

Additives in Transparent Glassy Polymers: Concentration Profiles Obtained by Solvent Diffusion Technique

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Synopsis

Concentration profiles of additives, introduced in transparent glassy polymers by solvent diffusion technique, are analyzed by measuring refractive index profiles. Such profiles depend not only on the diffusion conditions (temperature, time, kind of solvent, concentration), but also on the conditions of solvent desorption from the polymer (temperature, pressure, solvent, and additive volatilities). In particular, poly(methyl methacrylate) (PMMA) samples modified in an outer shell by zinc chloride carried by methanol are considered.

INTRODUCTION

A technique for manufacturing glassy polymers objects modified by suitable additives in the outer shell, whose thickness ranges from a few micrometers to a few millimeters, has been developed in our laboratories.¹⁻³ According to this method, a solute is carried by a volatile solvent able to swell the polymer; once the solvent has been removed, a polymer modified in the external region is obtained.

Concentration profiles relative to solvent-swelling polymers have already been described. The experimental results are relative to the variations of refractive index, caused by solvent diffusion in polymers⁴⁻⁶ and to color density induced in the treated shell, by a very low concentration of iodine in the solvent.⁷ Theoretical studies on concentration profiles of solvents in polymers have also been reported.⁸ The aim of this paper is to describe concentration profiles of additives introduced in transparent glassy polymers by solvent diffusion technique.

These profiles depend not only on the diffusion conditions (temperature, time, kind of solvent, concentration),⁹ but also on the conditions of solvent desorption from the polymer (temperature, pressure, solvent, and additive volatility). The knowledge of the additive concentration profiles in the outer modified layer of the polymer and of their dependence on treatment conditions is essential for a better understanding of the product properties. In particular, in this paper, poly(methyl methacrylate) (PMMA) samples, modified in an outer shell by zinc chloride carried by methanol, are considered. The use of nonvolatile additive allows an easy separation of the effects of the solvent and of the additive on the refractive index profiles. The optical technique used is a slight modification of the interferometric method proposed by Robinson.⁴

EXPERIMENTAL

Materials, Diffusion, and Measurement Techniques

Poly(methyl methacrylate) (PMMA) specimens were cut from commercial sheets of VEDRIL, produced by Montepolimeri S.p.A. The sample dimensions were nearly $30 \text{ mm} \times 6 \text{ mm} \times 1 \text{ mm}$. Reagent grade methanol and zinc chloride were obtained from Carlo Erba S.p.A. and were used without further purification. To simplify the interpretation of the interferometric patterns, the two principal surfaces of the PMMA samples were shielded by clamped glass plates, during the immersion in the diffusion bath, so that the solution could penetrate only through the lateral surfaces.

The treated samples have (with reference to Fig. 1) refractive index gradient along the x - and z -directions, while the refractive index is nearly constant in the y -direction. Introducing the central part of the sample in an interferometric arm, with the laser beam parallel to the y -direction, refractive index profiles caused only by diffusion along the x -direction can be obtained.

PMMA samples were immersed in methanol solutions and maintained at 60°C ($\pm 0.1^\circ\text{C}$) for a time varying between 15 min and 90 min. The constraint of the glass plates does not prevent thickness changes in the y -direction. These thickness changes are minimized (less than $5 \mu\text{m}$) by a thermal pretreatment: prior to immersion in the diffusing solution, the specimens were annealed for 2 h at 130°C . (The annealing procedure caused a 4% thickness increase with a corresponding reduction in the other directions.)

A Mach-Zender interferometer¹⁰ (Fig. 2) has been used; the apparatus allows

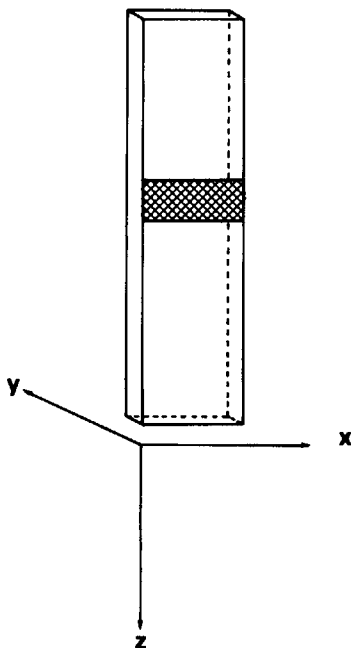


Fig. 1. Reference axes used to describe the diffusion and measurement technique. The diffusion is along x and z directions only. The refractive index profiles, measured in the y direction for the central part of the sample (dashed in the figure), are caused only by diffusion along the x direction.

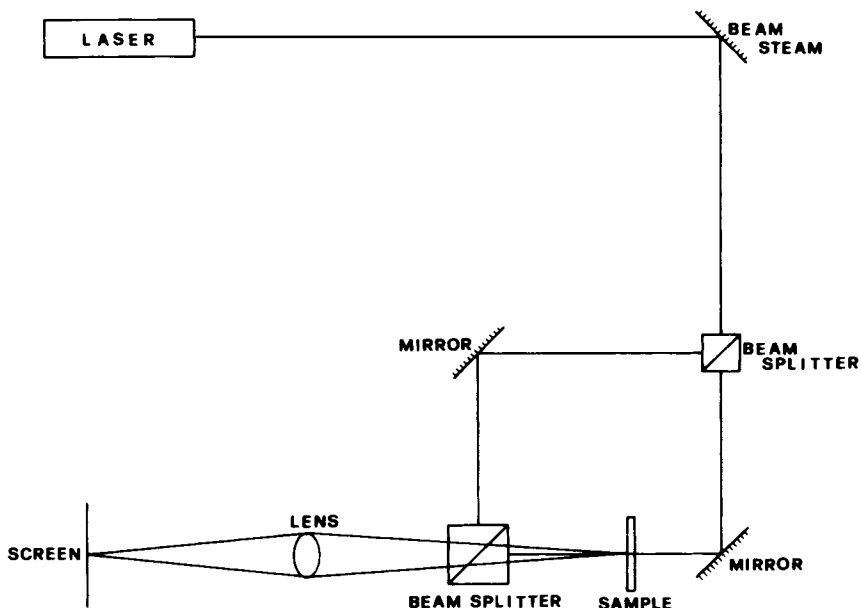


Fig. 2. A schematic diagram of the Mach-Zehnder interferometer.

to measure the variations of the refractive index with an error less than 10^{-4} . The introduction of a transparent graded index sample in an arm of the interferometer produces optical path differences visualized by local displacements of the interference fringes. The optical path differences are in general dependent on the local sample thickness and on the local sample refractive index (in the y -direction with reference to Fig. 1). The samples, during the measurements, were immersed in a mixture with the same refractive index of PMMA ($n \approx 1.49$), in order to make the refractive index measurements independent on the local thickness variations. The components of the mixture were benzylic alcohol ($n = 1.539$) and diethylene glycol ($n = 1.477$) in an appropriate ratio to avoid displacements of the fringes for an untreated specimen.

The measurements were made on at least partially desiccated samples, in which the diffusion rates of the mixture at room temperature are extremely low: no weight variation of the samples is observed after the measuring procedure. A thin copper wire ($\sim 100 \mu$) was used as reference for the scale factors for the interferometric patterns recorded on photographic plates. In Figure 3, as an example, a photo of the interferometric fringes characteristic of a PMMA sample with ZnCl_2 additive is reported. From these patterns the following can be obtained:

(a) the scale factor:

$$F = \Phi_A / \Phi_P$$

where Φ_A is the actual diameter of the reference copper wire and Φ_P the wire diameter as measured on the pattern.

(b) the penetration depth of the additive:

$$\Delta P = L_{\Delta P} \times F$$

where $L_{\Delta P}$ is the modified-layer depth measured on the pattern.

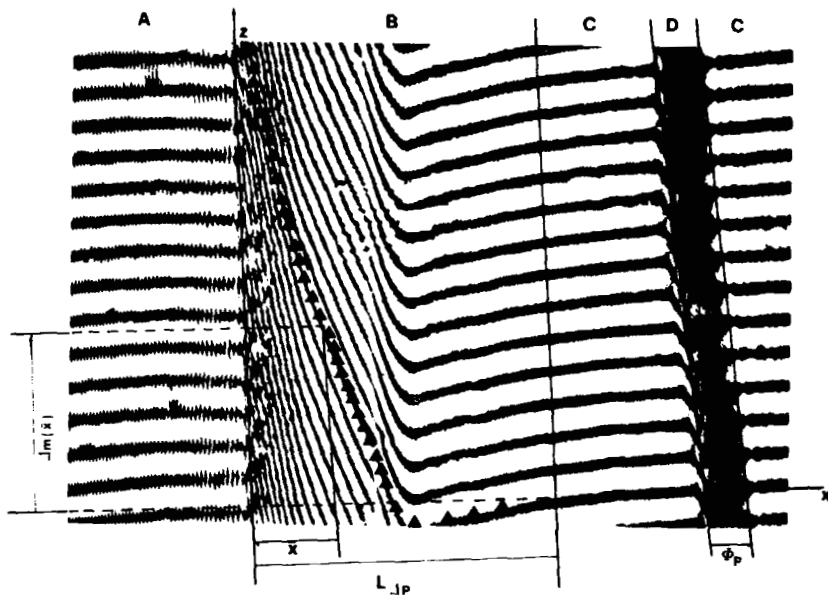


Fig. 3. A typical interferometric pattern. The correspondence between the regions of the photo and the regions of the sample is the following: (A) mixture adapting the external refractive index; (B) modified shell of the sample; (C) untreated core of the sample; (D) reference copper wire. For the meaning of the symbols x , $\Delta m(x)$, $L_{\Delta P}$, Φ_P , see the text.

(c) the refractive index variation:

$$\Delta n(x) = (\lambda_0/\delta)\Delta m(x)$$

where $\Delta m(x)$ is the local fringe displacement expressed as number of fringes, λ_0 the laser beam wavelength ($0.6328 \mu\text{m}$), and δ the average thickness of the sample.

Absolute values for refractive indexes were obtained, assuming the refractive index of the internal unperturbed region of the PMMA samples equal to 1.490.

Concentration Profiles from Refractive Index Profiles

The refractive index of a mixture is related to the refractive indexes of its components⁵ through the equation

$$n = n_A x_A + n_B x_B \quad (1)$$

where x_A and x_B are the volume fractions of components A and B. Such relation is valid only if the volumes are additive. For example, Gurnee⁶ puts in evidence for the styrene-divinylbenzene copolymer swollen by bromoform that the refractive index of the unswollen beads is considerably less than that found by extrapolation from the swollen state. The presence of "free volume" in the bulk polymer generates a refractive index less than what might be expected from the chain polarizabilities.

In our case, from gravimetric and volumetric measurements, it has been shown that the volumes of methanol and PMMA are additive, for samples previously annealed above the glass transition temperature.³ Moreover, the interferometric

measurements were carried out on partially desiccated samples characterized by a small volume fraction of solvent. As a consequence, the relation (1) has been assumed as valid, and the refractive index profiles have been considered as profiles of the volume fraction of the additive, as long as only one additive is present in the modified outer shell of the polymer sheet.

Unidirectional diffusion of solvents into a polymer sheet generates birefringence phenomena. The method of determining concentration gradients by the interference patterns is applicable provided that such birefringence is low with respect to the measured refractive index differences. The birefringence developed during partial swelling of PMMA specimens in methanol, and during successive solvent desorption, has been studied by Thomas and Windle.¹¹ The largest birefringence values at the center of the swollen layer (developed on desorption for smaller penetration depths) are less than 5×10^{-4} . For long diffusion times, high refractive index differences are generated ($\sim 10^{-2}$); on the other hand, larger penetration depths, and correspondingly lower birefringence values, are obtained. Hence we have assumed that for sufficiently long diffusion times the influence of the birefringence on the refractive index measurements is not relevant.

RESULTS

Interferometric Patterns Resulting from Methanol Diffusion and Desorption

A series of preliminary measurements on samples, in which pure methanol was diffused, has been performed, in order to obtain correct interpretations of the interference figures. The refractive index profiles, for PMMA samples immersed in pure methanol, are reported in Figure 4. The continuous and the

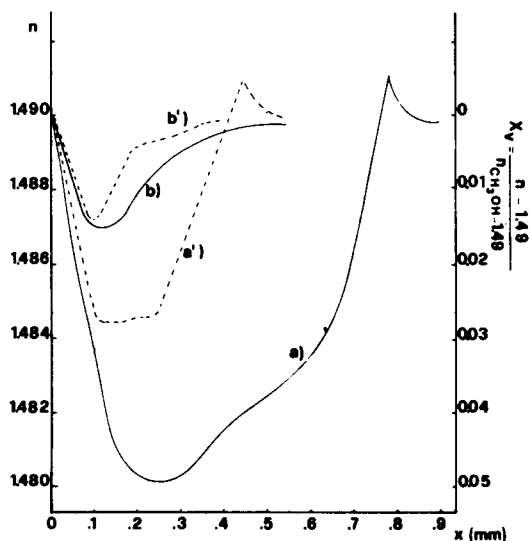


Fig. 4. Refractive index profiles for PMMA samples, immersed in methanol at 60°C for 60 min (—) and for 15 min (---). The letters close to the curves indicate the methanol desorption conditions: (a) at room temperature for 2 days; (b) at 70°C for 2 days. On the right of the figure the volume fraction of methanol in the polymer is indicated.

dashed lines refer to diffusion times of 60 min and 15 min, respectively, in samples subsequently desiccated in air at room temperature for 2 days or in an oven at 70°C, for 2 days again. According to the assumptions described in the previous paragraph, these refractive profiles can be considered as concentration profiles (more accurately for the higher diffusion time), the volume fraction of methanol in the polymer being indicated on the right-hand side of the figure. From methanol desorption curves at 60°C, it has been previously shown³ that the initially high desorption rate, of methanol from PMMA, is decreasing when the diffusion time increases and that a residual alcohol content is present in the polymer, also for long desorption times. The concentration profiles of Figure 4 indicate that the methanol desorption is faster from the outer region of the treated shell.

As the solvent desorbs, the dry polymer on the surface of the sheets constitutes a barrier for further desorption of the methanol; on the other hand, the methanol concentration is decreasing with desorption time, as a result, also the driving force for the diffusion decreases.

In fact, while the methanol concentration is almost zero on the specimen surfaces, it is not negligible at suitable depths, also for long desorption times at 70°C (which is above the boiling point of methanol, $T_b = 65^\circ\text{C}$). For example for 60 min of diffusion time, also after 2 days of desiccation at 70°C, at a depth

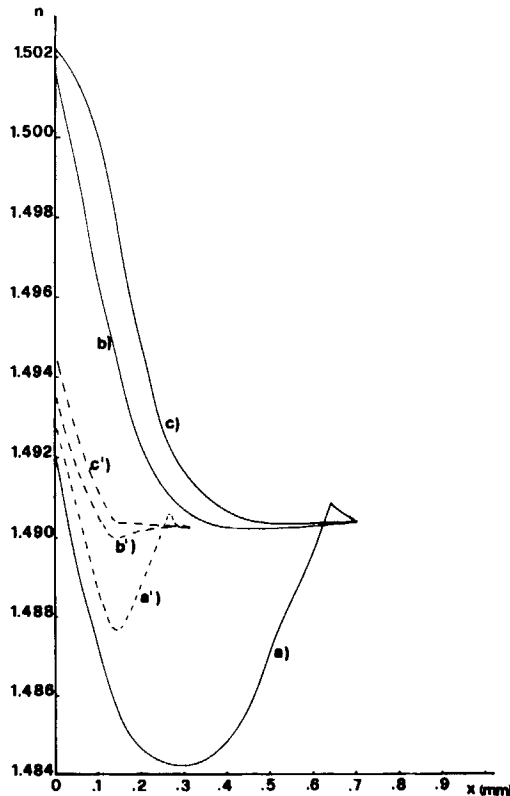


Fig. 5. Refractive index profiles for samples treated in 20% (b.w.) solutions of ZnCl_2 in methanol, for 60 min (—) and for 15 min (---). The letters near the curves indicate the desorption conditions: (a) at room temperature for 2 days; (b) at 70°C for 2 days; (c) at 130°C for 2 h.

of $100\ \mu$, there is still a local methanol concentration of almost 1% in volume. The alcohol can be completely removed only desiccating the samples at high temperatures, above the glass transition of the polymer. In such a case no significant variation in the refractive index, inside the treated samples, is observed.

An obvious result outcoming from the curves of Figure 4 is the increase with the diffusion time of the penetration depth and of the local concentration. In particular, the increase of the local concentrations of the solvent with the diffusion time clearly indicates that for this polymer-solvent system the transport mechanism at 60°C cannot be classified as case II diffusion, as already outlined.^{7,12,3}

For the samples desiccated only at room temperature small peaks close to the unaltered core in the interferometric figures are observed. These peaks could be tentatively attributed to the birefringence generated in the swollen polymer, during absorption, which is maximum near the advancing front, and can be still present in partially swollen samples.¹¹

Interferometric Patterns Resulting from Addition by Solvent Diffusion Technique, of Zinc Chloride

A nonvolatile additive such as ZnCl_2 ($T_m = 283^\circ\text{C}$) has been considered. Such an additive is not removed when the solvent driver is desorbed also at high temperature ($T = 130^\circ\text{C}$). The use of a nonvolatile additive allows us to separate the effects of the solvent and of the additive on the refractive index profiles, and hence allows us to easily obtain concentration profiles. The refractive index profiles of samples, treated at 60°C in 20% in weight solutions of ZnCl_2 , are reported in Figure 5. The continue and the dashed lines refer to different diffusion

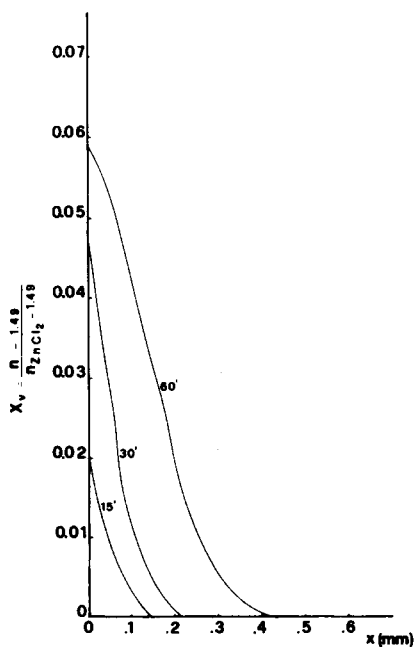


Fig. 6. Concentration profiles of ZnCl_2 in samples treated in 20% (b.w.) solution of the salt in methanol and then desiccated at 130°C . The diffusion times are indicated near the curves.

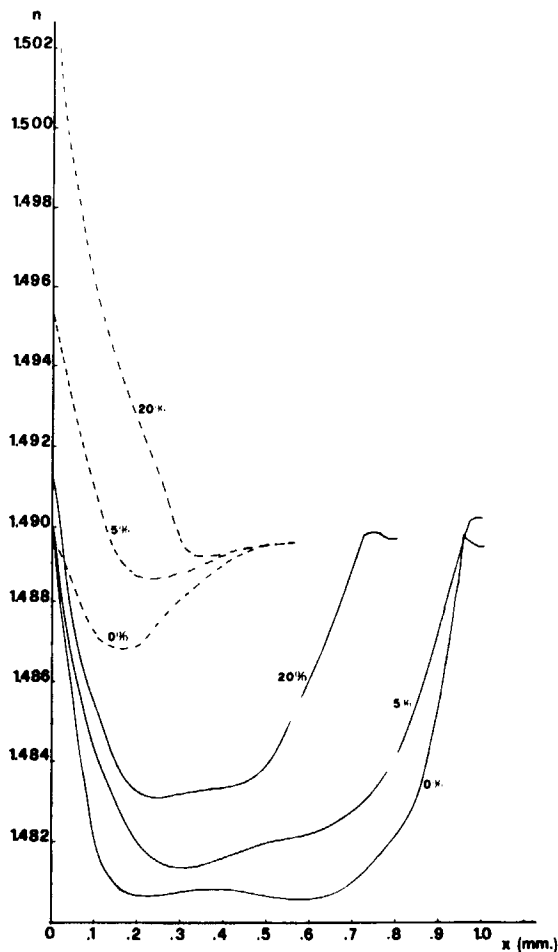


Fig. 7. Refractive index profiles for samples treated for 90 min with ZnCl_2 solutions in methanol and then desiccated for 2 days at room temperature (—) and at 70°C (---). The percent (b.w.) of ZnCl_2 in the diffusion baths is reported near the curves.

times, 60 min and 15 min, respectively. The interferometric patterns refer to samples desiccated at room temperature for 2 days (a) or at 70°C for 2 days (b) or at 130°C for 2 h (c). In the sample desiccated at room temperature, the high residual alcohol content reduces the refractive index of the polymers. After desiccation at 70°C , the alcohol content is greatly reduced, and, in nearly the whole modified shell, the effect of ZnCl_2 ($n = 1.69$), increasing the refractive index, prevails. Since at 130°C the alcohol can be completely removed, the corresponding refractive index profiles give the concentration profiles of ZnCl_2 in the polymer directly (Fig. 6). It is interesting to note that for the intermediate curve of Fig. 6 the additive concentration on the surface ($\sim 5\%$) is nearly twice the average concentration in the treated thickness ($\sim 2.5\%$) and is high compared to the concentration relative to a whole sample 3 mm thick (0.3%). These high surface concentrations can be responsible for the clear improvements of the flame retardant characteristics of polymer sheets reached by this technique.²

In Figure 7 refractive index profiles relative to samples immersed in solutions

at different concentration of ZnCl_2 are reported. The ZnCl_2 concentrations in the diffusion baths are indicated near the curves; the temperature and the time of diffusion are 60°C and 90 min. The continuous and the dashed curves are referred to samples desiccated for 2 days at room temperature and at 70°C , respectively. The increase of the additive concentration only slightly reduces the solvent diffusion rate but greatly increases the value of the refractive index inside the modified shell, that is, the local additive concentration.

CONCLUSIONS

The interferometric technique adopted is a useful tool for the characterization of transparent samples treated in the outer shell by diffusion technique. It is possible, in suitable conditions, to determine the amount and distribution of the residual solvent, the depth of the modified layer, and the additive concentration profile. It is possible to change these characteristics of the treated shells, varying the process conditions such as time and temperature of diffusion and of solvent desorption, or the concentration of the diffusion baths. The characterization of the concentration profiles leads to a better understanding of the action mechanism of the additives and of the manufactured product properties as a consequence of the additive penetration.

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