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# POSITRON ANNIHILATION STUDIES OF POLYETHYLENE–CARBON BLACK COMPOSITES

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Results of investigations of the angular correlation of annihilation radiation and positron annihilation lifetime measurements are presented for polyethylene–carbon black composites. The inhibition of positronium formation due to the carbon black introduction is evidenced by a decrease in intensities of the narrow component in angular correlation of annihilation radiation curves and of the longest-lived components in positron annihilation lifetime spectra. A qualitative interpretation of the data in terms of the free-volumes model is proposed.

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## 1. Introduction

Positron annihilation spectroscopy (PAS) has been widely applied to polymeric solids, particularly to polyethylene. The influence of different physical parameters such as crystallinity, density, temperature, pressure, electric or magnetic field, irradiation dose, etc., has been examined within this context to study structural changes and primarily to identify the origin of the various lifetime components (e.g. [1–9]). In general, the positron annihilation lifetime (PAL) spectra in polymers have been resolved into three or four components. For example, according to the four components analysis for teflon performed by Kindl et al. [2, 3], the longest component includes all the positrons forming ortho-positronium (o-Ps) and annihilation via electron pick-off; the intermediate long-lived component arises from positrons bound in the amorphous domains; the intermediate short-lived component is exclusively due to free positrons; the shortest component is partly due to para-positronium (p-Ps) self-annihilation and partly to a bound positron state of short lifetime. The former authors come to the conclusion that the intermediate long-lived component may be also due to a positronium (Ps) state.

Recently, the PAS has been developed to characterize the free-volume properties of polymers [10, 11]. The unique capability of PAS to probe free-volume properties is from the fact that Ps atom is preferentially trapped in the atomic-scale holes (voids) which have a size ranging from 0.1 to 1 nm. PAL measurements give direct information about the dimension, content and hole-size distributions of free-volume. The Ps formation has been also confirmed by the appearance of the narrow component in the angular correlation of annihilation radiation (ACAR) curves. ACAR curves give additional information about the shape of the voids in oriented polymeric materials.

Conductive polymer composites have found wide-spread application in the electronic industry (polymer thick film resistors, housings for shielding of electromagnetic interference, threshold switches etc.). In simple terms, a composite can be defined as a combination of several distinct materials, designed to achieve a set of properties not possessed by any of the components alone (see e.g. [12] and references therein).

In the present work, we have preliminarily examined by PAS a composite which consists of two component materials, one of them forming continuous phase (polyethylene matrix) and the second one forming discrete regions dispersed in polyethylene (carbon black particles). To our knowledge, only a few positron experiments have been carried out in polymer composites [13, 14]. A simple composite model for positron annihilation has been proposed in which the role of the ratio of the densities of two components as well as the size of the filler particles were emphasized.

## 2. Experiments

As a basic polymer, a polyethylene (Politen II/003/GO produced by Blachownia) of density 0.918 g/cm$^3$ and an average molecular weight of 158980 was used. The crystallinity of polyethylene was estimated to be 62%. The extra-conductive (EC) carbon black (Chezacarb EC produced by Chemopetrol Litvinow) was used. Some properties of the EC filler were: density 0.14 g/cm$^3$, specific surface area 900 m$^2$/g, pure carbon content 99 wt.%. The composite components were mixed in a two-roller laboratory mill for 25 minutes at 423 K. The composite samples with a different carbon content (up to 25 wt.%) were compressed under increasing pressure 2 MPa/5 min, 10 MPa/3 min, and 30 MPa/2 min to make a film of 2 mm in thickness. The samples were made in the Institute of Chemistry of Opole University.

ACAR curves were determined at room temperature with the conventional parallel long-slit annihilation spectrometer using a 5 mCi $^{22}$Na source placed on one side of the samples. The full width at half-maximum of the resolution function was about 1 mrad. Data were accumulated with the step of 0.5 mrad in the range from $-25$ to $+25$ mrad. The number of coincidences per point near the center was about $3 \times 10^4$.

PAL spectra were obtained using a conventional fast-slow coincidence system with high-efficiency $BaF_2$ scintillators. The time resolution of the device was determined to be 190 ps from the prompt curve of a $^{60}$Co source. The 90° geometry of detectors was applied. A 30 $\mu$Ci $^{22}$Na positron source sealed by kapton foils (1.08 mg/cm$^2$) was placed between two plates of the same samples. At least two millions of counts were collected for each spectrum.

## 3. Results and discussion

In absence of a better model, each ACAR curve was fitted with the sum of an inverted parabola (narrow component) and a Gaussian. One parabola plus one Gaussian fit turned out to be a reasonable one taking into account a chi-square test. In Fig. 1 the normalized intensity $I_N$ of narrow component is plotted against the carbon black weight fraction.

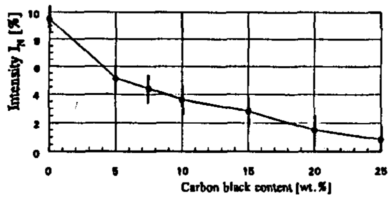


Fig. 1. Variation of the normalized intensities of narrow component versus the carbon black weight fraction. The curve is a guide to the eye.

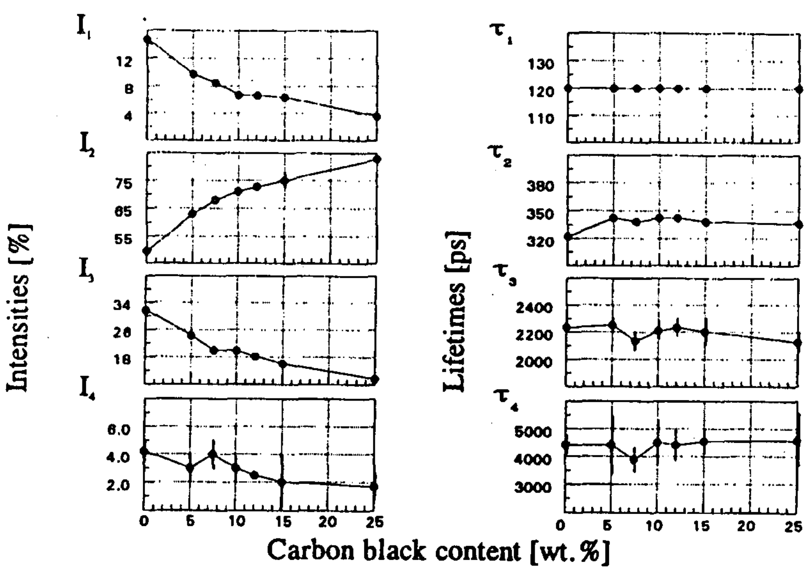


Fig. 2. Positron lifetimes and the relative intensities as function of the carbon black weight fraction. The curves are a guide to the eye.

PAL spectra corrected for positron annihilation in the source were fitted by a sum of four exponential functions convoluted with the resolution function of spectrometer (one Gaussian), plus a constant linear background. The computer program given by Kansy [15], instead of the commonly used Positronfit, was applied because of the simplicity with which it can be operated. Note that in our analysis one constraint ($\tau_1$ = 120 ps) was done. The results of fitting analysis, i.e. the lifetimes and the intensities against the carbon black weight fraction are collected in Fig. 2.

As Fig. 1 shows, the intensities of narrow component of ACAR decrease with increasing carbon black content. As it follows from Fig. 2, the intensities $I_1$, $I_3$ and $I_4$ show a similar behavior. On the other hand, the increase in $I_2$ with increasing filler content is evident. The lifetime values are unaffected by the carbon black content.

The outcome of these measurements suggests two main areas for discussion. One is connected with a general question of the nature of states occupied by thermalized positrons in the investigated composites, while the other is associated with the effect of the carbon black content.

The results of the ACAR analysis indicate that the narrow p-Ps component ($I_N$) decreases from 10% (pure polyethylene) to about 1% at 25 wt.% of filler. One can conclude that the incorporation of a reinforcing filler such as carbon black strongly inhibits the Ps formation in polyethylene.

As mentioned previously, the nature of positron states in polyethylene is not yet clear. Three or four lifetime components have been reported. Unconstrained analysis of PAL on 4 components is always a difficult task and the results are frequently uncertain. Therefore, some constraints are usually adopted. To summarize, a simple model involving o-Ps trapping by the free-volumes (voids) placed in the crystalline or non-crystalline phases has been mainly suggested. It is hence not unreasonable to assume tentatively a similar approach to filled polyethylene samples.

In this paper 4-component analysis with one constraint ($\tau_1$ = 120 ps) has been made and the data to be derived may be qualitatively interpreted as follows:

(a) the longest and the second longest-lived components are due to o-Ps (formed in the two types of voids) pick-off annihilation,

(b) a reinforcing filler such as carbon black fills the voids in polyethylene matrix and hence affects Ps formation possibility,

(c) the intermediate short-lived component may be ascribed to positron trapped at the interfaces,

(d) the shortest component may be due to p-Ps or free positron annihilation.

Thus, the intensities ratio $I_1/(I_3 + I_4)$ should be nearly equal 1/3 as far as the first possibility given in (d) is concerned. In the calculations performed none of these intensities has been fixed. It is enhancing the interest in checking this conclusion. The obtained results are given in Table.

As can be seen, the equation $I_1 = (I_3 + I_4)/3$ is nearly achieved which confirms the interpretation being proposed. It is necessary to mention that the equation should be fulfilled if the shortest component in the PAL spectra corresponds to the p-Ps while the two very long components there, are the result from the pick-off annihilation of o-Ps.

TABLE

Relation between $I_1$ and $(I_3 + I_4)/3$ as a function of carbon black weight fraction.

| Carbon black content [wt.%] | $I_1$ [%] | $(I_3 + I_4)/3$ [%] |
|---|---|---|
| 0 | 14.7 (0.6)* | 11.9 (0.5) |
| 5 | 9.7 (0.5) | 9.1 (0.6) |
| 7.5 | 8.5 (0.4) | 8.0 (0.7) |
| 10 | 6.7 (0.6) | 7.6 (0.6) |
| 12 | 6.6 (0.5) | 6.9 (0.5) |
| 15 | 6.4 (0.4) | 6.0 (1.0) |
| 25 | 3.6 (0.4) | 4.5 (0.5) |

*Standard deviations of measured quantities are given in round brackets.

## 4. Conclusion

A clear understanding of the nature of positron states in the carbon black filled polyethylene and its components is yet to be assessed. As the present results are preliminary, we can propose only a qualitative interpretation of the positron annihilation data basing on the simple free-volumes model. It is possible to assume that the positron annihilation signal contains a valuable information concerning the microstructure of composites. However, our interpretation needs support from the more comprehensive PAS experiments.

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