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## Positron lifetime measurements in polyethylene under different conditions

G. BRAUER, Th. DANIEL\*, W. FAUST\*\*, Z. MICHNO\*\*\* and H. SCHNEIDER\*\*

*Research Centre Rossendorf Inc., WIP Project, P.O. Box 510119, 01314 Dresden, Germany*

*\* Phys. Chem. Institut*

*\*\* Strahlenzentrum, Univ. Giessen, 35392 Giessen, Germany*

*\*\*\* Technical University Opole, Poland*

### Abstract

Positron lifetime measurements were performed on polyethylene probes of different dose densities under various atmospheric conditions within a  $\gamma$ -dose range from 0 kGy up to 1460 kGy. We present here experiments non destroying the sample. Four components could be resolved in each lifetime spectrum; the components consist each of a lifetime  $\tau$  and an intensity  $I$ . In the dose range investigated the behaviour of the lifetime parameters of the longest-lived ( $\tau_4$ ,  $I_4$ ) and the second long-lived ( $\tau_3$ ,  $I_3$ ) component, respectively, could be explained by the  $\gamma$ -induced recrystallisation and the creation of hydroperoxides. The average free volume as a function of the dose may be calculated out of the lifetime of the fourth component ( $\tau_4$ ).

### Introduction

Among organic solids, polyethylene (PE) repeatedly has been subject by different positron annihilation techniques [1-7]. Of the four resolved positron lifetimes the longest one ( $\tau_4 \approx 2,5$  ns) is associated with ortho-positronium (o-Ps), the shortest one ( $\tau_1 \approx 0,1$  ns) is - at least partially - associated with para-positronium (p-Ps), and an intermediate one ( $\tau_2 \approx 0,3$  ns) with free positrons not forming positronium (Ps). The origin of the third component ( $\tau_3 \approx 1$  ns) has been under debate, i.e. it should be due to either a positron or o-Ps bound to a molecule. However, at present it seems that there exists more evidence in favor of the latter interpretation of  $\tau_3$  [8].

Changes of PE materials properties during irradiation have been studied by positron annihilation and could be well correlated with the results of other methods [9-12]. Thereby a general real-time state-of-matter description of polymers during irradiation has been suggested.

Here we present experiments on high density PE for doses up to 1460 kGy to study the irradiation induced effects non-destructive by the positron lifetime technique.

### Results and Discussion

PE (Lupolen 4261 A, from BASF Ludwigshafen, Germany) with a density of  $0,942$  g cm<sup>-3</sup> and a crystallinity of 59% was used [13] as starting material for  $\gamma$ -irradiations with the <sup>60</sup>Co source at the Strahlenzentrum of the Universität Giessen. Separate sample pairs (50 mm x 50 mm x 5 mm) were cut from larger plates (0,5 m<sup>2</sup>) for each irradiation taking place in air at room temperature with a dose rate of  $0,54$  kGy h<sup>-1</sup>. Positron lifetime measurements (with a <sup>22</sup>Na-source

between two 7.5  $\mu\text{m}$  thick Ni-foils) were carried out up to a number of at least more than  $1 \times 10^6$  integral counts. The measurements were performed with a positron lifetime spectrometer based on  $\text{BaF}_2$ -scintillators (Harshow Chemie, Wermelskirchen, Germany) and XP2020Q (Valvo, Hamburg, Germany) photomultipliers having a time resolution of about 400 ps FWHM. The final analysis was performed with four components and the constraints (i)  $3I_1 = I_3 + I_4$ , and (ii) e.g.  $\tau_1 = 120$  ps. The lifetimes and intensities of the components vary with the degree of irradiation /13/.

The longest-lived component ( $\tau_4$ ,  $I_4$ ) shows the pick-off annihilation of ortho-positronium atoms (o-Ps) primarily in the amorphous regions (in the free volumes).

Due to the  $\gamma$ -irradiation in the polymer chains there may be produced radicals by kicking off H-atoms /14/. Subsequently different chemical reactions (recrystallisation, creating of hydroperoxides, crosslinking, degradation) are induced. Immediately after the beginning of irradiation the oxygen, dissolved in polyethylene, may be bound forming hydroperoxides at the polymer chains in the amorphous regions. More oxygen for this reaction is supplied by diffusing from the air into the sample /15/.

By increasing the dose, cross-linking of the polyethylene /15/ together with disarranged folding in the amorphous regions is induced, and consequently the created hydroperoxides are screened off by polymer chains. At doses higher than 500 kGy the degradation prevails /15/ (preferentially in the amorphous regions of the polyethylene), and furtheron disarranged folding takes place. But now previously screened off hydroperoxides get available for reactions.

Because of the disarranged folding of the polymer chains in the amorphous regions there is induced a recrystallisation /3/. Consequently the fraction of amorphous regions is reduced with increasing dose. This effect can be seen by the decreasing of  $I_4$  /5/ and on the behaviour of the reciprocal density  $\rho^{-1}$ . It is found that  $\rho^{-1}$  (measured by BASF) correlates with changes of the intensity  $I_4$  as a function of the applied  $\gamma$ -dose (fig. 1).

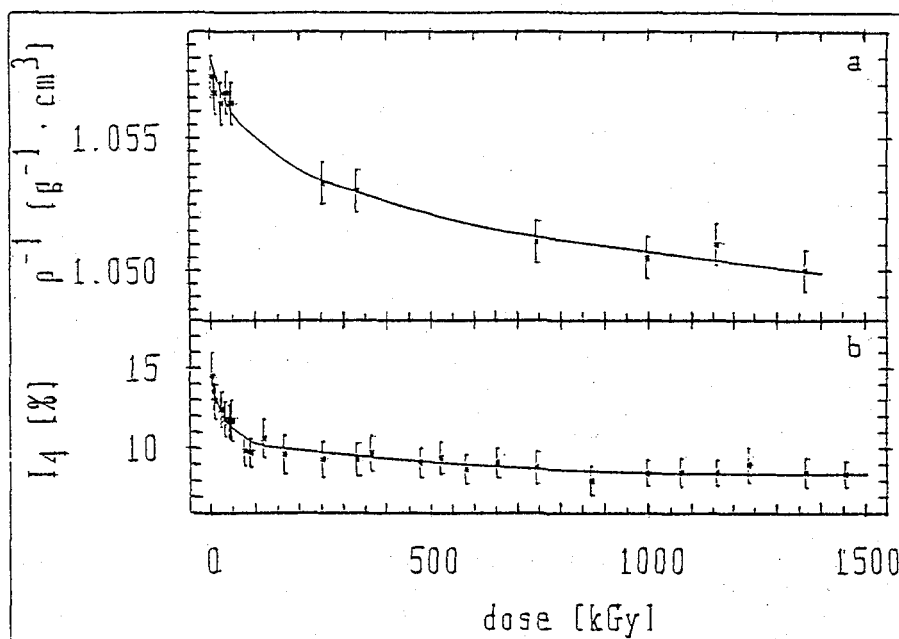


Fig. 1. Behaviour of the reciprocal density  $\rho^{-1}$  (a) and of the intensity  $I_4$  (b) (relative units) as a function of the  $^{60}\text{Co}$ - $\gamma$ -dose.

The lifetime of the fourth component ( $\tau_4$ ) depends on the free volume (i.e. from the crystallinity /7/, /13/). In /16/ there is given a model to calculate the lifetime of o-Ps atoms inside the free volume ( $V = 4\pi R_0^2/3$ ;  $R_0$  = Free volume radius).

To decide on the reproducibility of results (c.p. /17/) and possible aging effects of unirradiated materials "old" (1990) and "new" (1992) Lupolen samples have been studied. E.g. with a time resolution of about 215 ps and different statistics /18/, a constraint free analysis of all spectra gave the averages collected in Table 1.

Table 1. Global averages of the components ( $\tau$  [ps], I [%]) /13/

	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$	I <sub>3</sub>	I <sub>4</sub>
"Old"	85±10	307±5	1100±22	2620±33	12.46±0.30	16.15±0.38
"NRW"	80±15	308±5	955±16	2581±10	12.14±0.35	16.18±0.15

It is found /18/ that the counting statistics has no significant influence on the final evaluations if more than  $3 \times 10^6$  counts are collected. The  $\tau_1$  values given are possibly a little too short compared to the p-Ps lifetime (125 ps) but not unreasonable. Except for the  $\tau_3$  value there are no changes in the measurable parameters due to the age of the samples.

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#### References

- /1/ M. Eldrup, in: Positron Solid-State Physics, Proc. Internat. School of Physics "Enrico Fermi", Course LXXXIII, Varenna on Lake Como 1981, Ed. W. Brandt, 644, North Holland, Amsterdam (1983).
- /2/ P. Kindl, Habil. thesis, university of Graz (1983).
- /3/ P. Kindl, G. Reiter, phys. stat. sol. (a) **104**, 707 (1987).
- /4/ G. Reiter, Ph D thesis, university of Graz (1987).
- /5/ J. Ch. Abbé, G. Duplâtre, J. Serna, in: Positron Annihilation, L. Dorikens-Vanpraet, M. Dorikens, D. Segers (Eds.), 796, World Scientific, Singapore (1989).
- /6/ A. Badia, J. Ch. Abbé, G. Duplâtre, ICPA-9, 9<sup>th</sup> Int. Conf. on Positron Annihilation, D10, Szombathely, August, 26th-31th, (1991).
- /7/ F.H.J. Maurer and M. Welander, J. Adhesion Sci. Technol. Vol. 5, No. 6, pp. 425-437 (1991).
- /8/ A. Cornaz, J. Brunner, E. Cartier, in: Positron Annihilation, L. Dorikens-Vanpraet, M. Dorikens, D. Segers (Eds.), 793, World Scientific, Singapore (1989).
- /9/ G. Brauer, W. Hertle, A.G. Balogh, phys. stat. sol. (a) **105**, K7 (1988).
- /10/ G. Brauer, W. Hertle, E. Müller, W. Tzscheutschler, Radiat. Phys. Chem. **33**, 307 (1989).
- /11/ G. Brauer, W. Hertle, 'Kunststoffe' **78**, 424 (1988).
- /12/ G. Brauer, W. Hertle, E. Müller, W. Tzscheutschler, Report ZfK-678, Zentralinstitut für Kernforschung Rossendorf (1989).
- /13/ W. Faust, Ph D thesis, university of Giessen (1991).
- /14/ E. Köhnlein; in 'Kunststoffe', 65th year, no. 9 (1975).
- /15/ H.U. Voigt, F. Wizcnerowicz; Energiewirtschaftl. Tagesfragen (ET) **11** 524 (1974).
- /16/ Y.C. Jean; Microchem. J. **42**, 72 (1990); Nucl. Instr. and Meth. **B56/57**, 615 (1991).
- /17/ L. Dorikens-Vanpraet, D. Segers, M. Dorikens, Appl. Phys. **23**, 149 (1980).
- /18/ G. Duplâtre, private communication (1993).