimens annealed for 10, 25, and 100 hr at 120°C.
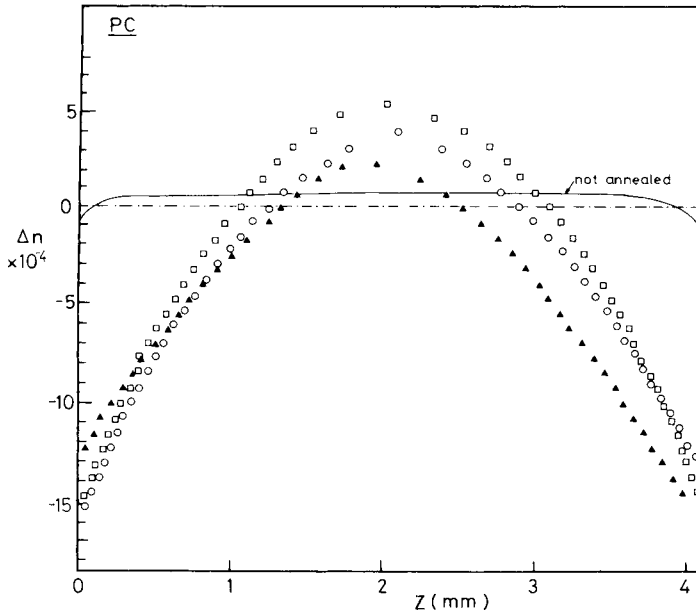
Fig. 11. Residual orientation component of birefringence for the 4-mm polycarbonate sheets in Fig. 8, all annealed at 120°C. Key symbols as in Fig. 8.

residual orientation in PC is greater for the slowly cooled sheets. For it is apparent that some relaxations of internal stress to create residual orientation could occur during slow cooling in the glassy state. However, we cannot be completely confident of this interpretation. The last experiment to be reported is the annealing of as-extruded polycarbonate sheets. In Figure 12 we see that the overall birefringence pattern is asymmetric. This asymmetry was observed in 2-, 3-,
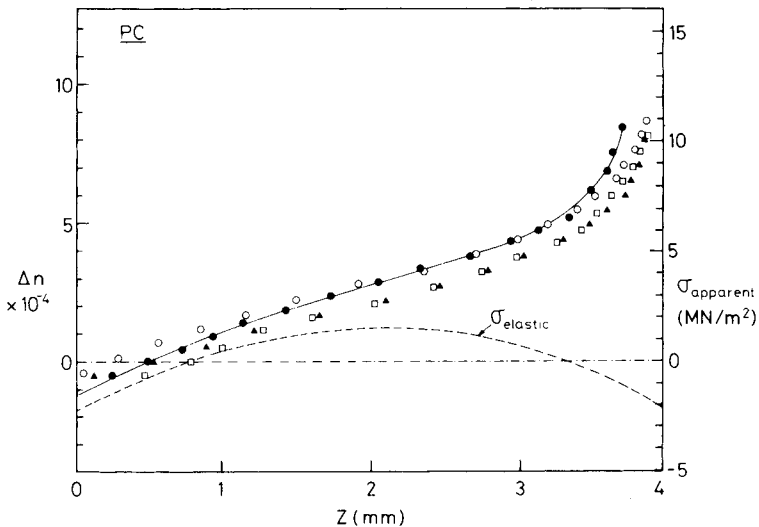

Fig. 12. Decay of the as-measured birefringence in extruded 4-mm polycarbonate sheet when annealed at 120°C as follows: (-●-) unannealed; (○) 10 hr; (□) 25 hr; (▲) 100 hr. Dashed line is the separated elastic stress component which does not noticeably change on annealing.

4-, and 6-mm extruded sheets and has been reported elsewhere.[10] The separated elastic stress is about $-2MN/m^2$ at the surface and does not noticeably decay upon annealing; the birefringence technique used here has a resolution of about $0.5MN/m^2$ for these PC specimens, so a slight decay on annealing might go undetected. The elastic stress distribution is the same as that measured using the bending technique of Treuting and Read[12] for extruded Lexan sheets.[10]

The difference between the elastic stress component and the total birefringence is the residual orientation, which is the source of the birefringence asymmetry. This residual orientation on one surface can be relieved by heating the sheets back into the rubbery state but apparently cannot be relaxed below T_g, except possibly with very long anneals. This residual orientation could be either anelastic or plastic: these experiments cannot separate which is the case because of the limited annealing times. Investigators studying polycarbonate who assume that as-extruded sheets are homogeneous must consider any possible errors in their work due to this small asymmetric orientational component.

DISCUSSION AND CONCLUSIONS

Elastic Internal Stresses

This new procedure for separating the elastic stress and the residual orientation from the overall birefringence pattern produces results that are consistent with previous studies of the elastic stress state of quenched polymer sheets, determined by mechanical methods.[4] Furthermore, we now see that the magnitude of the birefringence generated by the elastic stresses in the z (through-thickness) direction is small when compared to the contribution to the birefringence from the residual orientation.

Whereas we are not the first to suggest that prediction of elastic (tempering) stress generation in polymer glasses should be amenable to continuum mechanical approaches, we can offer further support to the legitimacy of this generalized approach:

(1) Although polycarbonate and PMMA display quite different mechanical properties, they both show the similar magnitudes of internal stresses for similar quenching rates through the glass transition.

(2) Both conductive and convective cooling methods produce parabolic elastic (tempering) stress distributions.

(3) When the elastic stress distribution is plotted against the thickness, both the shape and the magnitude of the distribution are independent of sample thickness.

(4) The location, in reduced thickness parameters, of the zero elastic stress is constant ($\pm5\%$), irrespective of sample thickness, cooling medium, cooling rate, and choice of polymer. This is a simple test of the constancy of the parabolic shape of the elastic stress distribution. A more rigorous test would be to plot the squared-elastic stress against the thickness: this should be a straight line.

Residual Molecular Orientation and Elastic Stresses

The residual molecular orientation is much larger in PMMA than in PC. Whereas the generated elastic stresses are nearly independent of the specific polymer, the residual molecular orientation is dependent on the form of the response of the specific polymer in the glassification region during cooling. Since the expansivity in the rubber and the glass (which induces the residual orientation) is about the same for both PMMA and PC, the difference in residual orientation appears to imply that PC can relax induced strains much faster than PMMA in the transition region. This conclusion is consistent with the observed relaxation behavior of the two polymers near T_g; for instance, whereas PMMA sheets can be heated in ovens at $T_g + 40°$ before thermoforming, PC sheets rapidly sag under their own weight when similarly preheated.

The residual molecular orientation in polycarbonate does not relax on annealing, unlike the elastic stresses. At short annealing times (e.g., 1 hr at 120°C), the volume and enthalpy have mostly relaxed, and the sample has embrittled. However, cold-drawn polycarbonate requires almost five decades more time for strain recovery.[13] This difference in relaxation times for these two sources of birefringence is not unexpected, since relaxation times depend on both the temperature and the method of deformation as well as the form of the permissible modes of recovery, which is controlled by the experimental setup and the sample dimensions.

Elastic Stress as a Toughness Criterion

An explanation for the toughness of polycarbonate was recently proposed by Broutman,[4] invoking the same argument as that for tempered inorganic glasses. Namely, brittle fracture initiates at the surface, so if the surface is in compression (i.e., the sheets are rapidly quenched), then crack propagation will be hindered, permitting a ductile yield mechanism to prevail rather than brittle fracture. The toughness of polycarbonate can be destroyed either by slow cooling or by subsequent annealing, both of which lead to a reduction of compressive elastic stresses in the sheet surfaces.

However, this work has demonstrated that as-extruded sheet shows a low surface compressive stress which, upon annealing, hardly changes, whereas even extruded sheets embrittle upon annealing, showing that the elastic internal stress distribution is not a sufficient criterion for defining the toughness in polycarbonate. These two observations are not difficult to reconcile. When a large deformation is imposed on polycarbonate, it must either craze and fracture in a brittle mode, or it must yield in a ductile mode. The choice between these two mechanisms is dependent on many parameters: the molecular weight,[6] temperature,[11] orientation, thermal history,[4,6,10,11] strain rate,[14] sample thickness,[14] stress concentrations,[14] and local elastic stress states.[4,10] However, not all of these parameters can be varied independently. In particular, it is not easy to vary thermal history without affecting internal stress and orientation. Thus, whereas the existence of a correlation between toughness and different internal stress states (produced by different heat treatments) is clearly apparent for the annealing of quenched sheets, it does not preclude the possibility that the thermal history is influencing toughness by a route other than internal stress, such as by affecting the ability of the polymer to absorb energy at a crack tip.

The fact that the correlation between internal stress and toughness does not hold for extruded sheet is a positive indication that the influence of annealing in reducing toughness cannot primarily be accounted for in terms of changes in internal stress.

The Industrial Relevance of This Work

From the results of this work, we can offer some advice to molders and end-users of polymer glasses, especially to molders of polycarbonate.

(1) The temperature of injection and thermoforming molds for polycarbonate has a strong effect on the elastic (tempering) stresses, especially in the region of mold temperatures between 80 and 120°C. A slightly increased mold temperature will greatly reduce the generated elastic (tempering) stresses, without an unacceptable increase in cycle times.

(2) The use of birefringence to follow the effectiveness of postforming anneals is not advised. Because of the two sources of birefringence with their different relaxation times, we cannot be sure that we are monitoring just the elastic stress relaxation. This is especially true in thick-walled sections, where the relaxing elastic stresses revert to strains, which may be recoverable at very long annealing times. The use of oil anneals[7] at 120°C to erase all birefringence is a most effective method for ensuring consistently brittle parts. It is recommended that the undesirable elastic stresses be avoided by proper molding and machining and not by postforming anneals.

(3) Thick-walled sections (i.e., >4 mm) of rapidly quenched polycarbonate show dimensional stability with aging because of the self-imposed constraints of the bulk sheet. However, very thin sheets (e.g., 1 mm) will distort as the quenched-in elastic stresses are relaxed during aging. The best solution to this problem of dimensional stability with aging is to avoid elastic stresses by reducing the cooling rate through the glass transition (150°C for polycarbonate), which usually means slower cycle times.

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