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## The Aging Process in Polymers, Positron Annihilation Lifetime Studies

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### Final Technical Report

Our research effort on this project investigated the capability of positron annihilation lifetime (PAL) spectroscopy to characterize quantitatively the molecular-level structural disorder in the amorphous phase of polymer materials and to enhance our understanding of the relationships between molecular disorder and the functional properties of such materials. A particular interest was to characterize the change in free volume during isothermal annealing, which is the origin of the well-known physical aging effect in mechanical properties of polymeric glasses such as embrittlement. Thermalised positrons, following injection into a polymeric material from a radioactive source such as  $\text{Na}^{22}$ , are annihilated in one of three mechanisms<sup>1</sup>: (a) formation and self-annihilation of parapositronium (pPs), with probability  $I_1$  and lifetime  $\tau_1$ ; annihilation as free positrons ( $e^+$ ), with probability  $I_2$  and lifetime  $\tau_2$ ; and formation and 'pick-off' annihilation of oPs, with probability  $I_3$  and lifetime  $\tau_3$ . Theoretical arguments,<sup>2,3</sup> and much circumstantial evidence from several laboratories<sup>4-8</sup> has shown that there is a relationship between the oPs annihilation parameters,  $I_3$  and  $\tau_3$ , and the free volume characteristics of amorphous polymers. Specifically,  $I_3$ , which is a measure of the probability of oPs formation, appears to be proportional to the number of free volume holes, and  $\tau_3$  is related to the hole radius,  $R$ , by an equation of the form<sup>2,3</sup>:

$$\tau_3 = 0.5[1 - R/R_0 + (\sin 2\pi(R/R_0)/2\pi)]^{-1}$$

where  $R_0$  is an empirical parameter. Our first task was to make quantitative comparisons between free volume parameters extracted from oPs annihilation lifetime spectra and an independent estimate of free volume. In our investigations<sup>9-20</sup>, we used a free volume function,  $h(P,T)$ , extracted from PVT data for the polymer chosen for study, using a statistical mechanical model due to Simha and Somcynski<sup>21</sup>. With this approach, we were able to demonstrate excellent quantitative agreement between a fractional free volume,  $f$ , estimated from oPs data via the equation:

$$f = K I_3 (4/3\pi R^3),$$

where  $K$  is an empirical constant, and the theoretical  $h(P,T)$  function in the equilibrium melt for several pure polymers<sup>9-13</sup>, including polyvinylacetate<sup>9</sup>, the polycarbonate of bisphenol A<sup>10-12</sup>, and polystyrene<sup>13</sup>. Most interestingly, significant deviations were found in the non-equilibrium glassy state, which were traced to deficiencies in the theory<sup>13</sup>. Thus, an empirical free volume function, numerically consistent with the statistical  $h$ -function in the melt, was found to be quantitatively consistent with the oPs  $f$ -values in both melt and glass<sup>13-15</sup>. We were thus the first to definitively establish a quantitative correlation between a well-defined theoretical free volume function and o-PS annihilation lifetime parameters  $I_3$  and  $\tau_3$  in both melt and glass.

For the above polymers, as well as certain well-specified miscible polymer blends, it was further established that a correlation exists between the oPs free volume and bulk properties, such as physical aging of stress relaxation<sup>16</sup>, and the composition dependence of the glass transition temperature<sup>17</sup>. The latter study<sup>17</sup> is particularly interesting because, using oPs annihilation parameters, we were able to validate a well-known theoretical argument that the composition dependence of the glass transition temperature of an athermal miscible blend, for which the volume change on mixing is also close to zero, can be predicted based on the free volume characteristics of the pure components. Changes in free volume on cross-linking elastomers were investigated and universal scaling parameters for free volume parameters at the glass transition temperature were described<sup>18</sup>. The temperature-dependence of free volume was measured in two commercially-important, wholly-aromatic copolyesters of hydroxybenzoic acid and hydroxynaphthoic acid, and their blends<sup>19</sup>. At room temperature,  $I_3$  and  $\tau_3$  were exceedingly small compared to typical amorphous flexible polymers, but each showed a very large increase with temperature up to the melting point. The onset of the increase in oPs free volume was observed at a temperature in the solid state where there is a transition in mechanical properties. The unusually small values of  $\tau_3$  may reflect the fact that the free volume holes in these fibrous polymers are prolate rather than spherical in shape, since theory suggests that the annihilation lifetime of prolate holes is determined by the shorter dimension.

We were the first to carry out an *in situ* PAL study of free volume changes in a glassy polymer (polycarbonate) under well-specified tensile deformation, using a custom-built miniature load cell<sup>20</sup>. The oPs free volume increased with applied strain in a fashion numerically consistent with that calculated from the above-mentioned empirical free volume function of Simha-Somcynsky<sup>21</sup> based on the known value of the Poissons ratio for polycarbonate. This gives us confidence that the PAL method can be applied to probe changes in the structural disorder of the amorphous component in polymer composites and stiff-chain polymers induced by mechanical deformation or other physical perturbations.

There is great interest in the possibility of using PAL to gain information about the distribution of free volume hole sizes in polymers through analysis of the oPs lifetime distribution. Indeed, a number of reports of such measurements have been published<sup>22,23</sup>. Several concerns exist with regard to these studies. First, we have proposed theoretical

arguments<sup>24</sup> that, because of the possibility of tunneling of oPs between holes, the oPs lifetime distribution may not reflect a complete picture of the hole distribution. Subsequent theoretical analysis<sup>25</sup>, however, suggests that the tunneling effect may be negligible. Even if this is true, it is not clear that the measured hole size distributions are accurate. For example, the published distributions invariably are based on fits where the quantum mechanically-required ratio between pPs and oPs annihilation probabilities, viz.  $I_1/I_3 = 1/3$ , is not satisfied. Our own simulations<sup>11</sup> of positron annihilation spectra containing distributions of  $\tau_3$  values indicate this discrepancy arises because some of the short-lived oPs intensity is being counted as pPs or  $e^+$  in the fitted spectra. Moreover, the same simulations indicate that, if the time resolution function is as large as 260 psec, as typical for most of these studies, there will be significant errors in the mean oPS lifetimes and intensities even for spectra with very low noise levels. Moreover, in most of the cited studies of oPs distributions, it is not made clear that the associated spectral fits are statistically better than fits to a single oPs lifetime. If this is not so, then the obtained oPs lifetime distributions do not contain meaningful information. From our modelling studies<sup>11</sup>, analyses of oPs lifetime distributions are questionable unless one uses a time resolution function with a width below 200 psec, and the above-discussed fitting criteria are met. Note that these considerations do not preclude the application of mean oPs lifetimes to characterise average free volumes. Our simulations demonstrate<sup>11</sup> that the loss of short-time oPs information does not introduce significant errors into the mean oPs lifetimes,  $\langle \tau_3 \rangle$ , which correspond to an intensity-weighted average,  $\langle \tau_3 \rangle = \sum I_{3i} \tau_{3i} / \sum I_{3i}$ . Finally, to obtain adequate signal to noise ratio for optimal analysis of PAL spectra, it is necessary to record an exceptionally large number of annihilation events which increases the possibility of radiation damage to the specimen<sup>26</sup>. Such damage results in anomalous behavior of the oPs intensities, but does not affect the mean lifetime measured<sup>26,27</sup>. It is not clear if such long term radiation damage leads to artifacts in attempts to resolve intensity-based distributions of oPs lifetimes.

In conclusion, we explored the use of oPs lifetime measurements to investigate changes in free volume during physical aging of polymeric materials. Early reports of decreases in the number of free volume holes during isothermal annealing of polystyrene<sup>28</sup> and polyvinylacetate<sup>9</sup>, based on an observed decrease in oPS intensity, proved to be due to radiation damage rather than a change in free volume. Subsequently, we carried out measurements on glassy polycarbonate<sup>10</sup> in which the polymer specimen was separated from the positron source during annealing and found a decrease in both oPS lifetime and intensity, which we assign to a true measure of the decrease in free volume associated with the aging process.

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