Birefringence and internal stress in polystyrene optical fibers

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The radial variations of the birefringence of the core of polystyrene optical fibers have been observed and characterized. Variations are much more important on the edge than along the axis, and they introduce a positive radial gradient of the ordinary refractive index that essentially governs light propagation. To explain the existence of such a birefringence, the conditions of the cooling of fibers during their drawing have been simulated. The radial variations of the temperature between the axis and the edge may increase by 10° and, because of the fast variation of the viscosity of polymers in the neighborhood of their glass transition, an important molecular orientation may result in the regions in which this transition first ocurs during the drawing. Comparison is performed between the behavior of polystyrene and poly(methyl methacrylate) core fibers.

During the manufacturing process of plastic optical fibers, organic glass [poly(methyl metacrylate), PMMA, and polystyrene] that constitutes the core is first heated to approximately 200 °C. This temperature is much higher than the glass transition temperature (approximately 100 °C) at which the material undergoes a transition from its glassy state to a rubbery state. In the latter state the viscosity decreases when the temperature is increased. At approximately 200 °C, if the molecular mass of polymeric chains is not too high, the density of chain entanglements is weak, so that the viscosity is weak enough to consider the material as a liquid; it can be poured and can generate a fiber. Then this fiber cools rapidly so that the constituting material is quenched. However the cooling takes place from the wall to the axis, and, since the plastic optical fibers generally have large diameters, the inner part of the fibers reaches the glassy state slightly later than the side of the fiber. This difference is sufficient to create internal stress that could result in birefringence in these amorphous polymers.

It is well known that stress-induced birefringence is greater for polystyrene than for PMMA. Besides, both organic glasses always have negative birefringence.[1] The birefringence of PMMA core fibers may be easily seen when one observes an uncoated fiber inserted between crossed polarizers at 45° to their axes. As expected the optical axis is parallel to the drawing direction, i.e., along the fiber axis. However in these fibers the birefringence is too weak to be easily measured. On the other hand we have been able to study it quantitatively in polystyrene (PS) core fibers. Such fibers are not currently in use; they are generally doped with scintillating molecules in order to be used for the detection of nuclear particles.

Approximately 1-cm-long pieces of uncoated PS core fiber, the diameter of which is 1 mm, were carefully cut lengthwise with a diamond saw in order to keep a thin plate on each side of the meridian plane. The plate thickness was generally approximately 0.1 mm. When the plate was inserted between crossed polarizers and lit with white light, colored interference fringes were observed with a microscope. These isochromates are parallel to the fiber axis. A broad dark blue fringe lies in the middle, and two narrow red fringes are observed at the sample edge. The corresponding birefringence variations $\delta n = n_e - n_o$ versus the distance to the axis are easily evaluated with Newton's color scale. A typical example is shown in Fig. 1. One observes that the birefringence is more important near the fiber wall, i.e., in the region that was cooled first. The apparent slight dissymmetry of the experimental points may be attributed to a weak defect of the parallelism of the plate. A thickness variation of

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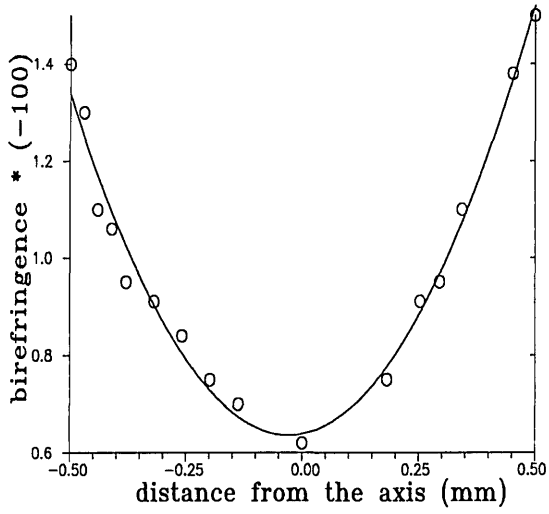

Fig. 1. Variation of the birefringence along the diameter of a PS core optical fiber: ○, experimental points.

several micrometers from one edge to the other is sufficient to explain this dissymmetry.

A numerical best fit has been performed by using a parabolic model, and agreement with the experimental values is quite correct. Taking the value of 1.591 as the mean refractive index n for D sodium lines for amorphous isotropic polystyrene[2] at room temperature, one obtains the values of ordinary and extraordinary indices n_o and n_e, respectively. Their radial variations are reported in Fig. 2.

It is first important to note that, in an optical fiber, the light propagates essentially with the ordinary refractive index n_o since the rays are weakly tilted from the axis. Even in the case of fibers studied here, which are clad with PMMA and for which the theoretical numerical aperture is slightly higher than 0.5, the tilt of rays inside the core is always lower than 20°. So, for any incidence the useful refractive index is always higher at the outer part of the core and thus,

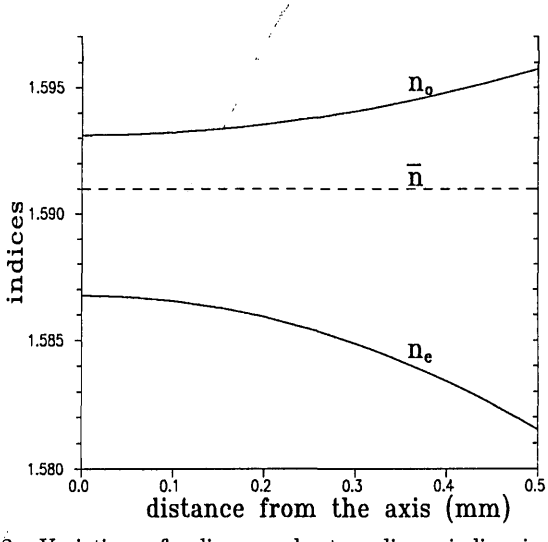

Fig. 2. Variations of ordinary and extraordinary indices in a PS core optical fiber.

in these fibers, it exists as a negative natural index gradient that is always disadvantageous because it tends to confine the rays in the outer part of the core.

Why does such a gradient exist? The kinetic theory of rubberlike elasticity (see, for example, Ref. 3) leads to a proportionality between birefringence and stress produced during axial extension σ: $\delta n = \mathrm{SOC}\sigma$, where the so-called stress optical coefficient (SOC) is independent of the extension ratio. Our observations show that a gradient of internal stress exists in the core. It has been induced during the drawing either by too fast cooling or by fiber stretching or both processes simultaneously.

Greener and Kenyon[4] have studied the effects of free quenching on rods of PS and PMMA, the diameter of which is 1 in. (2.54 cm). They first observed that when quenching from higher to lower temperatures than T_g, the resulting birefringence profiles were opposite in these polymers. In the case of PS, the birefringence is negative near the axis and becomes positive near the outer part, showing the presence of compressive and tensile layers. However, its absolute value always remains lower than some 10^{-4}. So it may be thought that in optical fibers, the diameter of which is weaker and for which the quenching performed during the drawing is not so hard, such effects would be still less. Then it may be considered that, even if the drawing process begins at approximately 200 °C when the material is almost liquid, it continues at a lower temperature when the viscosity progressively increases. It then induces a preferential orientation of the molecular chains that remains frozen because the drawing speed is too high and the cooling is too fast.

However it may be thought that during the drawing process, taking into account the small diameter of the fibers, the radial temperature gradient is weak enough to consider that the rheological behavior of the material is uniform in the whole cross section. Our observations demonstrate that this is not the case and that the temperature radial gradient existing in the fiber during its drawing is sufficient to explain the resulting radial variations of internal stress.

To evaluate how temperature varies in the fiber during the drawing process, it is necessary to solve the heat conduction equation with the thermal characteristics of the relevant material and to take into account the convection exchanges with the surrounding atmosphere. Then the evaluation of the surface heat transfer coefficient h is the major difficulty. The heat transfer coefficient has no data, and it is a well-known phenomenon in heat convective exchange problems that the smaller the objects, the more important the convection effects.

In order to evaluate h we used an optical pyrometer to measure the variations of the temperature of the wall of long PMMA cylindrical rods (in order to have surface radiative conditions as alike as possible to PS), the diameter of which is in the 3–14-mm range.

The characteristics of the pyrometer did not allow us to perform measurements on smaller diameters. The rods were first heated in an oven and the measurements were performed after they had been quickly removed. The temperature decrease of the rod surface was recorded versus time; the rod was kept in a vertical position in the ambient. Then, the heat conduction equation was resolved numerically by proceeding by trial and error to choose the value of the surface heat transfer coefficient h that gives the best fit with the experimental temperature decrease.

The value of h for a 1-mm-diameter fiber was obtained by extrapolation. However because of the rapid variations of h when the diameter is weak, such an extrapolation is difficult and leads to values with rough accuracy. The best empirical law we found had the form $h = 9.4 + 94/d^{1,27}$, where h is in W m^{-2} K^{-1} and d, the rod diameter, is in millimeters. The fit with experimental results may be observed in Fig. 3. Such a relation is advantageous for asymptotic values of approximately 10 W m^{-2} K^{-1} for large diameter rods, which corresponds to the value generally accepted for large objects in natural convection. For the fiber we used the value of $h = 100$ W m^{-2} K^{-1} and solved the heat conduction equation with the thermal data of PS, i.e., $\lambda = 0.13$ W m^{-1} K^{-1} for its thermal conductivity, $c = 1260$ J kg^{-1} K^{-1} for its heat capacity, and $\rho = 1.05 \times 10^3$ kg m^{-3} for its specific mass.[2] We assumed that the variations of these characteristics with temperature were weak enough to be neglected.

Figure 4 shows the trend of radial variations of temperature in the fiber versus cooling time with an initial temperature of 200 °C. It may be observed that, as long as the mean temperature of the fibers is higher than T_g, the temperature difference between the axis and the wall remains between approximately 20 and 25 °C. This means that the viscosity of the outer region of the core is always much higher.

The viscosity of all linear polymers at temperatures

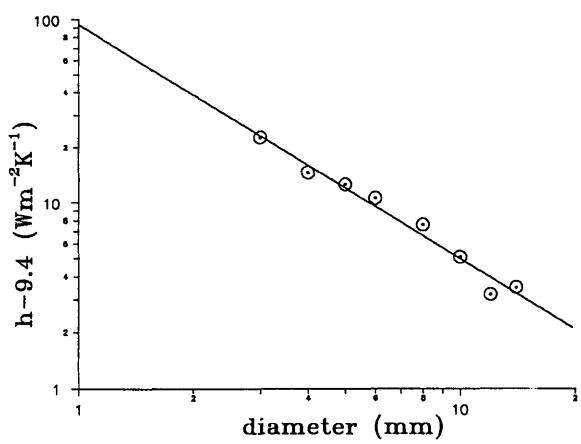

Fig. 3. Variation of the mean surface heat transfer coefficient h determined from the temperature decrease of the wall of long rods of PMMA, previously heated to 140 °C then cooled in a vertical position in ambient.

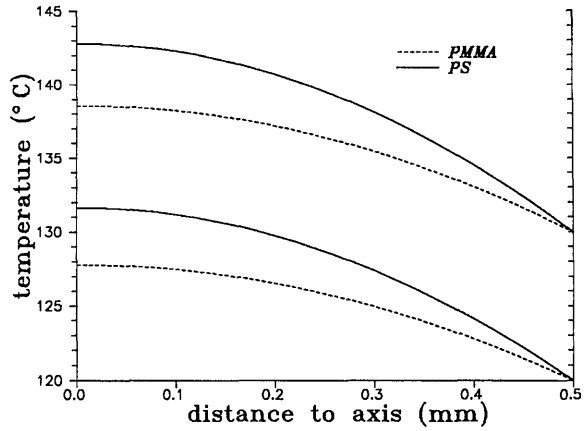

Fig. 4. Calculated temperature radial variations in 1-mm-diameter PS and PMMA core optical fibers. The initial temperature was 200 °C and the represented variations were obtained after cooling durations of 2.58 and 3.15 s for PS and 3.24 and 3.91 s for PMMA. These durations were such that the wall temperatures reach 130 and 120 °C.

higher than their T_g is based on the William, Landel, and Ferry equation, the form of which is

$$\ln \nu(T)/\nu_o = -c_{1o}(T - T_o)/(c_{2o} + T - T_o),$$

where ν_o is the viscosity at a convenient reference temperature T_o. If one uses T_g for this temperature, $c_{1o} = c_{1g} = 12.5$ and $c_{2o} = c_{2g} = 50°$ for the PS.[5]

Figure 5 represents the calculated relative radial variations of the viscosity in the core when the wall temperatures are 120 and 130 °C and the temperatures on the axis are 131.6 and 142.8 °C. One can see that the viscosity is approximately 20 or 30 times higher on the wall than on the axis, and such an important variation is sufficient to explain the existence of the stress gradient. The outer part undergoes the effects of the drawing more than the innner part. In addition, in this inner part, the temperature remains higher for a longer time so that the

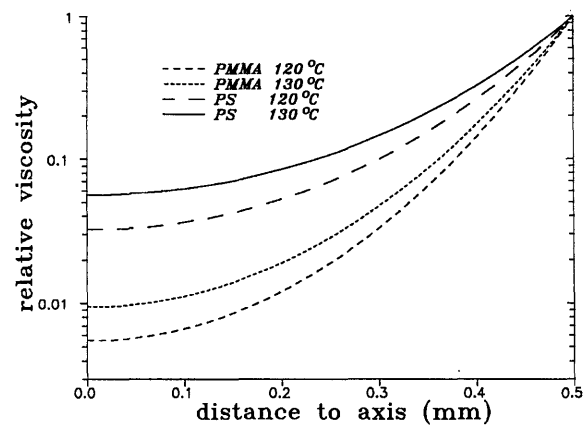

Fig. 5. Calculated radial variations of the relative viscosity of PS and PMMA using the William, Landel, and Ferry equation and the temperatures given in the caption to Fig. 4.

molecular mobility permits the rearrangement of the molecules and destroys their preferential orientation.

Although no experiment has been performed on PMMA core fibers, it may be considered that in these fibers the mechanical consequences of the cooling during their drawing are analogous. On the one hand, essentially because of the higher thermal conductivity of PMMA ($\lambda = 0.19\ W\ m^{-1}\ K^{-1}$), the thermal radial gradient is slightly lower (Fig. 4) whereas its viscosity varies much faster versus temperature (Fig. 5). However, even if it exists as an important internal stress gradient, because the SOC of the PMMA is approximately ten times weaker than the PS one, the resulting birefringence is too weak to be observed easily.

In conclusion, an important radial gradient of internal stress is created in plastic optical fibers during the manufacturing process. This probably contributes to better elastic properties and to less brittle fibers. This probably also contributes to the enhancement of optical losses by mode-coupling processes, essentially through unavoidable fluctuations of symmetry.

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