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Positron Annihilation Lifetime Spectroscopy for Measuring Free Volume during Physical Aging of Polycarbonate

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ABSTRACT: Free volume relaxation of polycarbonate (PC) as a function of aging time was investigated by means of positron annihilation lifetime spectroscopy at three different temperatures below the PC glass transition temperature. A clear decrease of the intensity of orthopositronium (o-Ps) was observed, while the o-Ps lifetime remained substantially unchanged. This was attributed to a decrease in the number of cavities in the system. The process was successfully modeled according to the Struik model, which describes a relaxation time dependent on both the temperature and the distance from equilibrium.

1. Introduction

Amorphous glassy polymers pass through a nonequilibrium state when cooled from the rubbery phase as demonstrated many years ago by Simon[1] and Kovacs.[2,3] This state is characterized by excess thermodynamic quantities (volume, enthalpy, entropy, etc.) and appears to be a nonequilibrium state of matter. The subsequent evolution of the system toward the equilibrium is known as physical aging. This phenomenon is of great practical importance, since it leads to a change in the polymer properties (mechanical, dielectric, volumetric, etc.). From a thermodynamic point of view, the process is outlined in Figure 1, where a volume−temperature plot is shown for a typical amorphous polymer.

Because of reduced mobility, volume contraction upon cooling cannot follow the equilibrium line below the glass transition temperature (T_g), and the contraction of the polymer will be much less pronounced. Substantial structural changes take place after the cooling process from the melt and during the subsequent isothermal conditions, where the volume will slowly approach its equilibrium value. Many studies have been presented on the kinetics of this process. Some of them are based on the measurement of the rate of evolution of polymer thermodynamics properties like volume[2,4−15] and enthalpy[13,16−19] during the aging process, while others deal with the strong effect on the polymer mechanical properties like creep, stress relaxation, yield, and dynamic behavior.[20−28] Other attempts to clarify the aging process have been done through fluorescence spectroscopy,[29−31] electron spin resonance spectroscopy,[32] and various scattering techniques.[33−35] A review of all these methods is given by Hutchinson.[36]

From a microscopic point of view, volume reduction has to be attributed, at least partly, to a decrease in the free volume. Free volume plays a main role in the aging process, since the segmental mobility itself strongly depends on this property; namely, the mobility decreases with decreasing free volume. Based on this picture, several models have been presented in the literature.[21,37−39] All of them are based on the experimental evidence that aging is divided in two main processes: (i) a thermally activated process that is described by an Arrhenius equation; (ii) a process that is driven by the excess free volume present in the system, i.e., by the distance from thermodynamic equilibrium. This means that, at each temperature, the rate of free volume relaxation is determined by the segmental mobility, M, that is determined by the amount of free volume, v_f, in a closed-loop scheme:

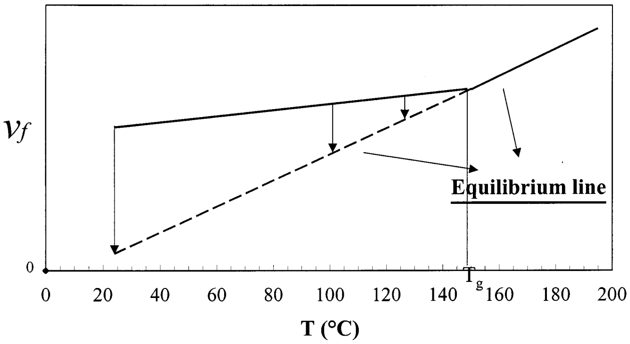

Figure 1. Schematic representation of the free volume changes of an amorphous polymer subjected to a fast cooling rate from the melt.

$$\begin{tikzcd} v_f \arrow[r] & M \arrow[r] & dv_f/dt \arrow[ll, bend left] \end{tikzcd} \tag{1}$$

This scheme implies that aging is a nonlinear process, based on a strong increase in the relaxation time upon free volume reduction. According to this scheme, the differential equation that describes the process of free volume relaxation is

$$\frac{\mathrm{d}v_\mathrm{f}}{\mathrm{d}t} = -\frac{v_\mathrm{f} - v_{\mathrm{f}\infty}}{\tau(T,v_\mathrm{f})} \tag{2}$$

where $\mathrm{d}v_\mathrm{f}/\mathrm{d}t$ is the aging rate, v_f is the actual free volume, $v_{\mathrm{f}\infty}$ is the equilibrium free volume, and τ is the actual relaxation time.

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Among the models present in the literature, an attempt to describe the relaxation time of this process was made by Struik,[21] who proposed a relaxation time, that is a function both of temperature, according to the Arrhenius equation, and of the excess free volume ($v_f - v_{f\infty}$):

$$\ln \tau = \ln \tau_0 + \frac{\Delta G}{kT} - \gamma(v_f - v_{f\infty}) \tag{3}$$

where ΔG is the activation energy, $\ln \tau_0$ is a preexponential factor, and γ is a constant.

It is clear from this picture that aging is a self-retarding process; i.e., it is characterized by an increasing relaxation time due to a decrease in the excess free volume. The highest value of the relaxation time is reached at the equilibrium (dashed line in Figure 1), when the term ($v_f - v_{f\infty}$) vanishes to zero. It is worth remarking that the dependence of the relaxation time on the excess free volume is exponential, and as the process goes on, the increase of the relaxation time will be dramatic. This is why, except for temperatures very close to the T_g, equilibrium is never reached, at least over a time scale of years.

The direct measurement of the free volume, a crucial parameter in the aging process, is probably the most attractive approach to study aging. This can be done using positron annihilation lifetime spectroscopy (PALS). This technique enables the detection of free volume "voids" in polymers at an atomic scale. Positrons, when injected in a polymer, are likely to form positronium (Ps) in the two states ortho- and parapositronium (o-Ps and p-Ps, respectively), the triplet and the singlet state of the bound positron−electron pair.[40] The p-Ps state has a very short lifetime (about 125 ps in a vacuum), and rapid annihilation occurs with the emission of two γ-rays at 511 keV. On the other hand, o-Ps is a long living system with a lifetime of about 142 ns in a vacuum, and annihilation occurs with the emission of three γ-rays. However, in condensed matter such as polymers, o-Ps is easily trapped in the potential well of free volume cavities. In this case annihilation occurs after localization of the positron with an electron of opposite spin on the wall of the cavity. This process, known as the pick-off reaction, strongly reduces the lifetime of o-Ps, τ_{o-Ps}, to values between 1 and 5 ns. Since τ_{o-Ps} is inversely proportional to the square of the overlap of the positron component of the Ps wave function with the cavity wall electron wave function, it is therefore correlated to the size of the cavity itself. A semiempirical equation has been derived to obtain to correlate τ_{o-Ps} with the radius of the cavity, R. This is obtained by using a spherical potential of radius R_0 with an electron layer of thickness $R - R_0 = 1.656$ Å:[41]

$$\tau_{o-Ps} = \frac{1}{2}\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \tag{4}$$

In this equation the lifetime is given in nanoseconds.

The probability of o-Ps formation is called the intensity o-Ps, I_{o-Ps}, and is proportional to the number of cavities in the system.[42] In this manner, the total free volume can be evaluated from the following equation:

$$v_f = A I_{o-Ps} \frac{4}{3}\pi R^3 \tag{5}$$

It has to be remarked that I_{o-Ps} can be influenced by prolonged positron irradiation. In the past, several studies concerning aging of PC and other amorphous polymers using PALS have been presented.[43−45] Unfortunately, all of them suffer from artifacts due to a false interpretation of the measured intensity drop of I_{o-Ps}. As a matter of fact, the relaxation times obtained in these aging studies are far too short to be attributed to molecular rearrangement, and instead they have to be attributed to the radiation (charging) effects, which reduce the probability of o-Ps formation. Therefore, while the free volume remains substantially unchanged the measured intensity decreases due to charging after prolonged irradiation of the sample. The main reason for this is that a single sample was used for the entire aging study, which ultimately leads to a modification of the structure of the sample in terms of the internal electric field and the free radical concentration. These radiation effects, which interfere with the probability of o-Ps formation, have been extensively studied over the past 10 years.[46−51]

In the present study, the free volume reduction of PC is investigated by means of PALS at three different temperatures. To avoid any artifact due to the buildup of charge, the samples are used only for one measurement, thereby avoiding any reduction in I_{o-Ps} due to prolonged exposure to the source of positrons. The number of counts collected for each sample was 2×10^6, which is low enough to avoid any significant effect of charging.[51] An attempt to model PALS data according to the Struik model of free volume relaxation is carried out. To achieve this aim, the initial relaxation time, at various temperatures, is evaluated using PALS experiments. The equilibrium relaxation times are also evaluated through dynamic−mechanical measurements carried out in the proximity of T_g and extrapolated to lower temperatures. By comparing these results, using eq 3, we can obtain information on the initial value of the excess free volume vs temperature.

2. Experimental Section

2.1. Materials and Sample Preparation. PC from General Electric (Lexan 161) was used for all the experiments. The polymer was first dried at about 120 °C under vacuum and compression-molded to obtain sheets of 4 mm thickness. Specimens of about 1 cm^2 area were obtained from the sheet. Before starting aging experiment, PC samples were thermally rejuvenated at about 170 °C and cooled in ice. A large number of samples were subjected to aging at three different temperatures: 25, 100, and 128 °C. These were used for the PALS experiments (performed at room temperature) after different aging times.

2.2. PALS Experiments. PALS measurements were performed at room temperature on all the above-mentioned samples, by exposing them to the radioactive ^{22}NaCl with an activity of 10 μC. A fast−fast coincidence circuit of the PALS spectrometer at the IRI-TU Delft, with a lifetime resolution of 240 ps as monitored by using a ^{60}Co source, was used to record all PALS spectra. The counting rate was about 70 cps. Each spectrum was collected to a fixed total count of 2×10^6, which is high enough to get a good analysis but at the same time low enough to avoid any substantial radiation effects. The spectrum is analyzed using the program POSITRONFIT, which describes the spectrum as a convolution of the instrument resolution function and a finite number of negative exponentials plus the background as described by the following equation:[52]

$$y(t) = R(t) \otimes (N\sum_{i=1}^{n} I_i\lambda_i \exp(-\lambda_i t) + B) \tag{6}$$

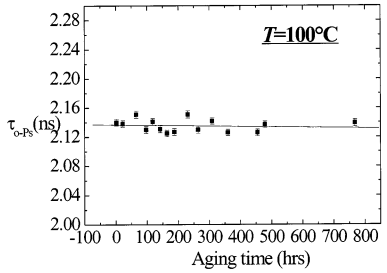

Figure 2. Relaxation of τ_{o-Ps} for samples aged at 100 °C.

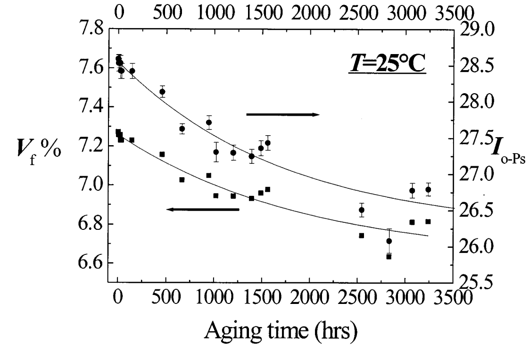

Figure 3. Decreasing intensity for the o-Ps pick-off annihilation I_{o-Ps} and the free volume relaxation for samples aged at 25 °C.

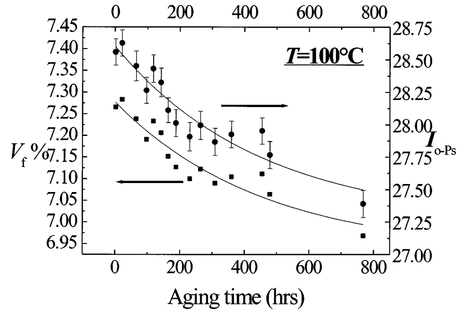

Figure 4. As for Figure 3, but at 100 °C.

Here $R(t)$ is the resolution function of the system, λ_i is the inverse of the annihilation time (annihilation rate), and B is the background signal. All spectra were resolved in three lifetime components: a short one of 125 ps related to p-Ps annihilation, an intermediate one of 400 ps related to free positron annihilation, and a long one component (τ_{o-Ps}) related to o-Ps annihilation.

2.3. Dynamic−Mechanical Measurements. Dynamic−mechanical thermal analysis was performed using a Dynamic analyzer RDA II from Rheometrics, in the frequency−temperature sweep mode. In particular, a frequency sweep between 0.1 and 100 rad/s was done between 130 and 160 °C at temperature intervals of 2.5 °C. Tests were performed on rectangular water-free PC specimens in torsion mode with a strain varying from 0.02 to 1.6% depending on the temperature.

3. Results and Discussion

The evolution of I_{o-Ps} with time is shown in Figures 3−5 for all the investigated temperatures. While the o-Ps lifetime, τ_{o-Ps}, shown in Figure 2, does not present any variation with aging time, I_{o-Ps} clearly decays with time at a different rate for each temperature. According to these results, no change of the cavity size can be observed, while the concentration of the free volume cavities clearly decreases with time.

From these results it appears that rather well-defined free volume sites are present in PC during the aging process. This raises several questions concerning the nature of the relaxation mechanism. It is possible that the distribution of the free volume changes during the aging process, either becoming more narrow or broadening, or it may even split into a bimodal distribution, while its average mainly remains constant. However, further investigation is needed to elucidate the details of the aging process.

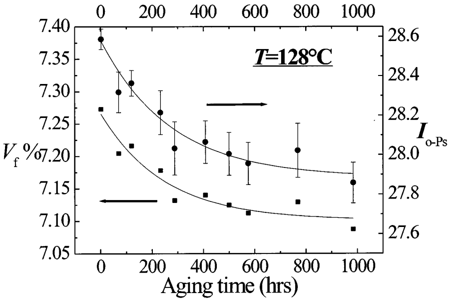

Figure 5. As for Figure 3, but at 128 °C.

Table 1. Zero-Time Relaxation Times As Obtained by PALS

temperature (°C)	25	100	128
τ (s)	5.70×10^7	7.39×10^6	4.61×10^6

From the evolution of I_{o-Ps} decrease, free volume relaxation was derived from eq 5, where $A = 0.0023$ was taken from literature data,[53] and the radius was calculated from eq 4. As the radius is practically constant during the course of aging, the free volume relaxation strongly resembles the I_{o-Ps} decay, as shown in Figures 3−5 (left scale).

Free volume relaxation data as obtained by PALS were processed to obtain the relaxation times at the beginning of the aging process, i.e., when relaxation times are as short as possible. The initial relaxation time is in fact, according to the Struik model, strongly reduced by the term $v_f - v_{f\infty}$, as it has the largest value at the beginning of the aging process, when the free volume has the largest value for the temperature under examination. The calculated values of the relaxation times are summarized in Table 1.

From these results we observe that the increase of the relaxation time by reducing the temperature is rather limited. From a qualitative point of view, this means that the effect of a temperature decrease on the initial relaxation time is strongly compensated by the increasing excess free volume in the system.

To quantitatively analyze the agreement of the Struik model with PALS data, eq 3 was used to determine the term $\gamma(v_f - v_{f\infty})$ at the three investigated temperatures. According to Figure 1, $\gamma(v_f - v_{f\infty})$ should decrease linearly with decreasing the temperature distance from equilibrium. However, to evaluate $\gamma(v_f - v_{f\infty})$ from the PALS data, the constants $\Delta G/k$ and $\ln \tau_0$ need to be calculated. The determination of the relaxation times at the thermodynamic equilibrium allows the calculation of these constants from the Struik equation, which, in this case, reduces to an Arrhenius equation, since the term $v_f - v_{f\infty}$ vanishes to zero. For this purpose, dynamic−mechanical measurements were carried out in proximity of the T_g, where equilibrium relaxation times are small enough to be evaluated over reasonably short observation times. Applying an oscillatory strain a stress $\sigma = \epsilon_0(G' \sin(\omega t) + G'' \sin(\omega t))$ is measured, where the maximum of the out-of-phase relaxation

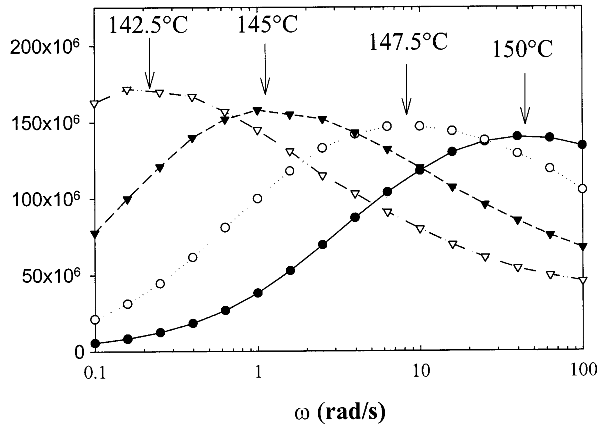

Figure 6. Variation of the T_g value with frequency as obtained from the localization of the G'' peak.

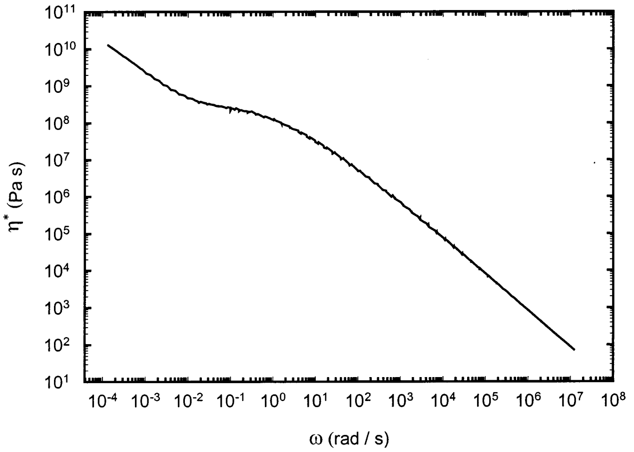

Figure 7. Viscosity master curve for PC as constructed from the DMTA results.

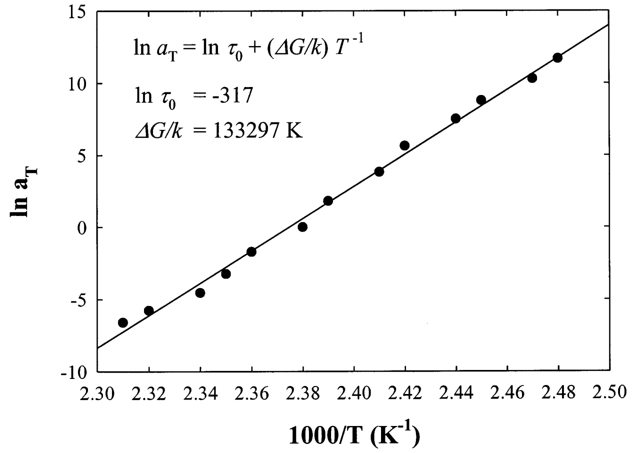

Figure 8. Arrhenius law variation of relaxation times with temperature for two different activation energies compared with the relaxation time at the beginning of the aging process as probed by PALS.

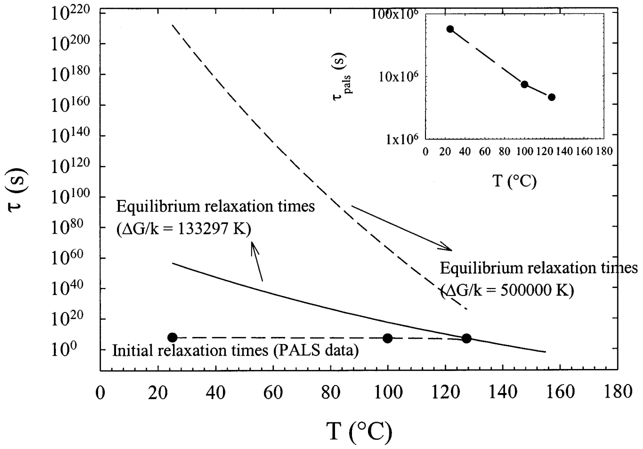

Figure 9. Comparison between equilibrium relaxation times evaluated by extrapolation of dynamic–mechanical measurements ($\Delta G/k = 133297K$), and using a larger sub-T_g activation energy ($\Delta G/k = 500000K$), with the initial relaxation times as probed by PALS.

modulus G'' corresponds to the glass transition at the angular frequency ω.

The first result of the dynamic–mechanical characterization was the determination of the T_g at various angular frequencies. This is shown in Figure 6, where the G'' peak is shown for different temperatures.

We observe that the T_g shifts by about 3 °C per decade, with a value of 147.5 °C for a frequency of about 6 rad/s that correspond to relaxation times of about 1 s. To have an accurate determination of the equilibrium relaxation times of PC, using the time–temperature superposition principle,[54] the viscosity master curve was constructed in Figure 7, with $T_g = 147.5$ °C as reference temperature. From this plot the shift factor a_T was obtained. Since the complex viscosity is proportional to the relaxation time, from the slope and the intercept of $\ln(\eta^*_T/\eta^*_{T_g}) = \ln a_T = \ln \tau_T$ $(\tau_{T_g} = 1)$ vs $1/T$, respectively $\Delta G/k$ and $\ln \tau_0$ were obtained, as shown in Figure 8. The resulting values of $\Delta G/k$ and $\ln \tau_0$ are $133297K$ and -317.

The knowledge of these two constants allowed the prediction of the equilibrium relaxation times at different temperatures. This is shown in Figure 9, where the equilibrium relaxation times (solid line) are compared with the initial relaxation times as probed by PALS. The striking feature in this figure is the huge difference between the initial relaxation times and the equilibrium Arrhenius values. This is true at lower temperatures, where the contribution of the excess free volume is more pronounced. These results explain why equilibrium is never reached except for temperatures close to T_g. Self-retardation, as described by Struik, allows a relatively fast relaxation at the beginning of the process, but as $v_f - v_{f\infty}$ decreases in the course of aging, a huge increase of the relaxation time occurs. For example, according to equilibrium relaxation time of PC at room temperature, total free volume recovery will take place in 1.1×10^{49} years, i.e., substantially longer than the lifetime of the universe.

From a quantitative point of view, the effect of the excess free volume on the reduction of the relaxation times is shown in Figure 10, where $\gamma(v_f - v_{f\infty})$, calculated from eq 3 where τ is the PALS value, is plotted vs temperature (lower plot). This plot shows a linear relation between the excess free volume and the temperature difference with T_g, which means that the Struik model appears to provide a good way to describe the observed influence of temperature on the physical aging dynamics.

However, if we examine the details of the above figure, there is still a discrepancy. The drawn line (lower one) obtained plotting $\gamma(v_f - v_{f\infty})$ with the temperature does not intersect the zero excess free volume axes at the T_g, while the excess free volume should be zero at that temperature (see Figure 1). The weak point of the

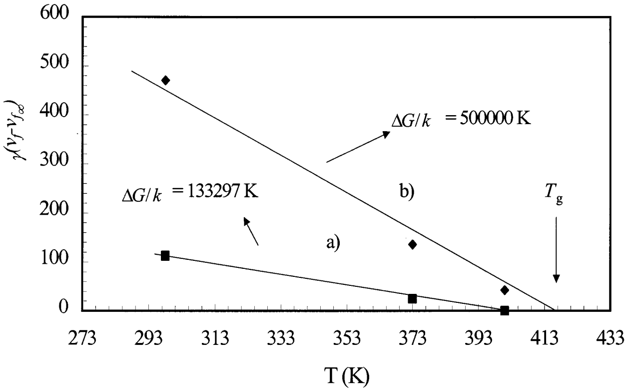

Figure 10. The term $\gamma(v_f - v_{f\infty})$ at the three investigated temperatures is plotted vs temperature for two different values of the activation energy: (a) the one obtained from dynamic–mechanical measurements around T_g; (b) the one that fits the requirement of $\gamma(v_f - v_{f\infty}) = 0$ at T_g.

treatment described above is that $\gamma(v_f - v_{f\infty})$ was evaluated employing the activation energy as obtained from dynamic–mechanical measurements around T_g. In reality, the activation energy is temperature-dependent and was successfully modeled above T_g in the past by Williams–Landel–Ferry[54] and by the Vogel–Tamman–Fulcher[55] equations, which indicate a decreasing activation energy with increasing temperature. However, at temperatures far below T_g the two models will fail to predict the real behavior of amorphous materials. On the basis of this, if we employ a value of the activation energy about 3 times higher ($\Delta G/k = 500000K$), the straight line obtained plotting $\gamma(v_f - v_{f\infty})$ vs temperature intersects the zero excess free volume axes at the T_g, as clearly shown in Figure 10 (upper curve). This means that this higher value of the activation energy is more reasonable to use for modeling of phenomena far below T_g.

Finally, it is worth noticing that in this study we have employed the Struik model for reasons of simplicity; however, a quantitatively more accurate treatment can be done employing more complicated models. For example, if the Moynihan–Tool–Narayanaswamy model[37] is used, a similar picture to the one shown in Figure 10 is obtained, but with somewhat better agreement with the data.

On the basis of the new value of the equilibrium relaxation time employed for the deeply glassy state, the relaxation times plotted in Figure 9 are recalculated (dashed line). The values of the relaxation time in this case are even larger than with the previous activation energy, but from a practical point, we can conclude that in either case a total volume recovery cannot take place in a reasonable time scale.

4. Conclusions

Physical aging of PC was studied by means of PALS, which allows the direct determination of the free volume of the system. Three different temperatures below T_g were chosen to follow the kinetics of free volume recovery. The striking feature of the PALS data was that the intensity of o-Ps decreases in the course of aging, while o-Ps lifetime as measured at room temperature on all samples remains constant. An attempt to model the free volume recovery through the Struik model was performed. As expected, an inverse proportionality between the excess free volume and the temperature was found, and the excess free volume drops to zero at the T_g, if a reasonable value of the activation energy is chosen. Further investigation on the nature of the relaxation mechanism is needed in order to clarify the underlying physical phenomena governing the relaxation during physical aging.

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