Is Kapton* Really That Simple?

C. Dauwe[a,†], J. De Baerdemaeker[a], N. Djourelov[a,b],
N. Laforest[a,c] and B. Van Waeyenberge[a]

[a]Ghent University, Department of Subatomic and Radiation Physics
Proeftuinstraat 86, B-9000 Gent, Belgium
[b]Institute of Nuclear Research and Nuclear Energy
72 Tzarigradsko Shoosse, 1784 Sofia, Bulgaria
[c] LMOPS — Université de Savoie, LMOPS — UMR 5041
Campus Scientifique, 73376 Le Bourget-du Lac, France

Age momentum correlation experiments in kapton has revealed the existence of two positron states corresponding to the trapping of positrons on the partially negatively charged O and/or N sites in the polymer chain. A young age broadening of the annihilation line shape is also observed and is attributed to the annihilation in flight of the positrons.

PACS numbers: 34.80.Lx, 41.75.Fr, 36.10.Dr, 82.30.Gg

1. Introduction

Kapton occupies a very special place in the characterization of polymers with positron annihilation spectroscopy (PAS). It is the only known amorphous polymer that does not form positronium and thus it is the only polymer that allows us to study states and dynamics of positrons, without being perturbed by the positronium. The lifetime spectrum of kapton is reported to contain one component [1–3] which is not dependent on temperature [4]. Kapton is also insensitive to irradiation damage by the energetic positrons emitted by the ²²Na sources. Brusa et al. [5] studied the motion of positrons in kapton by observing the drift of positrons towards the outer layer in function of an external electrical field. They found an extremely low value for the positron diffusion constant of $D_+ = 2.5 \times 10^{-5}$ cm²/s from which they concluded that the positrons are trapped in the negative sites of the polymer chain, i.e. on the nitrogen and/or oxygen sites. Recent *ab initio* calculations [6] have indeed found strong negative partial charges on the N and O sites in kapton; the results are presented in Fig. 1. Because of their stronger

---

*Kapton is a registered trademark of DuPont, Chemical Co.
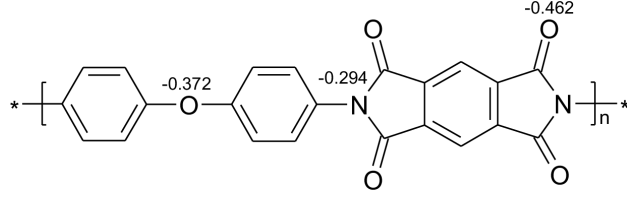†corresponding author; e-mail: charles.dauwe@UGent.be

Fig. 1.   Chemical structure for kapton, with the partial charges of the N and O sites in eV according to Pinel et al. [6].

negative partial charges it is reasonable to consider the 2 different O sites as the main trapping centers. Dlubek et al. have reported [7] that the lifetime spectra of Kapton may be decomposed into two components. The shorter-lived one had a lifetime of approximately 220 ps and intensity of 14%, and the longer-lived component was 376 ps. As usual, this author considers the shorter-lived component to be an artefact of a broad distribution of lifetimes due to the fact that the positron is supposed to be trapped into the intermolecular free spaces and free volume holes (fvh). While it is known that positronium (Ps) is efficiently trapped into these fvh, there is no experimental evidence that this is also true for free positrons. On the other hand, if the two lifetimes correspond to two real and distinguishable positron states, then we may expect these states to have distinguishable values for the S- or line shape parameters.

2. Experimental

We obtained an age momentum correlation (AMOC) relief for kapton at the Stuttgart pelletron facility. The experimental setup, and the procedures for AMOC experiments with the high-energy positron beam was described elsewhere by Stoll [8]. The AMOC data set contained 2.2×10^7 counts. Summation of the data over the energy axis generates the overall experimental lifetime spectrum $\Lambda_{\exp}(t)$ and the line shape curve $S_{\exp}(t)$ is obtained by calculating the line shape parameter for each time channel. In order to obtain a constant statistical quality the energy data were grouped along the time axis, in order that each energy spectrum contains at least 4×10^5 counts.

The theoretical lifetime spectrum $\Lambda(t)$ and the line shape curve $S(t)$ can be written as

$$\begin{cases} \Lambda(t) = \sum L_j(t) \quad \text{with} \quad L_j(t) = I_j \lambda_j \exp(-\lambda_j t), \\ S(t) = \sum S_j(t) \frac{L_j(t)}{\Lambda(t)}, \end{cases} \tag{1}$$

where the index j stands for all positron states. Generally, the $S_j(t)$ coefficients may be function of the positron age t. However, if we assume that the trapping of e^+ on the negative potential sites is immediate, then each contribution has a characteristic constant S_j value. The combined variance $\chi^2_{\tau,S} = 0.5(\chi^2_\tau + \chi^2_S)$ of the fit is calculated from the residues both in the lifetime (LT) and the line shape (S) spectra

$$\chi^2_{\tau,S} = \frac{1}{2\nu_{\mathrm{t}}} \sum \frac{[\Lambda(t_i) - \Lambda_{\exp}(t_i)]^2}{\Lambda_{\exp}(t_i)} + \frac{1}{2\nu_{\mathrm{s}}} \sum \frac{[S(t_i) - S_{\exp}(t_i)]^2}{\sigma^2_{\mathrm{s}}(t_i)}, \qquad (2)$$

where ν_{t} and ν_{s} are the number of degrees of freedom in te LT- and the S-fitting and $\sigma_{\mathrm{s}}(t_i)$ is the standard deviation of the experimental S-value at t_i. A non-linear least squares computer program was written to fit Eq. (1) to the experimental data. The non-linear fitting parameters are the decay constants λ_j; the linear parameters are I_j and S_j.

3. Results and discussion

The experimental line shape versus positron age data $S_{\exp}(t)$ are shown in Fig. 2. We see that these data are not compatible with a single-state system. There must be at least two states and the positron state with the shorter lifetime has the lower S-value. Therefore we first fitted Eq. (1) with two components. The result of this fitting is $[\tau_i] = [153, 372]$ ps, $[I_i] = [7.0, 93.0]\%$ and $[S_i] = [0.4589, 0.4910]$. The variances of the fit are $[\chi^2_{\tau,S}, \chi^2_\tau, \chi^2_S] = [1.31, 1.36, 1.26]$. The resulting fitted $S(t)$ curve is shown as the dashed line in Fig. 2. Both variances χ^2_τ, χ^2_S indicate that the two-component model is not acceptable. Also the S-value of the shorter-lived component is very small with respect to the one for the longer component. N and O have very similar electronic structure and positrons localized on either of them are expected to have barely distinguishable line shapes, and a small difference in their S-parameters. The experimental data around zero age also seem to indicate the existence of a juvenile broadening of the line shape. Juvenile broadening has been observed exclusively in materials which form positronium and it would be due to the finite thermalization time of the newly formed Ps. In the non-Ps material kapton the juvenile broadening must be due to some alternative process.

Within the limited energy range of an S-parameter analysis, the in-flight annihilation of the injected positrons yields an approximately constant contribution. The S parameter of a constant contribution is simply $S_{\mathrm{flight}} = N_{\mathrm{C}}/N_{\mathrm{T}}$, where N_{C} and N_{T} are the number of channels for the central and the total summation in the determination of the experimental S-values. Recently, do Nascimento et al. [9] found a 0.066% contribution of in-flight annihilation in a source based 2D Doppler experiment in aluminium. A new model with 3 contributions was fitted to our AMOC data. The first contribution was a "prompt" curve i.e. with $\tau_1 = 0$ and $S_1 = 0.35$ which constitutes the in-flight annihilation, and the other 2 have free fitting parameters. The result of this fitting is shown on the $S(t)$ curve as the solid line in Fig. 2. The obtained model parameters are $[\tau_i] = [0, 229, 378]$ ps, $[I_i] = [0.6, 12.0, 87.4]\%$ and $[S_i] = [0.35, 0.4818, 0.4908]$. The variances of the fit are $[\chi^2_{\tau,S}, \chi^2_\tau, \chi^2_S] = [0.98, 1.15, 0.81]$.

The results for the lifetimes τ_2 and τ_3 and their intensities are now in very good agreement with the ones found by Dlubek et al. [7]. It is also clear now that S_2 is only slightly smaller than S_3 which could correspond to the 2 different O sites. The intensity of the in-flight contribution is 0.6%. The total probability for
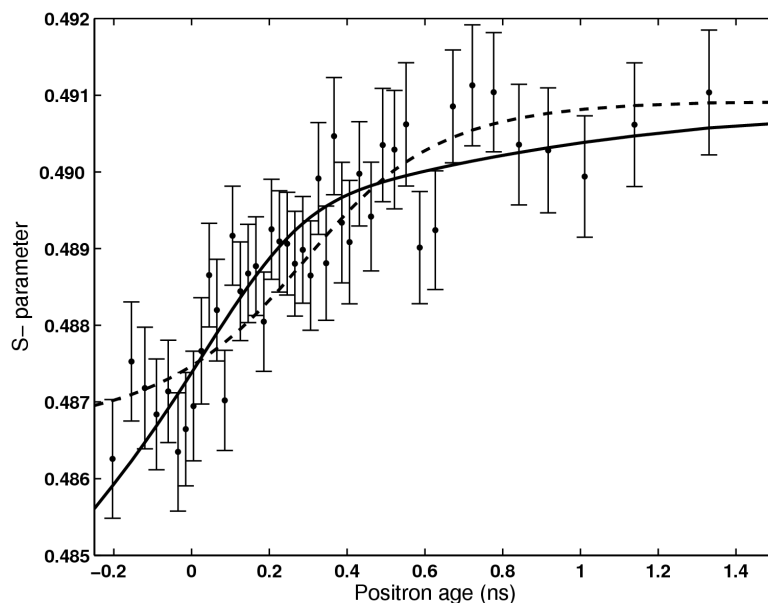
Fig. 2.   Experimental and fitted line shape curves for kapton. The dashed line is the two-component fit, the solid line corresponds to the two-component plus in-flight annihilation model.

in-flight annihilation, $P_{\text{flight}}(E_+, Z)$ is a function of the positron energy and the atomic number of the material, and was calculated by Azuelos and Kitching [10]. For low-Z material this probability is $\approx 0.5\%$ at the energy of 200 keV which is the mean positron energy from a ^{22}Na source. This means that do Nascimento observed approximately 10% of all in-flight events. At 3.5 MeV, the energy of the positrons in our experiment, the total in-flight probability increased to $\approx 8\%$. Because of the improper geometry for observing the 511 keV peak, this observed in-flight annihilation fraction will be much lower than 8%. Thus we also observed 10% of the in-flight annihilations.

4. Acknowledgments

References

[1] I.K. MacKenzie, in: *Positron Solid State Physics. Proc. LXXXIII Int. School of Physics "Enrico Fermi"*, Eds. W. Brandt, A. Dupasquier, North Holland, Amsterdam 1983, p. 210.
[2] M.A. Monge, J. del Rio, *Il Nuovo Cimento D* **10**, 933 (1988).

[3] K. Plotkowski, T.J. Panek, J. Kansy, *J. Phys., Condens. Matter* **6**, 2643 (1994).

[4] H. Weisberg, S. Berko, *Phys. Rev.* **154**, 249 (1967).

[5] R.S. Brusa, A. Dupasquier, E. Galvanetto, A. Zecca, *Appl. Phys. A* **54**, 233 (1992).

[6] E. Pinel, D. Brown, C. Bas, R. Mercier, N.D. Albérola, S. Neyertz, *Macromolecules* **27**, 10198 (2002).

[7] G. Dlubek, R. Buchhold, Ch. Hübner, A. Nakladal, K. Sahre, *J. Polym. Sci. Part B: Polym. Phys.* **37**, 2539 (1999).

[8] H. Stoll, P. Castellaz, A. Siegle, in: *Principles and Applications of Positron and Positronium Chemistry*, Eds. Y.C. Jean, P.E. Mallon, D.M. Schrader, World Scientific, Singapore 2003, p. 362.

[9] E. do Nascimento, O. Helene, C. Takiya, V.R. Vanin, *Nucl. Instrum. Methods Phys. Res. A* **538**, 723 (2005).

[10] G. Azuelos, J.E. Kitching, *At. Data Nucl. Data Tables* **17**, 103 (1976).