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(22) The temperature of 60 °C was chosen for the isothermal demixing process, because the rate of spinodal decomposition and subsequent coarsening processes occur sufficiently slow, which makes it easy to control the initial condition for the concentration fluctuations for the subsequent experiment on the uniaxial compression. Needless to say, the wavelength of the dominant mode of the fluctuations depends on time as well as temperature.[5]

Free Volume and Physical Aging of Poly(vinyl acetate) Studied by Positron Annihilation

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ABSTRACT: The positron lifetime technique was used to study the free-volume properties of poly(vinyl acetate) (PVAc) in the liquid and the glass as a function of temperature and aging time. The average hole volume $\langle v_f \rangle$ at each temperature was determined from the orthopositronium (o-Ps) lifetime τ_3 by using an equation of Nakanishi, based on a theoretical model of Tao. The temperature dependence of the product of the intensity of the o-Ps component I_3 and $\langle v_f \rangle$ agrees well with the free-volume fraction h computed from equation-of-state data via the statistical mechanical theory of Simha and Somcynsky. This observation suggests that I_3 is a measure of the number of holes in a polymer matrix. Changes in I_3 during physical aging were found to be proportionately greater than changes in τ_3, in agreement with previous studies. The results indicate that positron annihilation can be a reliable method for monitoring not only free-volume changes but also changes in the distribution of free-volume elements in polymers.

1. Introduction

Physical aging of an amorphous polymer refers to a progressive change of its properties without the intervention of chemical agents. This process occurs in the glassy state, having its origin in the nonequilibrium character of this state and the consequent relaxation toward equilibrium.[1] A convenient phenomenological description can be developed within the classical free-volume concept. The distance from equilibrium can be related to the excess free volume of the glass, and the aging rate can be related to the time evolution of the free-volume distribution. Classical aging experiments have involved well-specified temperature jumps with subsequent observations of macroscopic quantities such as volume, enthalpy, or mechanical properties such as stress relaxation.

The statistical mechanical theory of Simha and Somcynsky[2] provides a powerful vehicle for correlating and predicting aging effects on different materials. The thermodynamic properties of the bulk polymeric state are expressed in terms of a free-volume function, h. However, numerical evaluation of this quantity requires P-V-T information as a function of thermal and pressure history of the specimen under study.[3,4] A more convenient application of the theory as an analytical tool requires a more direct and rapid means of numerically determining h.

Positrons have been successfully used for materials research since it was discovered in the late 1960s that the positron lifetime in a variety of materials is extremely sensitive to phase transitions and to the presence of defects and other inhomogeneities. The utility of positrons in polymer studies is enhanced by the fact that the positron can capture an electron and form a bound system, an atom of positronium (Ps).[5,6] Ps has an atomic radius similar to hydrogen, except that it rapidly decays by positron–electron annihilation. Orthopositronium (o-Ps), where the spins of the two particles are parallel, has a mean lifetime of 142 ns under vacuum. Parapositronium (p-Ps), where the spins of the two particles are antiparallel, has a mean lifetime of only 123 ps. The difference in the o-Ps and p-Ps lifetimes under vacuum is due to the fact that, to conserve spin angular momentum, o-Ps (spin = 1) must produce three photons upon annihilation while p-Ps (spin = 0) only produces two. In condensed matter, the o-Ps lifetime is shortened to a few nanoseconds or less, because of pickoff of the positron by electrons of antiparallel spin in the surrounding medium. However, this lifetime is considerably longer than that of a free positron in the same medium, because the electron in o-Ps partially shields its positron from those electrons with antiparallel spin, which would annihilate it more rapidly. Because of the relatively long lifetime of o-Ps, its component is well-defined in a lifetime spectrum. Therefore, it is possible to make a rather precise determination of the o-Ps lifetime and its intensity (the fraction of positrons that annihilate as o-Ps).

The other important feature of the o-Ps atom in a polymer is that this species is preferentially trapped or formed in regions of low electron density, or holes. Since the annihilation rate of o-Ps is proportional to the overlap of the positron and the pickoff electron wave functions,[7] it is expected that the o-Ps lifetime will strongly depend upon the size of the hole. Numerous experiments[7-13] have

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shown the increase of o-Ps lifetime with temperature. This phenomenon has been interpreted in terms of an increase of the free volume with temperature. It has also been shown that the intensity of the o-Ps component, or, in other words, the probability of formation of o-Ps, may be related to the number of free-volume sites in the polymer.[7]

In the present study, the authors have determined positron lifetime parameters of poly(vinyl acetate) (PVAc) as a function of temperature and aging time. PVAc was selected since a significant amount of information exists on the volume aging behavior. Furthermore, connections between volume aging and the aging of viscoelastic shift parameters have been established via the *h* parameter of the Simha–Somcynsky theory. The aim of this study was to establish a quantitative relation between the positron lifetimes and the free-volume fraction, *h*, of an amorphous polymer and to make numerical connections between free-volume measurements by positron annihilation and the time evolution of the mechanical properties of the polymer during isothermal annealing below the glass transition temperature, T_g.

2. Experimental Section

A commercial poly(vinyl acetate) sample (Mowilith 40), supplied by DSM, Geleen, The Netherlands, was used in this study. The glass transition temperature was determined to be 32 °C by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.

The positron source consisted of approximately 50 μCi of ^{22}NaCl deposited onto a thin (1.7 mg/cm^2) piece of aluminum foil. The foil was sandwiched between two rectangular pieces (1 cm × 2 cm × 3 mm) of PVAc, which were prepared by compression molding under vacuum at 80 °C. The sample temperature was regulated within 1 °C by a temperature controller from Lake Shore Cryogenics (DTC500-sp) with a diode sensor also from Lake Shore (DT-470-sd). In order to minimize possible error resulting from different thermal histories,[10] the sample was annealed at 60 °C for at least 30 min before each quench and subsequent data accumulation. Blowing cold, dry nitrogen gas into the sample cell permitted a quench to be completed within 10 min.

Positron lifetime spectra were obtained with a conventional fast–fast coincidence system by determining the time interval between the 1.28-MeV γ-ray due to nuclear decay and one of the 0.511-MeV annihilation γ-rays. In the present study, to get high efficiency and good timing performance simultaneously, two fluoride crystals were used as scintillators. A cesium fluoride crystal of cylindrical shape (diameter 3.8 cm, length 3.8 cm) coupled to a Hamamatsu H2431 photomultiplier tube was used to detect the 1.28-MeV γ-rays as start signals. A barium fluoride crystal of conical shape[14] (diameters 1.5 and 2.5 cm; length 2.5 cm) coupled to a Hamamatsu H2431Q photomultiplier tube by glycerol[15] was used to detect the 0.511-MeV γ-rays as stop signals. Following Rajainmaki,[16] short delay cables of length about 10 cm were used on the discriminators. The time resolution of the lifetime spectrometer was measured by a ^{60}Co source and found to be 210-ps full-width at half-maximum (fwhm).

The lifetime spectra were successfully resolved into three exponentially decaying components by two computer programs: POSITRONFIT EXTENDED[17] and EXPFIT. The latter program, developed by McGervey and Walters many years ago,[6] permits the resolution fwhm to be used as a fitting parameter. Both programs gave identical results for the lifetimes and intensities. The shortest lived component, with lifetime $\tau_1 \approx 0.14$ ns and intensity $I_1 \approx 0.15$, is attributed mainly to self-annihilation of p-Ps. The intermediate component with lifetime $\tau_2 \approx 0.39$ ns and intensity $I_2 \approx 0.58$ has been attributed to annihilation of free positrons. The longest lived component, with lifetime τ_3 ranging between 1.7 and 2.5 ns and intensity I_3 between 0.25 and 0.28, results from pick-off annihilation of o-Ps. The data analysis also accounted for the positrons that were annihilated in the source (about 11% of the total).[18]

3. Results and Discussion

3.1. Positron Lifetime vs Temperature.

Figure 1 shows the increase in o-Ps lifetime with increasing temperature throughout the entire temperature range studied. The slope is small and constant below about 20 °C, undergoes a transition in the range from 20 °C to about 45 °C, and then finally is steep and constant beyond this region. Extrapolation of the straight lines below 20 °C and above 45 °C gave a glass transition of about 32 °C. This value agrees well with the results of DSC. The variation of τ_3 with temperature has previously been studied for various polymers. Experiments reported on polystyrene,[8] epoxy resins,[13] poly(methyl methacrylate), and other methacrylates[12] show an abrupt change of the slope of τ_3 vs temperature at T_g. However, analyses of τ_3 versus temperature in polyethylene,[9] styrene–butadiene–styrene copolymer[19] and polyisoprene[10] show a broad change like the one shown in Figure 1. The reason for the occurrence of different types of transitions is not clear. However, the range of this transition in Figure 1 is in good agreement with the results of DSC, where the heat capacity showed a gradual increase in the region from 20 to 45 °C. A broad transition at T_g = 32 °C was also observed when we measured the temperature dependence of the emission intensity of the fluorescent probe Auramine O, dispersed in this PVAc sample.[20]

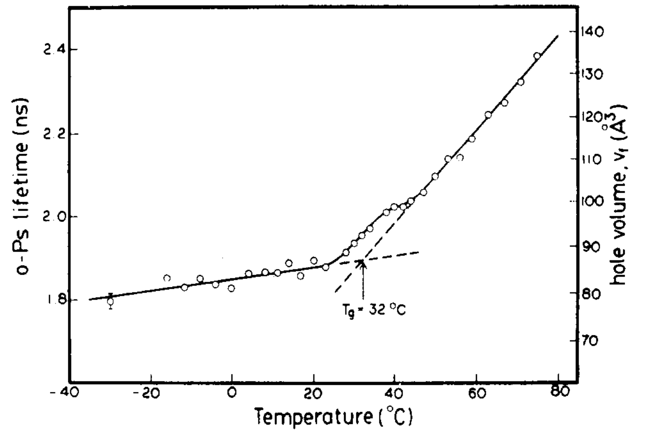

Figure 1. Ortho-positronium lifetime and calculated hole size versus temperature. The error bars are only for the lifetime. For all points above −30 °C the error bars are within the plotting symbols. All points below 60 °C were obtained after a quench from 60 °C. The data accumulation time for each point was 1 h.

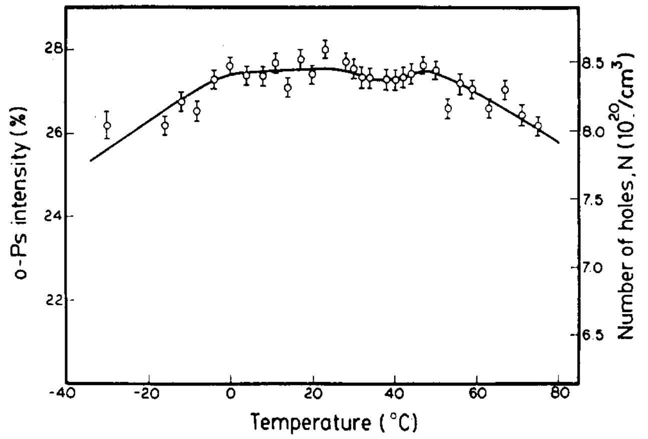

Figure 2. Ortho-positronium intensity and calculated hole density versus temperature. All points below 60 °C were obtained after a quench from 60 °C. The data accumulation time for each point was 1 h.

Figure 2 shows that the temperature dependence of I_3 is more complex than that of τ_3. Above 45 °C, where the o-Ps lifetime increases rapidly with temperature, I_3 actually decreases slightly with increasing temperature. Since Ps formation is believed to be correlated with the number of holes,[21,22] this decrease in I_3 suggests a decrease in the number density of holes with increasing temperature. We are therefore led to propose that, in the melt, the increase in total free volume with temperature involves growth in hole size rather than an increase in number of holes. On the other hand, since τ_3 decreases only slightly with temperature below T_g, while I_3 decreases relatively rapidly, it appears that in the glass the variation in free volume with increasing temperature primarily results from hole formation.

3.2. Positron Lifetime and Hole Size. The decrease in τ_3 with decreasing temperature indicates a decrease in free-volume hole size. The relation between hole size and positron lifetime was quantified in a model first used by Tao for molecular liquids.[23] Following Tao, we assume that the o-Ps atom in a hole in a polymer may be approximated by a particle in a spherical potential well of radius R_0. The potential is infinite for $r > R_0$ and constant for $r < R_0$. It is assumed that there is an electron layer in the region $R < r < R_0$, where $R = R_0 - \delta R$, and δR is an adjustable parameter. If we make the further reasonable assumption that the lifetime of the o-Ps in the electron layer is[23] the spin-averaged Ps lifetime of 0.5 ns, then the relation between R and the o-Ps lifetime τ_3 becomes[24]

$$\tau_3^{-1} = 2(\text{ns}^{-1})(1 - [R/R_0] + 0.159[\sin(2\pi R/R_0)]) \qquad (1)$$

Recently, Nakanishi[24] has shown that eq 1, with $\delta R = 0.1656$ nm, gives correct values of τ_3 for known hole sizes in porous materials. The same choice of δR gives the hole sizes shown on the right-hand scale in Figure 1. (Although this scale appears to be linear, it is not. It is only approximately linear over the range of values in question.) The hole volume, v_f, calculated as $(4/3)\pi R^3$, spans a range from 0.078 nm^3 at $T = 30$ °C to 0.134 nm^3 at $T = 75$ °C. This volume range corresponds to $0.26 \text{ nm} < R < 0.32$ nm.

Our problem that now arises is that in any given sample state the holes are not all the same size. The fact that we observe a well-defined lifetime τ_3 does not mean that the positrons are annihilating in holes of the same size. On the contrary, there is surely a distribution of holes of different sizes, and there is reason to believe that an o-Ps atom can sample a number of holes during its lifetime. In that case, all of the o-Ps atoms share the same mean lifetime (which is what we observe) even though the holes are of different sizes. The measured annihilation probability λ per unit time is then the sum of contributions from various holes, each contribution being proportional to the λ for that hole and to the probability of finding the o-Ps atom in that hole. To determine the effect of this summation on our results, let us consider two holes a and b and assume that the probability of finding the positron in either hole is proportional to the volume of the hole. Then a positron trapped in this pair would have a mean lifetime of

$$1/\lambda = \tau_{av} = [(V_a/\tau_a) + (V_b/\tau_b)]^{-1}(V_a + V_b) \qquad (2)$$

It is not obvious that τ_{av} is related to the average volume $\langle v_f \rangle$ of two holes in the same way that τ_3 is related to the volume of a single hole. However, for holes of the sizes expected in this study, eq 2 shows that τ_{av} differs very little from the lifetime given by eq 1 for a positron in one hole whose volume is the average volume of the two holes. For example, when the hole volumes are 0.070 and 0.140 nm^3, respectively, eq 1 and 2 give $\tau_{av} = 2.13$ ns. A positron having this same lifetime in a single hole would, according to eq 1, be in a hole whose volume is 0.109 nm^3, only 4% greater than the average of 0.070 and 0.140 nm^3. (Theory indicates that this is an extreme case and that most of the holes have volumes between these two values.) Therefore, with reasonable accuracy, we can say that eq 1 provides a relation between τ_3 and the *average* hole size.

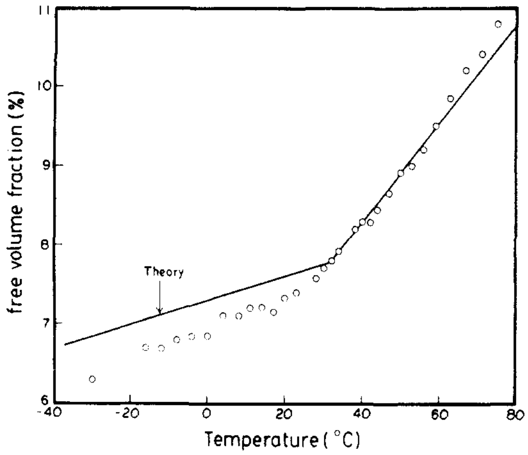

Figure 3. Free-volume fraction values (○) computed from positron annihilation data via eq 6 are compared with the solid line computed from volumetric data via the Simha–Somcynsky theory.

3.3. Determination of the Free-Volume Fraction h from Positron Lifetime Data. The free-volume fraction h can be written as

$$h = \int_0^\infty n(v_f)\, v_f\, dv_f = \langle v_f \rangle N \qquad (3)$$

where $n(v_f)\, dv_f$ is the number density of holes whose volume is between v_f and $v_f + dv_f$, $N = \int_0^\infty n(v_f)\, dv_f$ is the number of holes per unit volume, and $\langle v_f \rangle$ is the average hole size. We have seen (section 3.2. and eq 1) that the o-Ps lifetime can be related to the average hole size, and our results suggest that I_3 is proportional to N. If this is true, then the product of I_3 and τ_3 should be proportional to h. In other words, we can define a factor h_{ps} as

$$h_{ps} = C I_3 v_f(\tau_3) \qquad (4)$$

where C is a constant relating the o-Ps intensity to the total number of holes and $v_f(\tau_3)$ is the average free volume, related to τ_3 by eq 1.

The validity of eq 4 can be tested by comparing the values of h_{ps} obtained from our positron data with the values of h deduced from experimental P–V–T data for PVAc using the statistical mechanical theory of Simha and Somcynsky. Let us determine the constant C by using the positron data at 59 °C. From Figures 1 and 2, $v_f(\tau_3) \times I_3$ has a value of 30.91 at this temperature. According to McKinney and Simha,[4] the theoretical free-volume fraction, h^{th}, for PVAc at temperature T and atmospheric pressure can be obtained by

$$h^{th}(T) = a_0 + a_1(T/9419\text{ K}) + a_2(T/9419\text{ K})^2 \qquad (5)$$

Values of the coefficients a_0, a_1, and a_2 have been derived[4] from P–V–T data for PVAc in both liquid and glass[4] and are listed in Table I(b) of ref 4, referring to $\tilde{P} = 0$. Moreover, the relations designated PF (partition function) have been employed for the glass in Figure 6. At 59 °C this equation gives an h^{th} of 0.095. It follows that, if eq 4 is valid, the constant C is $0.095/30.91 = (0.325\text{ nm}^3)^{-1}$. Thus, our equation for h^{ps} is

$$h^{ps} = (0.325\text{ nm}^3)^{-1} I_3 v_f(\tau_3) \qquad (6)$$

Figure 3 shows the comparison of the free-volume fraction, h^{ps}, obtained by eq 6 with the theoretical values obtained from eq 5. The theoretical curve was calculated by assuming that the polymer is in equilibrium above T_g

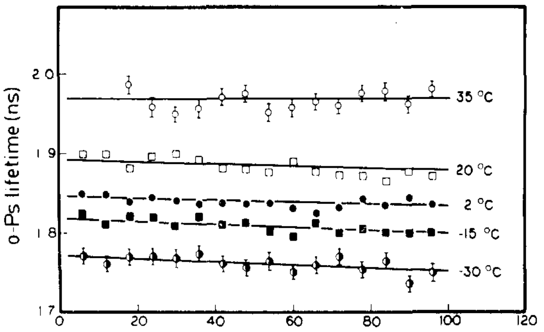

Figure 4. Ortho-positronium lifetime as a function of aging time for various temperatures. The error bars for the three intermediate temperatures are comparable to the size of the plotting symbol. The sample was annealed at 60 °C before the start of each run. The data accumulation time for each point was 6 h.

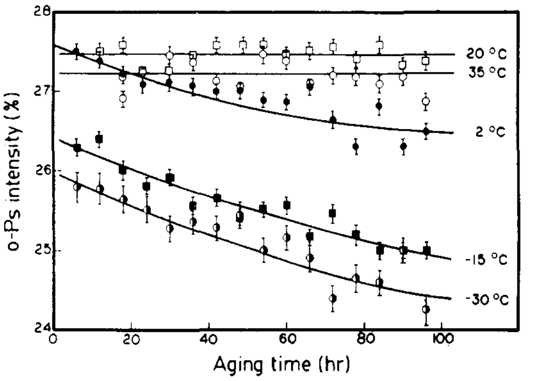

Figure 5. Ortho-positronium intensity versus aging time for various temperatures. The sample was annealed at 60 °C before the start of each run. The data accumulation time for each point was 6 h.

= 32 °C and is in the glassy state just after the quench below T_g. We can see in this figure that the experimental results obtained by eq 6 agree with the theory rather well in the entire temperature range. The systematic deviations of experimental points from the theoretical curve below T_g could be accounted for by considering the fact that $h^{\rm th}$ is derived from the instantaneous volume following a quench, whereas the smaller positron results, $h^{\rm ps}$, represent mean values obtained during the first hour after the quench and thus correspond effectively to a lower free-volume condition. This point requires further study.

We also note that the positron free-volume values lie systematically above theory at temperatures $T > 65$ °C. The origin of this effect is unclear, but one contributing factor could be that the relaxation times of smaller holes become shorter than the average o-Ps residence time and thus do not contribute to the measured free-volume function.

Since it was confirmed that eq 6 gives reasonable estimates of the free-volume fraction, we can use this equation to calculate the number of free-volume sites in PVAc near T_g. A typical value obtained for N is about 8.4×10^{20}/cm^3 or about 1 hole every 1.2 nm^3.

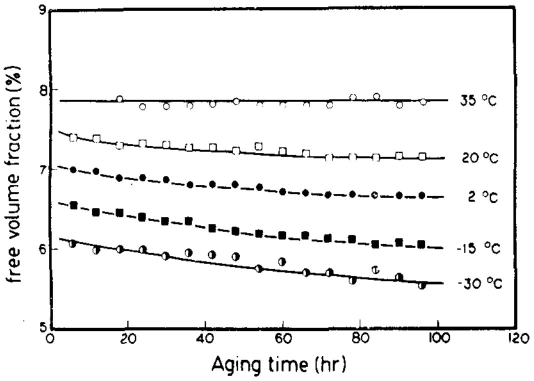

Figure 6. Free-volume fraction obtained from positron lifetime data versus aging time for various temperatures.

3.4. Study of Physical Aging by Positron Annihilation. Figures 4 and 5 show the change of τ_3 and I_3, respectively, during isothermal annealing after a quench to various temperatures below T_g. Although no clear variation of o-Ps intensity is seen at relatively high temperatures, a marked decrease is observed at low temperatures. Physical aging appears to have a greater effect on the intensity than on the lifetime of the o-Ps component. The same behavior has been reported for polystyrene[25] and in a more recent study of polycarbonate.[26] Thus, the consequences of physical aging appear to be qualitatively different from those of changing the temperature. As the quench temperature is changed, the holes change in size; as aging proceeds, the number of holes changes with little apparent change in hole size.

In order to confirm that this decrease in I_3 is really associated with physical aging, the following experiment was conducted. After the aging experiment at −15 °C in Figure 5, the sample was annealed at 60 °C and then quenched to −15 °C, and the positron lifetime spectrum was remeasured. It was found that the values of I_3 and τ_3 were reproducible within statistical error. This result is in agreement with the well-known fact that physical aging is a reversible process and suggests that the observed change in I_3 in Figure 5 is indeed a true physical aging process.

Figure 6 displays the plot of the free-volume fraction calculated by eq 6 against aging time. It should be noted that the errors contained in the data of Figure 6 are smaller than those in Figures 4 and 5. It appears that systematic errors in I_3 and τ_3 tend to cancel out in the calculation of h. From Figure 6 it is clearly seen that h decreases with aging time at all measured temperatures below T_g. Comparison of the results in Figures 4 and 5 suggests that the decrease of the free volume is mainly due to the disappearance of holes and not the shrinking of holes. Our results show that at −15 °C over an aging time of 96 h, the number density of holes decreases from 8.1×10^{20}/cm^3 to 7.7×10^{20}/cm^3 (−5%) while the hole size decreases from 0.0805 to 0.0786 nm^3 (−2.4%). The results suggest that the positron annihilation technique has a unique ability to separately identify contributions to variations in free volume from changes in the average hole size and in the number of holes.

Finally, it is pertinent to compare our free-volume results in Figure 6 to the mechanical properties of PVAc. As is well-known, the effect of aging on a viscoelastic response during isothermal annealing can be described to a major extent by considering only the shift of the time scale involved.[1] According to Lagasse et al.,[27] this shift factor for PVAc can be calculated from the free-volume fraction by the following Doolittle equation:

$$\ln a(t_a) = 10.5\left[\frac{1}{h(t_a)} - \frac{1}{h(0)}\right] \qquad (7)$$

Here $a(t_a)$ is defined as the time shift required for the response curve at aging time t_a to be superposed onto the curve of the reference state, and $h(t_a)$ and $h(0)$ are the free-volume fractions at aging time t_a and in the reference state, respectively. Figure 7 displays the change of the shift factor calculated by eq 7 with aging time. The reference state, where $\log a = 0$, was equilibrium at 35 °C. Our

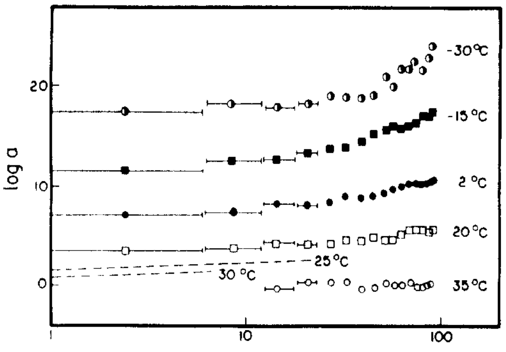

Figure 7. Shift factor $a(t_a)$ as a function of aging time t_a. Points are from positron data and eq 7. The horizontal bars show the data accumulation range for the preliminary points. Dashed lines are computed from volume data.[27] The reference state in both cases is equilibrium at 35 °C.

results reveal the strong temperature dependence of log $a(t_a)$ when plotted vs log t_a. Above T_g, log $a(t_a)$ is independent of aging time, but below T_g the dependence gets stronger with decreasing temperature until −15 °C, below which the aging effect is nearly constant. This is in agreement with the general character of physical aging.[1] For purposes of comparison we include calculated results for $a(t_a)$ based on volumetric data.[27] Clearly, the shift factors calculated for the positron free-volume parameter (eq 7) are of the correct order of magnitude. We note, however, that the nonlinearity in d log a/d log t_a seen in physical aging in deep quenches does not appear to be present in mechanical experiments,[1] although the latter are difficult to perform at temperatures far below T_g. This effect may be related to a limitation in the degree to which the Doolittle equation (eq 7) can describe the free-volume dependence of molecular relaxation times in amorphous polymers over wide ranges of free volume.[28]

4. Conclusions

The positron annihilation lifetime technique is a powerful tool to determine the free volume contained in a polymer matrix. Positron annihilation is also useful for separately identifying the contributions from changes in the hole size and the changes in the number of holes to the changes in the free-volume fraction *h*.

The *h* function has proven to be quite successful for analyzing results of experiments that measure only the total free volume. But in contrast to other techniques, the positron annihilation method yields two parameters, intensity and lifetime, which appear to be independent. The intensity varies with hole number, and the lifetime varies with hole size. Thus we have more information than is obtained by other methods. This information is in a form that demands further analysis before a direct comparison with theory can be made, but we have shown that it is possible to obtain a reasonable fit to known free-volume values from positron lifetime data.

Furthermore, our positron results show effects that could not be seen by simply measuring the total free volume or free-volume fraction. Although further work is needed to relate our results to a theoretical model, one feature of the data is clear: We have demonstrated that positron annihilation is capable of distinguishing between samples that are identical in composition and density.

This means that there are distinguishable points at which the sample has exactly the same free-volume fraction, for example, at −30 °C with minimal aging and at −15 °C after 4 days of aging. Polymer samples with different histories but having the same composition, volume, and temperature could in principle be produced; they would be indistinguishable by conventional measurements, but positron annihilation could readily distinguish between them. This conclusion is independent of the assumptions made in determining the actual value of the free volume in any state. Thus, it is clear that this technique has much to offer in polymer aging studies; it could conceivably lead to a way to predict the future of a sample as well as to interpret its past history.

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