

## On the consistency between positron annihilation lifetime and Doppler broadening results in polypropylene

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Polypropylene samples were measured as a function of the source exposure time at 20 K and as a function of the temperature (20–400 K) simultaneously by Positron Annihilation Lifetime (PAL) and Doppler Broadening (DB) spectroscopy. The peak shape parameter ( $S$ ) measured by DB can be calculated as a sum of contributions of specific parameters corresponding to each positron state. The contributions are obtained by analysis of the PAL spectra. The confinement of positronium (Ps) in a free volume hole (FVH) determines the self annihilation shape parameter  $S_{sa}$  of the para-Ps, the pick-off annihilation lifetime  $\tau_{po}$ , and supposes FVH size-dependence of the pick-off shape parameter  $S_{po}$ . The ortho-Ps lifetime and shape parameters are used to compute  $S_{sa}$ . In this way, the temperature and time dependences of the  $S$  parameter are modelled. The fit of this model to the experimental  $S$  parameter shows a stronger dependence of the  $S_{po}$  on the FVH size ( $R$ ) than the one as expected by taking into account only the Ps momentum. This result suggests that the penetration of Ps into the walls of the FVH must be properly considered and that the penetration depth depends on  $R$  itself.

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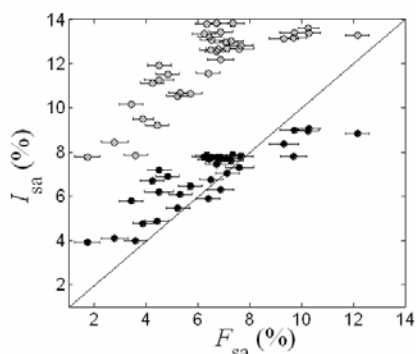
**1 Introduction** The positrons ( $e^+$ ) injected into a polymer may form positronium (Ps) which may get confined into free-volume holes (FVH). Ps exists in two states, triplet ortho-Ps (oPs) and singlet para-Ps (pPs) with lifetimes in vacuum  $\tau_{vo} = 142$  ns and  $\tau_{vp} = 0.125$  ns. It is widely reported that PAL spectra of various polymers can be fitted with three components but with unacceptable intensities ratio of pPs to oPs. Better fit gives a four-component analysis but usually requires a constraint on the intensities. A HPGe-detector is often used to detect the annihilation  $\gamma$ -line which is Doppler-broadened due to the annihilating pair momentum projection along the detection direction (DB spectroscopy). The extent of the broadening is usually evaluated by the peak shape ( $S$ ) parameter which is an integral characteristic.  $S$  parameter can be calculated as a sum of contributions of specific parameters corresponding to each  $e^+$  state. The contributions can be obtained reliably as output of the PAL analysis. The simulated peak shape parameter is compared to the experimental one in order to investigate the consistency between the PAL and DB results.

**2 Experimental** Two slabs of size  $10 \times 10 \times 2$  mm<sup>3</sup> of isotactic polypropylene (PP, 66% crystallinity) were attached to the source (1.5 MBq of <sup>22</sup>NaCl in 7- $\mu$ m-thick Kapton envelope) in sandwich geometry and mounted on the cold finger of a cryostat. The PAL measurements were carried out using a fast-fast coincidence system having a time resolution (full width at half maximum, FWHM) of 230 ps. For the

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DB measurements a HPGe detector with energy resolution of  $G_{1/2} = 1.06$  keV (FWHM of the 514-keV line of  $^{85}\text{Sr}$ ) was used. The spectra were recorded at every 2 h with statistics  $\sim 9 \times 10^5$  for PAL and  $8.5 \times 10^6$  counts in the 511-keV peak for DB. The PAL spectra were analyzed by 4 components by the LT code [1] with a constraint on the intensities either  $3I_1 = I_4$  or  $3I_1 = I_3 + I_4$ . The constraints are based on the assumptions that the third component ( $C_3$ ) is either due to a positron state (A) or to a Ps state (B). Both analyses showed relatively high scattering of  $\tau_3 = 0.5$ - $0.9$  ns and therefore we repeated the analyses with fixed  $\tau_3 = 0.7$  ns. The experimental  $S$  parameter was calculated as the sum of the counts in the central region ( $|\Delta E| < E_S = 0.7$  keV) of the photo peak relative to the total peak counts. For more detailed analysis, the photo peak ( $-1.6$  keV  $< \Delta E < 4.2$  keV) also was decomposed into three equi-centered Gaussians taking into account the HPGe detector resolution.

**3 Results and discussion** Both pPs and oPs confined in FVH may annihilate via self annihilation (sa) or by pick-off (po) annihilation with an electron from the surroundings. The branching ratio of the self annihilation is given by  $\beta(\eta, \tau_{\text{po}}, \tau_{\text{sa}}) = (\eta/\tau_{\text{sa}})/(\eta/\tau_{\text{sa}} + 1/\tau_{\text{po}})$ , where  $\eta$  is the Ps contact density [2] and  $\tau_{\text{sa}}$  is either  $\tau_{\text{vp}}$  for pPs or  $\tau_{\text{vo}}$  for oPs. From the typical values  $\tau_{\text{po}} \sim 2$ - $3$  ns and  $\eta \sim 0.5$ - $1$  [3] in polymers follows  $\beta(\eta, \tau_{\text{po}}, \tau_{\text{vo}}) \approx 0$ . The intensity of pPs self annihilation can be taken as  $^A I_{\text{sa}} = \beta(\eta, \tau_4, \tau_{\text{vp}})I_1$  for the case of PAL analysis A and  $^B I_{\text{sa}} = [\beta(\eta, \tau_3, \tau_{\text{vp}})I_3 + \beta(\eta, \tau_4, \tau_{\text{vp}})I_4]/3$  for analysis B. The fraction,  $F_{\text{sa}}$ , of the self annihilation of pPs localized in FVH can also be obtained as the intensity of the narrow Gaussian in the decomposition of the annihilation pair momentum distribution measured by DB technique [2].



**Fig. 1** Intensities,  $^A I_{\text{sa}}$  and  $^B I_{\text{sa}}$ , of the self annihilation of pPs as obtained from PAL analyses A and B, versus the intensity,  $F_{\text{sa}}$ , of the narrow Gaussian in the decomposition of the DB annihilation peak for the temperature ramp 20-400 K. The Ps contact density is taken as  $\eta = 0.7$  for the calculation of the self annihilation branching ratio,  $\beta$ .

The intensities,  $^A I_{\text{sa}}$  and  $^B I_{\text{sa}}$ , versus  $F_{\text{sa}}$  are plotted in Fig. 1. Only  $^A I_{\text{sa}}$  values agree satisfactorily with  $F_{\text{sa}}$  which means that the component  $C_3$  should not be considered as due to Ps confined in FVH. The sample temperature ( $T$ ) schedule together with  $\tau_{\text{po}} = \tau_4$ , and  $I_c = I_3$  and  $I_{\text{ps}} = I_1 + I_4$  from the PAL analysis A are presented in Fig. 2. The two short lifetimes were found being  $\tau_1 \sim 130$  ps and  $\tau_2 \sim 300$  ns.

On the assumption that  $C_3$  is due to  $e^+$  trapping (or  $e^+$  bound to molecule state) and by taking into account the pPs self annihilation the  $S$  parameter can be presented as

$$S = (I_{\text{ps}}/4)[\beta S_{\text{sa}} + (1-\beta)S_{\text{po}}] + (1 - I_c - I_{\text{ps}})S_+ + I_c S_c + (3I_{\text{ps}}/4)S_{\text{po}}, \quad (1)$$

where  $\beta = \beta(\eta, \tau_{\text{po}}, \tau_{\text{vp}})$ , and the indexes ‘+’ and ‘c’ denote the free  $e^+$  annihilation and trapped  $e^+$  annihilation, and  $I_c$  and  $I_{\text{ps}}$  are the fraction of trapped  $e^+$  and Ps yield. Generally,  $S_+$ ,  $S_c$ ,  $S_{\text{sa}}$  and  $S_{\text{po}}$  may vary with  $T$ . Free  $e^+$  and trapped  $e^+$  annihilations occur in the occupied volume of the polymer and the corresponding annihilation characteristics may change similarly to the thermal expansion of the occupied volume. Therefore, it is admissible to consider linear dependence on  $T$ , i.e.  $S_+ = S_+(0)(1 - \alpha_+ T)$  and  $S_c = S_c(0)(1 - \alpha_c T)$ .

The following correlation has been found  $\theta_{1/2}(R) = 0.424/(R + \delta R)$ , where  $\theta_{1/2}$ , here in keV, is the FWHM of the Ps linear momentum distribution ( $D_{\text{ps}}(R)$ ) represented by a narrow Gaussian in the DB peak decomposition,  $R$  is in nm, and  $\delta R = 0.1656$  nm [4]. From the experimental  $\tau_{\text{po}}$  we calculate  $R$  with

the help of the well-known Tao-Eldrup relation, after which we evaluate  $\theta_{1/2}(R)$  and finally the peak shape parameter  $S_{sa}(R)$  is obtained from

$$S_{sa}(R) = \text{erf}\{2.35E_s/[(\theta_{1/2}(R))^2 + (G_{1/2})^2]^{0.5}\}. \quad (2)$$

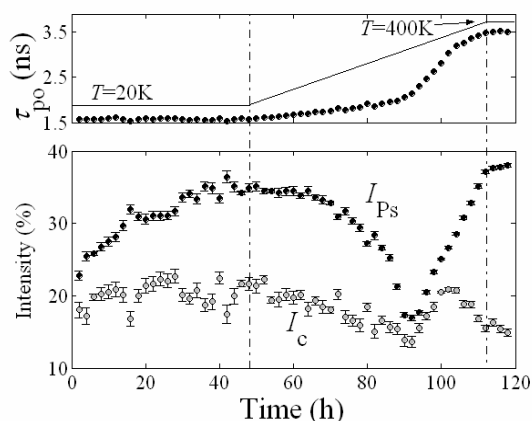
The pick-off annihilation occurs between the positron of Ps ( $e_{ps}^+$ ) and  $e^-$  of the surroundings of the FVH where Ps is confined. The momentum of the annihilating pair is the sum of the individual momenta of the annihilating  $e_{ps}^+$  and  $e^-$ . The momentum of  $e_{ps}^+$  in the laboratory system is composed of the  $e_{ps}^+$  momentum in respect to the Ps center-of-mass (internal  $e_{ps}^+$  momentum) and the Ps linear momentum in the laboratory system. Consequently, we can present the momentum distribution (MD) of the pick-off annihilation as  $D_{po}(R) = D_{ps}(R) \otimes D$ , where  $D$  represents the convolution of the internal  $e_{ps}^+$  MD with MD of  $e^-$  involved in the pick-off annihilation. The last MD will be independent on  $R$  if the Ps penetration (into the outer  $e^-$  shells of the atoms from the FVH wall) depth is considered independent on  $R$ . For estimation of  $S_{po}$  we may consider  $D$  as a Gaussian with FWHM of  $K_{1/2}$  and we obtain an equation similar to Eq. (2)

$$S_{po}(R) = \text{erf}\{2.35E_s/[(\theta_{1/2}(R))^2 + (K_{1/2})^2 + (G_{1/2})^2]^{0.5}\}. \quad (3)$$

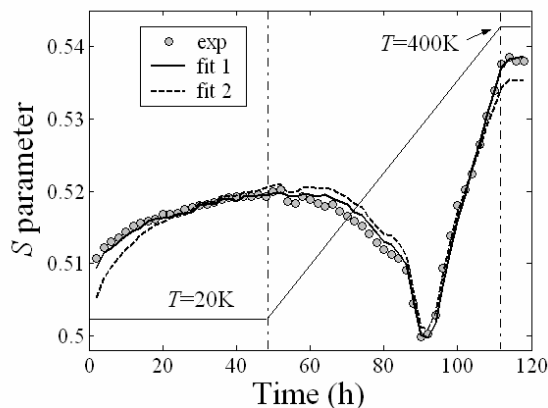
The Ps penetration depth may increase with the decrease of FVH size. In this case, we have to consider  $K_{1/2}$  as dependent on  $R$ . In order to simplify the calculation procedure, for parameterization of  $S_{po}(R)$  we used a more common function which fairly well interpolates also Eq. (3)

$$S_{po}(R) = S_{po}(\infty) \{1 - \exp[-(R+a)/b]\}, \quad (4)$$

where  $S_{po}(\infty)$ ,  $a$ , and  $b$  are parameters. By using Eq. (2) for calculation of  $S_{sa}$  and Eq. (4) for parameterization of  $S_{po}$  together with the experimental intensities  $I_c$  and  $I_{ps}$ , we fitted Eq. (1) to the experimental  $S$  parameter. The best fit (shown in Fig. 3 as fit 1) gave the following set of parameters [ $S_+(0) = 0.487$ ,  $\alpha_+ = 1.0 \times 10^{-4} \text{ K}^{-1}$ ,  $S_c(0) = 0.522$ ,  $\alpha_c = 0.8 \times 10^{-6} \text{ K}^{-1}$ ,  $S_{po}(\infty) = 0.65$ ,  $a = 0.112 \text{ nm}$ ,  $b = 0.245 \text{ nm}$ ].



**Fig. 2** Temperature schedule, pick-off annihilation lifetime  $\tau_{po}$ , and intensities  $I_{ps}$  and  $I_c$  for the PAL analysis A vs. the time.

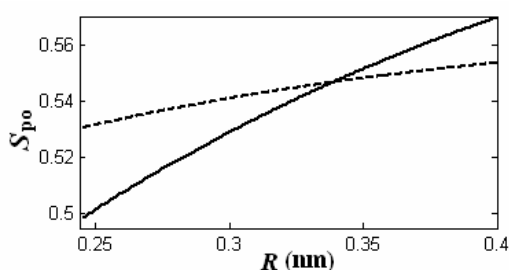


**Fig. 3**  $S$  parameter vs. the time (the black points). The fits are based on Eq. (1) and the output of PAL analysis B (see Fig. 2) by the use of Eq. (4) or Eq. (3) for  $S_{po}(R)$ , correspondingly fit 1 and fit 2.

The change in  $S_{po}$  as a function of  $R$  corresponding to Eq. (4) is plotted as solid line in Fig. 4. In order to make the further discussion easier, first we will report some of the results obtained in a separate DB experiment on Kapton. We found that  $S_{Kapton}$  decreases linearly with  $T$  (20–400 K), and we determined  $\alpha_{Kapton} = 4.4 \times 10^{-6} \text{ K}^{-1}$ . In Kapton all  $e^+$  are localized by forming  $e^+$ -molecule bound state ( $\text{Me}^+$ ) [5]. The  $e^+$  attachment and localization implies that the  $\text{Me}^+$  annihilation characteristics will be rather more sensitive to the chemistry of the nearest environment than to the macroscopic properties of the material. The

value of  $\alpha_{\text{Kapton}}$  is  $\sim 4$  times lower than the linear thermal expansion coefficient of Kapton ( $2 \times 10^{-5} \text{ K}^{-1}$ ). In our opinion, this indicates that the characteristic peak shape parameter of a  $\text{Me}^+$  state is almost insensitive to  $T$ . The last is confirmed by the obtained very low value of  $\alpha_c$  for PP. Both PP and polyethylene show high positron diffusion constants [6] and the estimated diffusion length is  $\sim 100$  nm which is of three orders longer than the typical interatomic distances. This indicates that free  $e^+$  are not localized and their wave functions feel relatively vast volume, consequently, their annihilation characteristics will be sensitive to the macroscopic properties. Therefore, the value of  $\alpha_+$  for PP is in excellent agreement with the reported linear thermal expansion coefficient ( $\sim 1 \times 10^{-4} \text{ K}^{-1}$ ) of the occupied volume in polymers [7, 8].

We performed another fit (fit 2 in Fig. 3) in which for  $S_{\text{po}}(R)$  we used Eq. (3) with the assumption that  $K_{1/2}$  is independent on  $R$ . The best fit resulted in  $K_{1/2} = 1.73$  keV and  $S_{\text{po}}(R)$  reproduced from Eq. (3) is plotted as dashed line in Fig. 4. However, the last fit shows obvious discrepancy in the low and high temperature regions. This implies that Ps wave function penetration depth increases with decreasing of  $R$ .



**Fig. 4**  $S_{\text{po}}$  parameter as a function of  $R$ . The dashed line corresponds to the simplified model of Eq. (3) with the assumption that  $K_{1/2}$  is independent on  $R$ . The solid line takes the variation of the Ps penetration into the FVH wall into account according to Eq. (4).

The described fitting procedure can likewise be performed on the assumption that the additional component  $C_3$  is due to Ps – molecule (MPs) bound state and the output of the PAL analysis B. The fitting result has led to similar dependences for  $S_+(T)$ , and  $S_{\text{po}}(R)$  as already reported, and to constant  $S_{\text{MPs}}$ .

**4 Conclusions** We have shown that coupled DB and PAL analysis is a critical tool for models and hypotheses about  $e^+$  and Ps states in polymer. Based on the reported experimental results, it is impossible to distinguish if the component  $C_3$  is due to  $\text{Me}^+$  or MPs, however, we have shown that it should not be considered as due to Ps confined in FVH. The best fit of the simulated  $S$  parameters set to the experimental one is obtained when the Ps wave function penetration depth is considered dependent on the FVH size. The experimentally determined change of  $S_{\text{po}}$  as a function of  $R$  could be a good base for a comparison with a theoretical calculation of the momentum distribution of the annihilation pair for the oPs pick-off annihilation. The best fit also reveals that  $S_+$  decreases linearly with the temperature with a coefficient close to the linear thermal expansion coefficient of the occupied volume, while  $S_c$  has been found being almost temperature independent.

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