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Refractive index: a probe for monitoring volume relaxation during physical aging of glassy polymers

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A positive correlation between refractive index and density has been experimentally illustrated in the literature for numerous materials, including polymers. This relationship was exploited in an attempt to follow the densification of a glassy polymer during the physical aging process. Atactic polystyrene films were aged at 74°C and the refractive index (n) was evaluated as a function of aging time (t_a) using an Abbe refractometer. The refractive index increased linearly with respect to log (t_a), and this dependence was used in conjunction with experimentally determined values of the thermal expansion coefficient in the glassy state and $(\partial n/\partial T)_{P,t_a}$ for unaged polystyrene to determine the volume relaxation rate at 74°C. This rate was similar to that obtained for the same polystyrene material using a precision dilatometer, indicating the possibility for using refractive index measurements to quantitatively assess volume relaxation during physical aging. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Optical properties are intimately related to the chemical composition and structural features of a polymeric material. Representative examples of such relationships are evident in the Lorentz–Lorenz expression for average refractive index ($\bar{n}$), an important optical property for polymer applications. One form of the Lorentz–Lorenz equation is as follows[1]:

$$\frac{\bar{n}^2-1}{\bar{n}^2+2}=\frac{\rho \mathrm{N_{av}} \sum n_i\bar{\alpha}_i}{3\mathrm{M_0}\epsilon_0} \tag{1}$$

where $\mathrm{N_{av}}$ is Avogadro's number, the molecular weight of the polymer repeat unit is denoted by $\mathrm{M_0}$, ϵ_0 is the permittivity of free space constant, the density of the polymer is represented by ρ, the average polarizability of the ith type chemical bond is given the symbol $\bar{\alpha}_i$, and n_i is the number of such bonds per repeat unit. It is clear from the above equation that increasing the average polarizability of the chemical bonds is expected to result in greater refractive index values, if all other factors remain constant. For a given chemical composition, the number of polarizable species per unit volume also influences the velocity of light through a material, hence a positive correlation between refractive index and density. Therefore, knowledge of refractive index changes for a polymer material can provide information concerning density changes.

There are numerous variables which indirectly influence the refractive index by altering the density of a polymer. As temperature is increased, a material expands volumetrically which results in a decrease in density and refractive index. The thermal expansion coefficient for a polymer in the glassy state is significantly lower than the coefficient for the polymer at temperatures above the glass transition region. The inflection in a plot of refractive index *versus* temperature can be used to determine the glass transition temperature associated with the heating/cooling conditions utilized, as has been detailed in the literature[2–4]. The crystalline phase of a semicrystalline polymer is typically more dense than its amorphous counterpart, and refractometry has additionally been used in assessing the degree of crystallinity for polymer films[5].

Physical aging of glassy polymers is another area where refractive index measurements can potentially be utilized to probe densification features. When an amorphous polymer is quenched from the liquid state to a temperature below the glass transition temperature region, attainment of thermodynamic equilibrium via structural rearrangement is initially denied due to kinetic considerations[6]. Relaxation can occur with time, and this process, known as physical aging, results in a decrease of the specific volume of the polymer towards the equilibrium state. Although the density changes during physical aging are typically quite small (the density of atactic polystyrene aged 15°C below T_g increases at an approximate rate of 0.0008 g/cc per decade of aging time[7]), volume relaxation during physical aging may be able to be followed using refractometry provided refractive index measurements can be made with adequate accuracy. Research employing refractometry to provide insight into the non-equilibrium nature of the glassy state has been very limited. The memory effect, first disclosed by the dilatometry experiments of Kovacs[8], has been investigated for inorganic glasses using refractometry[9–11] as opposed to dilatometry. Jenkel followed the physical aging of polystyrene using refractive index[12], but a direct quantitative link between refractive index changes and volume relaxation rates has not clearly been made for the physical aging of glassy polymers. This research investigates whether changes in refractive index for atactic polystyrene (a-PS) during isothermal physical aging can be quantitatively related to the corresponding volume changes.

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EXPERIMENTAL

The material used in this study was Styron 685D, an atactic polystyrene (a-PS) produced by Dow Chemical. This amorphous polymer has a number average molecular weight of 174 000 g/mol and a weight average molecular weight equal to 297 000 g/mol as assessed via gel permeation chromatography. The inflection glass transition temperature (T_g) for this material was determined to be 104°C at a heating rate of 10°C min using a differential scanning calorimeter (Perkin Elmer DSC-7). Films were generated by compression molding a-PS pellets in a picture frame mold at a temperature of 165°C using a laboratory press with heated platens produced by Pasadena Hydraulics Incorporated. The resulting films, possessing an average thickness of 0.1 mm, were cut into rectangles of suitable size (20 × 50 mm) for refractive index testing. In order to insure that the initial films were unaged and unoriented, the film samples were annealed at a temperature 50°C above T_g for 10 min and subsequently quenched between two plates at room temperature. The films were then placed into a vacuum oven held at 74°C, and samples were removed from the oven at various aging times for refractive index evaluation. Because the films were unoriented, the refractive index in any direction for the films should be equal to the average refractive index, and the symbols n and $\bar{n}$ will, therefore, be used interchangeably in this paper.

Refractive index measurements were made using an Abbe refractometer manufactured by Bellingham and Stanley Ltd (model 60/ED). The product literature provided for this instrument indicated that it provides refractive indices that are accurate to within 0.0001 refractive index units. A circulating water bath produced by Neslab Instruments Inc. (model Endocal RTE-100) was employed to maintain the temperature of the refractometer prisms and the enclosed sample at a constant value ± 0.1°C. Based on the sensitivity of refractive index to temperature in the glassy state for a-PS, this temperature fluctuation is expected to result in a refractive index error of $\pm 1.2 \times 10^{-5}$, a value negligible in comparison to the combined sample and instrument error to be detailed later. Prior to testing the polystyrene film samples, the refractometer was calibrated at 20°C using a contact liquid with a known refractive index of 1.5982 at this temperature. For all of the tests performed, the critical angles were determined with respect to the average Sodium D line (589.3 nm wavelength), and the corresponding refractive index (n_D) values were determined to the fifth decimal place using conversion tables for the instrument. In order to minimise diffuse reflection from the surfaces of the a-PS films, a contact fluid based upon hydrogenated terphenyl 1-bromonapthalene was utilised. The n_D of the particular fluid used was 1.6423 at 20°C which is a value between the refractive index of a-PS (~1.59) and that of the refractometer prisms (~1.89), in accordance with standard refractometry procedure[13]. To eliminate sample error, it would be desirable to determine the refractive index of a single a-PS film sample after various incremental aging times. However, the a-PS samples could only be tested once because it was necessary to expose the film samples to the contact fluid in order to make refractive index measurements. Since testing multiple films was unavoidable, five a-PS samples were tested for each aging condition to provide some measure of the statistical significance of the refractive index data.

Volume relaxation of the atactic polystyrene material during physical aging at 74°C was evaluated using a precision dilatometry apparatus constructed by Dr M. D. Shelby and described in detail elsewhere[14]. A solid bar of the a-PS material with the dimensions 13 × 13 × 38 mm was prepared in an analogous manner to the previously mentioned films. The bar sample was subsequently enclosed in a glass dilatometer containing a capillary with an inside diameter of 4.16 mm. The dilatometer, encasing the polymer sample, was filled with mercury and then degassed under vacuum for 48 h to remove any air bubbles. The degassed dilatometer was allowed to equilibrate for 24 h at room temperature after removal of the vacuum, annealed 10 min at a temperature 50°C above T_g in an oil bath, and then quenched using an ice bath. The a-PS sample in the dilatometer was then isothermally annealed at 74°C in a Haake model N4-B oil bath with temperature control fluctuations less than 0.01°C, and the height change of the mercury in the capillary was assessed with aging time using a calibrated linear voltage differential transducer and converted to volume change based on the cross sectional area of the capillary. This procedure was performed three times in order to determine a volume relaxation rate and its corresponding standard deviation for a-PS undergoing physical aging at 74°C. The thermal expansion coefficient for a-PS in the glassy state was also determined using dilatometry by cooling a sample from above the glass transition region to a temperature of 65°C in the dilatometer at an approximate rate of 1°C per min, recording the capillary height change during cooling, and subtracting the mercury volume change in order to assess the volume change attributed solely to the a-PS sample as a function of temperature.

RESULTS AND DISCUSSION

The discussion to follow will explore the potential for using refractive index measurements to monitor the densification of atactic polystyrene during physical aging. First, the experimental data concerning the influence of aging time on the refractive index of atactic polystyrene isothermally aged at 74°C will be presented. This will be followed by details pertaining to the development of two straightforward methods to utilize this data in the determination of the corresponding volume relaxation rate (β). The volume relaxation rates assessed using the two refractometry approaches will finally be compared to the analogous rate determined for the same a-PS material at the same aging conditions using dilatometry in order to provide an indication of the validity of the refractometry approach developed.

Effect of physical aging on refractive index

Film samples of atactic polystyrene were physically aged at 74°C following a quench from the equilibrium rubbery state ($T = T_g + 50°C$), and refractive index measurements were made as a function of aging time (t_a). After removal from the aging chamber, the film samples were cooled to room temperature and the refractive indices were determined at 20°C within 20 min from the time of oven removal. It was assumed that negligible additional physical aging occurred during the short 20-min duration after the samples were removed from the oven because the aging rate is expected to be extremely slow at 20°C relative to the rate at 74°C, a temperature which is much closer to the glass transition temperature region[7]. The effect of aging at 74°C on the refractive index of atactic polystyrene is indicated

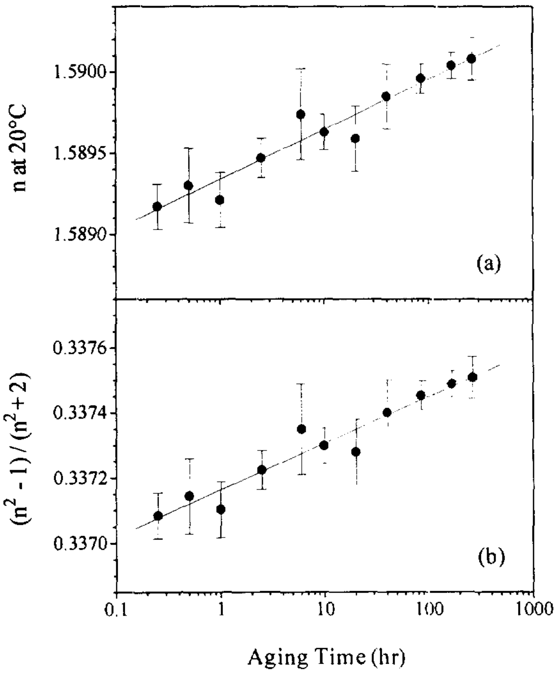

Figure 1 Refractive index at 20°C as a function of aging time for a-PS films aged at 74°C (a) and data replotted in the form of the Lorentz–Lorenz relationship (b). Straight lines represent linear fits to the data

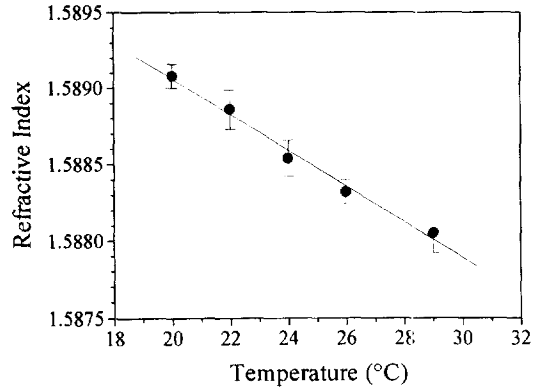

Figure 2 Refractive index as a function of temperature for unaged a-PS films. The solid line represents the linear fit used to determine $(\partial n/\partial T)_{P,t_a}$

in *Figure 1a*. The refractive index increased in a linear fashion when plotted as a function of log t_a and the slope of the linear fit to the data $(\partial n/\partial \log t_a)_{P,T}$ was found to be $(3.22 \pm 0.60) \times 10^{-4}$. The error bars indicated in this plot represent the standard deviations associated with the five samples tested at each aging time. The refractive index error, which represents a combination of instrument error (±0.0001) and sample error, possessed average and maximum values of 0.00015 and 0.00028, respectively. Despite the considerable magnitudes of the error bars, the linear dependence of refractive index on log t_a is statistically significant as is evident from the correlation coefficient (R^2) for the linear fit which is equal to 0.934.

It is often observed that density increases are linearly related to log t_a during isothermal aging, following a quench from above the glass transition temperature, due to the self-limiting nature of physical aging[15]. The Lorentz–Lorenz relationship (equation (1)) does not predict refractive index to be a linear function of density, and the experimental observation that refractive index has a linear dependence on aging time does not have a fundamental basis. The refractive index data was replotted in the form of the left-hand side of equation (1) as illustrated in *Figure 1b*. This plot implies that a linear increase in density with log t_a occurred during isothermal aging of a-PS at 74°C, as anticipated. However, the degree of linearity for the plot in *Figure 1b* ($R^2 = 0.934$) is identical to the linearity between refractive index and log t_a which suggests that either plot is suitable to describe the experimentally observed effect of aging on refractive index for the polymer material and conditions utilized in this study. In agreement with this observation, research evaluating the effect of density on refractive index for various polyolefins resulted in the conclusion that plotting refractive index or refractive index expressed in the form of Lorentz–Lorenz equation *versus* density provides similar degrees of linearity[13].

Determination of volume relaxation rate from refractive index data

The volume relaxation rate (β) is a parameter which can be used to represent the kinetics of volume relaxation during the isothermal physical aging of glassy materials. The volume relaxation rate can be expressed as follows[7]:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial \log t_a}\right)_{P,T} \tag{2}$$

The previously discussed increase in refractive index with aging time for atactic polystyrene is a consequence of the densification of the system. Therefore, the value of $(\partial n/\partial \log t_a)_{P,T}$ observed for a-PS physically aged at 74°C is influenced by the rate of volume relaxation and can potentially be used to determine β. The relationship between β and $(\partial n/\partial \log t_a)_{P,T}$ can be expressed mathematically using the chain rule of partial differentiation:

$$\begin{aligned}\beta &= -\frac{1}{V}\left(\frac{\partial V}{\partial \log t_a}\right)_{P,T}\\ &= -\left(\frac{\partial n}{\partial \log t_a}\right)_{P,T}\left(\frac{\partial T}{\partial n}\right)_{P,t_a}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,t_a}\end{aligned} \tag{3}$$

Using the definition of the thermal expansion coefficient in the glassy state (α_g), equation (3) can be rewritten as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial \log t_a}\right)_{P,T} = -\left(\frac{\partial n}{\partial \log t_a}\right)_{P,T}\left(\frac{\partial n}{\partial T}\right)_{P,t_a}^{-1}\alpha_g \tag{4}$$

This relationship allows determination of the volume relaxation rate from $(\partial n/\partial \log t_a)_{P,T}$ in conjunction with the change of refractive index with temperature for the unaged material in the glassy state $(\partial n/\partial T)_{P,t_a}$ and the glassy thermal expansion coefficient. Refractive index data for unaged a-PS is presented as a function of temperature in *Figure 2*. This data was used to determine the value for $(\partial n/\partial T)_{P,t_a}$ which was equal to $-(1.17 \pm 0.07) \times 10^{-4}\,\mathrm{K}^{-1}$, a value comparable to the value of $-1.2 \times 10^{-4}\,\mathrm{K}^{-1}$ reported in the literature[1]. Dilatometry was used to determine that $\alpha_g = (2.21 \pm 0.06) \times 10^{-4}\,\mathrm{K}^{-1}$ for the atactic polystyrene material investigated which is consistent with the range of values tabulated for this polymer[16]. Using the experimentally determined values for the parameters $(\partial n/\partial \log t_a)_{P,T}$, $(\partial n/\partial T)_{P,t_a}$, and α_g, and propagating their associated errors using a differential technique, the volume relaxation rate calculated via equation (4) was found to be equal to $(6.08 \pm 1.61) \times 10^{-4}$. A summary of the parameter values used in this calculation of volume relaxation rate can be found in the upper portion (Method 1) of *Table 1*.

Table 1 Summary of parameters used to calculate β from refractive index data

Method 1 Equation (4)	$\left(\frac{\partial n}{\partial \log t_a}\right)_{P,T}$	$\left(\frac{\partial n}{\partial T}\right)_{P,t_a}$ [K^{-1}]	α_g [K^{-1}]	β
	(3.22 ± 0.6)E-4	(− 1.17 ± 0.07)E-4	(2.21 ± 0.06)E-4	(6.08 ± 1.61)E-4
Method 2 Equation (5)	$\frac{n^2-1}{n^2+2}$ (average)	$\frac{\partial L}{\partial \log t_a})_{P,T}$ where $L=\frac{n^2-1}{n^2+2}$		β
	0.3373 ± 0.0002	(1.43 ± 0.06)E-4		(4.25 ± 0.38)E-4

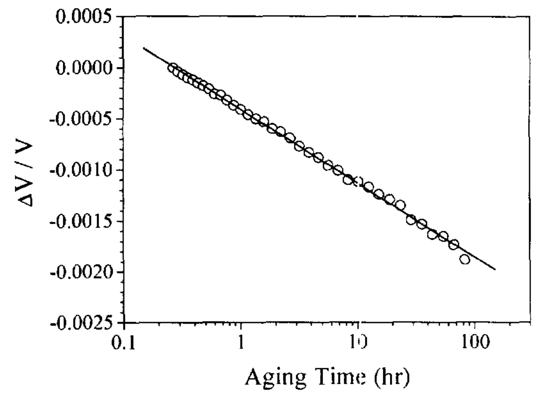

Figure 3 Volume relaxation plot for a-PS during aging at 74°C obtained using dilatometry. Volume changes referenced to $t_a = 0.25$ h. The slope of the linear fit is equal to $-\beta$

Irrespective of the changing thermodynamic state of the glassy polymer undergoing physical aging, the Lorentz–Lorenz expression should remain valid at any instant in time. Because the chemistry of the system is not changing during physical aging, all of the parameters on the right-hand side of equation (1) are constant except for density. Therefore, the following expression can be developed based upon this proportionality between density and the left hand side of the Lorentz–Lorenz equation:

$$\frac{1}{L}\left(\frac{\partial L}{\partial \log t_a}\right)_{P,T} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial \log t_a}\right)_{P,T} = \beta \text{ where } L = \frac{n^2-1}{n^2+2} \tag{5}$$

Using this approach (Method 2), the volume relaxation rate determined was equal to (4.25 ± 0.38) × 10^{-4} as is indicated in the lower half of *Table 1*. Direct use of the Lorentz–Lorenz expression (Method 2) slightly under-predicted the volume relaxation rate in comparison to Method 1, and the origin of this discrepancy is not known. As will be indicated, the β value determined from the refractive index data via Method 1 more closely agrees with the value obtained by dilatometry. (See Note Added to Proof.)

Comparison of β values determined by refractometry and dilatometry

Volume relaxation rates for glassy materials are commonly assessed through the use of dilatometry. The densification of a-PS during physical aging at 74°C was investigated using a precision mercury dilatometer, and a typical volume relaxation plot providing a slope of $-\beta$ is presented in *Figure 3*. The average volume relaxation rate for three dilatometry experiments was found to be (7.57 ± 0.41) × 10^{-4} which is within experimental error of the rate calculated based upon the refractive index data using Method 1 which was equal to (6.08 ± 1.61) × 10^{-4}. This suggests that the technique (Method 1) developed in this investigation for converting refractive index changes during physical aging of glassy polymers to the associated volume relaxation rates can be used quantitatively.

It is anticipated that improvements can be made in order to determine volume relaxation rates using the refractometry approach which more closely match the corresponding rates assessed using dilatometry. The use of a device which allows refractive index determinations with improved accuracy relative to the Abbe refractometer used in this study is expected to improve the agreement between the volume relaxation rates. Additionally, if refractive index measurements could be made on a single polymer film sample as it is incrementally aged, the sample error would be eliminated thus improving the experimental results and the volume relaxation rates calculated from them. A weak secondary relaxation, which occurs in the vicinity of 60°C for atactic polystyrene, has been shown to slightly increase the glassy thermal expansion coefficient above this temperature of 60°C relative to the glassy expansion coefficient observed near room temperature[17]. Although this difference is quite small, it implies that $(\partial n/\partial T)_{P,t_a}$ near the aging temperature of 74°C may have been slightly different than that determined for the lower temperature range used to determine this parameter, possibly influencing the β calculation. Overall, the best method would be to accurately follow the refractive index for a single polymer film sample *in situ* during the physical aging process and use values of the parameters $(\partial n/\partial T)_{P,t_a}$ and α_g determined near the aging temperature in the calculation of the volume relaxation rate using equation (4).

CONCLUSIONS

For atactic polystyrene isothermally aged at 74°C following a quench from above the glass transition temperature, the refractive index increased linearly with respect to log t_a due to the densification of the system during physical aging. This linear relationship was used with experimentally determined values of the thermal expansion coefficient in the glassy state and $(\partial n/\partial T)_{P,t_a}$ for the unaged polymer to determine the volume relaxation rate. This rate was equal to (6.08 ± 1.61) × 10^{-4}, a value within experimental error of the volume relaxation rate of (7.57 ± 0.41) × 10^{-4} determined by dilatometry. This technique developed for converting refractive index changes to the rate of volume relaxation appears to be a quantitative alternative to dilatometry for following the densification kinetics associated with physical aging. Due to the difficulty in constructing a dilatometry apparatus providing accurate volume change measurements and the lengthy procedures necessary to remove entrapped air from the dilatometer prior to testing, the refractometry approach explored in this study may in fact be an easier method of following volume relaxation as well.

NOTE ADDED TO PROOF

The development of Method 2 described in the text assumes that density does not influence the polarizability of the chemical bonds, and a possible interrelationship between density and polarizability may have resulted in the noted under-prediction of volume relaxation rate using this method. This possibility does not pose any problems when using Method 1 due to a canceling effect between density changes (and possible polarizability changes) induced by temperature changes and by physical aging.

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