Doppler broadening of positron annihilation radiation as a probe for the anisotropy of free-volume-holes in polymers

C. A. Palacio¹,², N. Djourelov¹,³, J. Kuriplach⁴, C. Dauwe¹, N. Laforest⁵, and D. Segers¹

¹ Dept. Subatomic and Radiation Physics, Ghent University, Proeftuinstraat 86, 9000 Gent, Belgium
² Institute of Physics, University of Antioquia, A. A. 1226, Medellín, Colombia
³ Institute of Nuclear Research and Nuclear Energy, 72 Tzarigradsko Shoosse, 1784 Sofia, Bulgaria
⁴ Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V. Holešovičkách 2, 180 00 Prague, Czech Republic
⁵ LMOPS, Université de Savoie, 73376 Le Bourget du Lac Cedex, France

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Doppler broadening of annihilation radiation (DBAR) measurements have been performed in uniaxially hot-drawn poly(methylmethacrylate) (PMMA) samples. The DBAR spectra were deconvoluted into three Gaussians. The full width at half-maximum of the narrow component which is due to para-Positronium (p-Ps) self-annihilation is under discussion. An anisotropy of the free volume holes (FVHs) has been detected by measuring the deformed samples at the stretching and transverse directions. The sample deformed at 280% was also measured as a function of the orientation angle (0°–90°) with respect to the stretching direction. The momentum distribution of p-Ps, which is considered as a structureless particle confined in FVH of ellipsoidal or cuboid shape, was calculated as a function of the potential well size and depth and compared with experiment.

1 Introduction

Positron annihilation lifetime spectroscopy (PALS) has been proven to be a very sensitive technique to study free-volume holes (FVHs) in polymers [1, 2]. When a positron (e⁺) enters condensed matter, after thermalization and diffusion, it eventually annihilates with an electron (e⁻) of the medium, mostly by two 511 keV gamma quanta. Before the annihilation, the e⁺ exists as a “free” positron (it annihilates directly with an e⁻ with a lifetime (τ) of ~ 0.3-0.5 ns), or forms a positronium (Ps). In condensed matter, the ortho-positronium (o-Ps) lifetime (τₒ–Ps), which is 142 ns in vacuum, is quenched to some nanoseconds as e⁺ of the o-Ps atom annihilates with e⁻ from the surrounding molecules (so-called pick-off process). There is a well-known correlation between the radius (R) of spherical FVH and τₒ–Ps derived from the Tao-Eldrup model [3].

The second most frequently used technique to detect open volume defects and to study their properties is the Doppler broadening of annihilation radiation (DBAR). In DBAR the interest is focussed on the 511 keV line, which is Doppler-broadened due to the momentum component $P_z$ of the $e^+ - e^-$ pair, where z is the detection direction. The peak is a superposition of a narrow (approximately a Gaussian) component due to the self-annihilation of para-positronium (p-Ps) and broader Gaussian-like distributions due to free $e^+$ and o-Ps pick-off annihilation [2, 3]. The narrow component reflects the localization momentum of the p-Ps inside FVH and according to the Heisenberg uncertainty principle, it is sensitive to the FVH size.

In a simple quantum-mechanical model, it is assumed that the Ps is confined in a spherically shaped potential well of infinite depth and radius R with a spatial overlap of the Ps wave function with molecules within a layer $\delta R$ of the potential wall. The relationship between $\delta R$ (the full width at half-maximum

* Corresponding author: e-mail: carlos.palacio@ugent.be, Phone: +32 9 264 65 66, Fax: +32 9 264 66 97

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performed at 128 °T

Triple is quenched from temperatures above the glass transition temperature, varying from 7.77 to 8.67 keV with intensity from 5.82 to 6.56 % is attributed to the momentum of the core

\[ R = 16.6/\theta - \delta R, \]

where \( \theta \) is in mrad (1keV = 3.913 mrad) and \( \delta R = 1.656 \) Å is an empirical parameter.

In glassy polymers, numerous temperature-dependent structural transitions can happen. When the sample is quenched from temperatures above the glass transition temperature, \( T_g \), a non-equilibrium structure is introduced into the glassy state, where the physical properties change over time (aging). For many years, several studies [5, 6] have been carried out on hot-drawn (i.e. stretched above \( T_g \)) polymers. When these hot-drawn polymers are quenched to temperatures below \( T_g \), their physical properties show anisotropy. Previous experiments performed with angular correlation of positron-annihilation radiation (ACAR) have shown anisotropy in FVHs of polymers [7–9], but until now, there are no measurements of anisotropy by means of the conventional DBAR technique.

For PMMA, no information about the sample deforming and quenching conditions was found in the literature. In the present study, PMMA samples were hot-drawn (\( T_g = 119.8 \) °C) to different elongations, \( \epsilon \), and were then quenched with liquid nitrogen vapors to freeze the stretched microstructure. If in a non-deformed sample the FVH is considered to have a spherical shape, a change (in the FVH shape) from an isotropic to an anisotropic structure is expected subsequently to the stretching along the tensile direction.

DBAR experiments at room temperature (RT) were performed in the machine (stretch) (MD) (0° with respect to the Ge detector) and transverse (TD) (90°) directions. The sample deformed to \( \epsilon = 280\% \) was also measured as a function of the orientation angle (0–90°).

### 2 Experimental

PMMA samples 3.0-mm-thick were supplied by Vink NV, \( T_g \sim 119.8 \) °C as determined by differential scanning calorimetry. The samples were cut in a bone shape and were heated at 128 °C for ~40 min to erase any previous thermal and mechanical history. Uniaxial deformations were also performed at 128 °C in a tensile machine, with a crosshead speed of 7.7 cm s \(^{-1} \) to elongations of 150, 185, 200, 220, and 280%. The deformation extent was obtained according to the formula \( \epsilon = (l - l_0)/l_0 \); where \( l_0 \) and \( l \) were the original and obtained length of the line-marked region in the specimen. Immediately after stretching, the samples were quenched below \( T_g \) with a blast of liquid nitrogen vapors.

The DBAR measurements were carried out with a HPGe detector with resolution of 1.28 keV on the 514 keV line of \(^{85}\)Sr. The used source was \(^{22}\)NaCl with activity of 12.9 µCi in 7-µm-thick Kapton envelope. The sample-source sandwich was mounted in the middle of a rotatable plate so that the measurements for the MD and TD could be performed by just rotating the plate 90°, and the source could therefore always be at the same distance with respect to the Ge detector. In addition, two DBAR measurements were performed for the sample 280% deformed at orientation angle 30° and 60° respect to the MD-detector axis. Each data point represents the analysis of 10 spectra recorded at every 1 hour with statistics in the peak of ~1.9 ×10 \(^6\) counts. The photo peak was decomposed into three Gaussians. The broadest one, with a FWHM varying from 7.77 to 8.67 keV with intensity from 5.82 to 6.56 % is attributed to the momentum of the core \( e^- \) annihilating with free \( e^+ \). The intermediate one, with a FWHM of 2.41 to 2.45 keV with intensity of ~ 83.99 to 84.55 %, is assigned to a superposition of wider distributions coming from the annihilation of free \( e^+ \) and o-Ps pick-off with \( e^- \) of the shallow orbitals. The narrow one, with a FWHM of ~ 1.11 to 1.14 keV with intensity of ~ 9.50 to 9.87 %, reflects the self-annihilation of p-Ps localized in FVHs. All spectra were initially fitted without constraints, but because the intensity values for the narrow Gaussian found by the fitting program did not vary extensively, and because they were very close to the theoretical one-third of the o-Ps intensities (~ 28.5 to 29.6 in PALS experiments), in the last analysis these values were fixed at one-third of the intensity values of o-Ps obtained by PALS.

### 3 Simulations of p-Ps DBAR response

Ps trapped in potential wells (PWs) of various shapes was studied theoretically. In the present work we consider the spherical/ellipsoidal and cubic/cuboid shapes of
PWs/FVs as limiting cases. Ps is considered as a structureless particle with a mass of $2m_e$, $m_e$ being the electron mass. From the quantum-mechanical point of view, this leads to the solution of a stationary Schrödinger equation in three dimensions. We solve the equation numerically and employ a conjugate gradient method \cite{10} as implemented in \cite{11}. The ground Ps state ($\psi$) is then, by means of the Fourier transform, converted into the momentum distribution ($\varrho$) using the formula

$$\varrho(p) = \left| \int \psi(r) \exp(-i \mathbf{p} \cdot \mathbf{r}) \, dr \right|^2,$$

(2)

where $p$ and $r$ are Ps momentum and position coordinate, respectively. The one dimensional momentum profile (MP) corresponding to measured DBAR profile is calculated as follows:

$$\varrho(p_z) = \int_{p_x} \int_{p_y} \varrho(p) \, dp_x \, dp_y$$

(3)

assuming that the measuring direction coincides with the $p_z$ axis. The FWHM of the calculated MP (i.e. $\theta_{1/2}$ in Eq. (1)) is finally determined.

The depth ($V_0$) of the Ps potential well is an important parameter for the calculations. There are only rough considerations presented in the literature (see e.g. \cite{12}) and $V_0$ is supposed to be in the range of several eV. We have found that $V_0$ ranges from 4.5 to 5.5 eV as this assumption leads to physically plausible results concerning the PW size and p-Ps energy. Figure 1 presents calculated $\theta_{1/2}$ for spherical and cubic PWs using the above specified values of $V_0$. The potential well size (i.e. diameter for spherical PWs and edge length for cubic PWs) ranges from about 1.5 to 10 Å. The character of the dependence of $\theta_{1/2}$ vs the size is very similar for both cases. The curves corresponding to the cubic PWs are somewhat shifted to lower sizes with respect to the spherical PWs. The solutions for $\theta_{1/2}$ gives two PW sizes. The smaller one is physically unacceptable because it results in a too high p-Ps energy.

In the next section, the fitted dependencies shown in Fig. 1 are used to determine the FVH size and anisotropy in PMMA. Figure 1 also shows the curve corresponding to Eq. (1) that is based on the assumption of the infinite spherical potential well \cite{4}. One can see that this curve agrees in the slope with those calculated for finite potential wells in the case of larger sizes. Otherwise the agreement is poor (except partly for cubic PWs). Further simulation results are presented in the next section for the purpose of the interpretation of experimental DBAR data.

4 Results and discussion

The average FVH size in PMMA was determined by two methods. The first one, by using Eq. (1), where the lowest and highest experimental values obtained from the FWHM ($\theta_{1/2}$) of the narrow Gaussians in the MD and TD for the deformed PPMA (1.11 and 1.14 keV respectively) results in FVH sizes ranging between \sim{} 4.09 and 4.31 Å, which agrees with the values found in \cite{1}. The second one, by means of the Fig. 1, where for example for the PW depth of 5.0 eV and for the same $\theta_{1/2}$ (1.1 and 1.14 keV), the resulting FVH sizes in the cubic PW are 3.94 Å for TD and 4.18 Å for MD while for the spherical PW it results in 5.08 Å for TD and 5.37 Å for MD (as indicated by vertical lines). Comparing the results obtained by both methods, it is clear that in the cubic PW, the size is about the same as the one obtained using the Eq. (1), whereas in the spherical PW the difference is bigger. This indicates that the shape of the hole (PW) is an important factor that influences the interpretation of the experimental results and that Eq. (1) can be used for rough estimates only.

Figure 2 displays the difference between $\theta_{1/2}$ of the narrow Gaussians for the TD and MD at different deformations as determined by means of DBAR. It becomes obvious that the difference increases with the elongation, which indicates a clear increasing of the anisotropy in the FVH shape. The above estimated size ranges can be also explained in terms of the anisotropy of FVs in PMMA between the TD and MD after the deformation. The detected FVH size anisotropies amount to 5–6 % in all cases. In principle, the anisotropy can be determined also by finding the PW sizes (considering ellipsoidal or cubic PWs).
Fig. 1 Calculated FWHMs of momentum profiles for spherical and cubic potential wells (size being the diameter for spherical PWs and edge length for cubic PWs). To compare, the curve plotted using Eq. (1) is also shown. The vertical lines are used to determine the FVH sizes in PMMA for TD and MD.

Fig. 2 The difference between the FWHMs of the narrow Gaussians for the transverse and machine directions as determined by means of DBAR.

Fig. 3 FWHM of the narrow Gaussian (p-Ps) obtained for the sample deformed 280% as a function of the orientation angle (0°–90°, 0° corresponding to the MD-detector axis). The data were fitted with an ellipsoidal curve (two lines were drawn at the maximum value found for the narrow Gaussian in MD).

to match simultaneously both experimental $\theta_{1/2}$ values for TD and MD. When such a procedure is used, the resulting anisotropy is about the same as determined above, which is due to the fact that the overall anisotropy of FVHs due to deformation is rather small in our case. Finally, the values of FWHM of the narrow Gaussian (p-Ps) obtained for the sample deformed at 280% and measured as a function of the orientation angle are shown in Fig. 3. This figure clearly confirms the anisotropy displayed in Fig. 2.

5 Conclusion The conventional DBAR technique has been shown to be a useful, sensitive, and fast technique for characterizing the free-volume holes in polymers. Anisotropy has been detected by measuring the deformed samples at the stretching and transverse directions and also as a function of the orientation angle. In addition, theoretical calculations considering the spherical/ellipsoidal and cubic/cuboid shapes of PWs/FVHs as limiting cases have been used to estimate the size of FVHs and their anisotropy induced by deformation. Our simulations indicate that the shape of the hole (Ps well) is an important factor that needs to be taken into account for the interpretation of experimental data.

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