

# Study of the Electric-Field Effect in Polyethylene by the Positron Annihilation Technique

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## SYNOPSIS

The positronium formation and the reversibility behavior of the electric field from 31.75 to 588.24 kV/cm were studied in high-density polyethylene (HDPE) using the positron annihilation lifetime technique. The lifetime measurements were performed using the conventional fast-fast coincidence timing system. The observed *ortho*-positronium lifetime  $\tau_3$  does not show significant variation from the corresponding values measured without the electric field. On the other hand, the corresponding intensity  $I_3$  increases with increasing the electric field strength in the range from  $\sim 100$  to 588.24 kV/cm. This result indicates a strong irreversible effect of the electric field. In addition, the effect of temperature on the sample stressed at 450 kV/cm was investigated. The structural changes on the heating and cooling cycles show reversible behavior. The thermal expansion coefficient has been deduced to be  $7.53 \times 10^{-3}/^\circ\text{C}$ . © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The study of electric breakdown mechanisms in solids are of utmost importance from the technological point of view. The electric breakdown in insulating materials is influenced by a large number of factors such as electric-field strength, temperature, type of voltage applied, time of voltage application, and material structure. Polyethylene is one of the organic polymeric materials frequently used in high-voltage cable insulation. One of the interesting fields in cable insulation industry is the study of the structure of polyethylene under different external conditions before breakdown.

Positron annihilation lifetime technique has been widely applied to polymeric solids, particularly to polyethylene.<sup>1-6</sup> In the present investigation, the positron annihilation lifetime (PAL) technique was applied to probe the microstructural changes occurring in the properties of free-volume holes in high-density polyethylene (HDPE) before breakdown. Whether the effect of low and high electric-field

strengths is reversible or irreversible was investigated. The investigation was carried out using a high-voltage supply (40 kV, 50 c/s). The maximum applied electric-field strength was about 588.24 kV/cm and the time duration of the electric stress was kept constant (10 min) for all the samples. The temperature effect on the free-volume holes in the sample stressed by 450 kV/cm was investigated and the thermal expansion coefficient was deduced.

## EXPERIMENTAL

Samples of HDPE ( $d = 0.963 \text{ g/cm}^3$ ) were stressed by ac high voltage for a duration time of 10 min using two parallel plate electrodes to obtain a uniform electric field. The details are shown in Table I.

The stressed samples are then measured by the conventional fast-fast coincidence system having a time resolution of 180 ps with energy windows set for <sup>60</sup>Co. The <sup>22</sup>Na positron source held in a 7  $\mu\text{m}$  Kapton foil (activity of 20  $\mu\text{Ci}$ ) was sandwiched between two identical pieces of the sample under investigation. The 1.275 MeV  $\gamma$ -ray from the decay of <sup>22</sup>Na isotope is taken as the start signal, whereas

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**Table I** Values of the Electric-field Strength Applied for Different Samples of HDPE

Sample No.	Thickness (cm)	High Voltage (kV)	Electric Field $E$ (kV/cm)
1	0.630	20	031.75
2	0.630	30	047.62
3	0.152	20	131.57
4	0.222	40	180.18
5	0.051	15	294.12
6	0.089	40	449.44
7	0.051	30	588.24

one of the 0.511 MeV  $\gamma$ -rays from the positron annihilation in the studied material is the stop signal. Thus, the time interval between the above two  $\gamma$ -rays is the lifetime of the positron in the material. The lifetime spectra were analyzed using the PAT-FIT program<sup>7</sup> with source corrections.

In the thermal measurements, the samples are heated up to 100°C. Temperatures are fixed for 2 h and varied in steps of 5°C. The same lifetime measurements are also performed during cooling the sample back to room temperature under the same above-mentioned conditions. The temperature is controlled by a NiCr-NiAl thermocouple that was placed between two samples and away from the positron source.

## RESULTS AND DISCUSSION

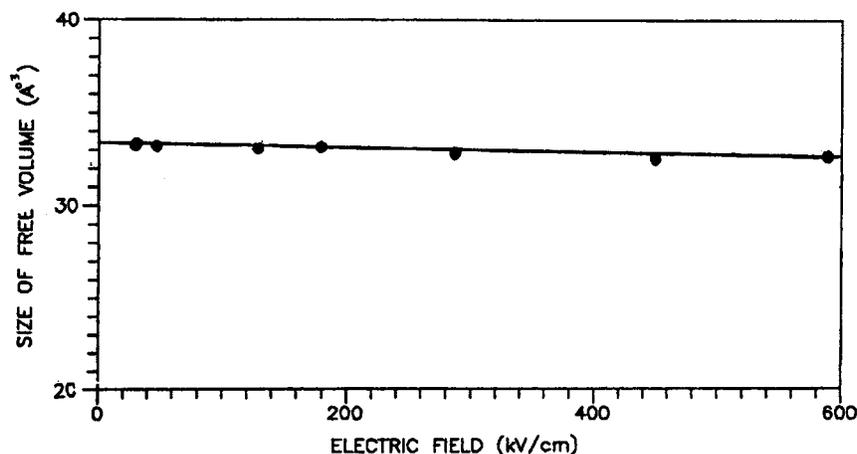
All the lifetime spectra have been resolved into three components: The shortest-lived component,  $\tau_1 = 130$

$\pm 2.1$  ps with intensity  $I_1 \approx 20\%$  is attributed to *para*-positronium (*p*-Ps) annihilation. These values did not show any appreciable variation with the electric field  $E$ . The intermediate-lived component,  $\tau_2 = 390 \pm 50$  ps, is due to the free positron and positron molecular annihilation. Its intensity  $I_2$  has been found to vary from 72 to 42%. The long-lived component  $\tau_3$  with intensity  $I_3$  is due to *ortho*-positronium (*o*-Ps) annihilation in free volumes. In accordance with the free-volume model,<sup>8</sup> the size and the fractional free volumes have been deduced.

### Electric-field Effect

Figure 1 shows the effect of the electric-field strength on the sizes of the free volumes. Before applying the electric field, the free-volume size was  $33.59 \pm 0.11 \text{ \AA}^3$ . This value did not change during the whole range of the electric-field stress from 31.75 to 588.24 kV/cm. Accordingly, it can be deduced that the thermal effect on the free volume is not appreciable. This result is quite consistent with the choice of a maximum electric-field strength of 588.24 kV/cm, which is less than 50% of the breakdown voltage strength at these conditions.

The variation of the fractional free volumes with the electric-field strength (Figure 2) gives an inflection point at  $\sim 100$  kV/cm. It can be noticed that the increase in the fractional free volumes does not exceed 2% until 31.75 kV/cm. However, from  $\sim 100$  to 588.24 kV/cm, there is an appreciable increase in the fractional free volumes from 10 to 37%. Since the PAL measurement is carried out after applying the high-voltage stress, it can be concluded that even before breakdown microstructural changes occur in the materials and that the effect of the elec-



**Figure 1** The free-volume sizes in HDPE as a function of the electric-field strength (errors are within the points).

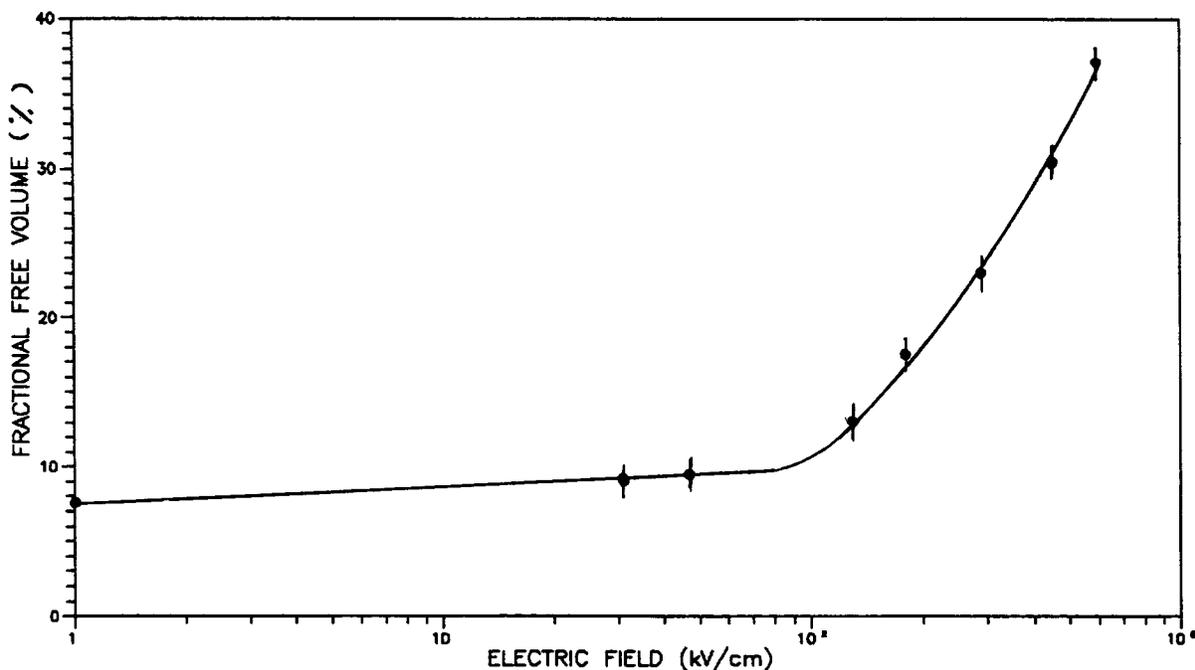


Figure 2 The dependence of the fractional free volumes on the electric-field strength.

tric field on polyethylene from  $\sim 100$  to 588.24 kV/cm is irreversible.

### Temperature Effect

The temperature dependencies of *ortho*-positronium lifetime  $\tau_3$  and its relative intensity  $I_3$  in the sample stressed by 450 kV/cm are shown in Figure 3. On increasing the temperature from 20 to 100°C,  $\tau_3$  increases linearly from 1.23 to 1.5 ns while its intensity  $I_3$  increases from 31 to 37.5%. The results of  $\tau_3$  and  $I_3$  obtained by cooling the samples back agree well with those measured in the heating cycle. As seen from Figure 3, the structural changes in  $\tau_3$  and  $I_3$  are reversible. The increase in  $\tau_3$  can be explained by the fact that due to the thermal expansion of the lattice the overlap between the positronium (Ps) and the electron wave functions decreases with increasing lattice spacings. At higher temperatures, lattice vibrations and density fluctuations will be more considerable. These thermal fluctuations lead to a smearing of the electron-density distribution in the lattice. The increase in  $I_3$  indicates an increase in the number of free-volume holes with temperature.

The thermal coefficient of the stressed sample can be determined by calculating the radius  $R$  of the free-volume hole according to the relation<sup>8</sup>

$$\tau_3^{-1} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin(2\pi R/R_0) \right]$$

which assumes a spherical shape for the free-volume hole. In the above equation,  $R = R_0 + \Delta R$ , where  $\Delta R$  is an empirical parameter that is determined by fitting the observed  $\tau_3$  with the known hole and cavity sizes in different molecular substrates. The deduced free volumes  $V$  are shown in Figure 4 as a function of temperature. The thermal expansion coefficient defined as

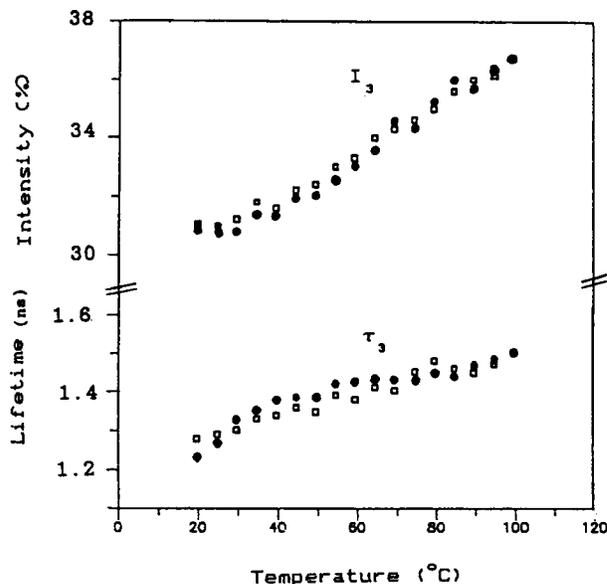
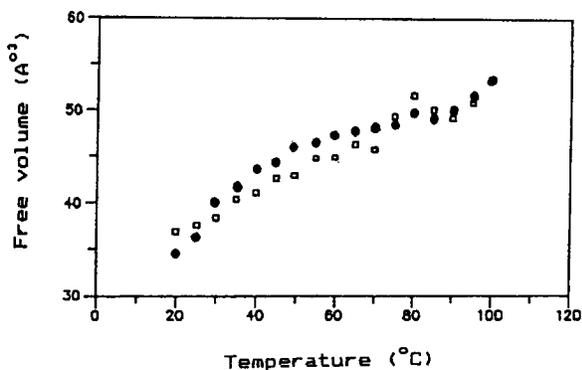


Figure 3 The intensities and the lifetimes of the long-lived component in HDPE stressed by 450 kV/cm: (●) heating cycle; (□) cooling cycle.



**Figure 4** The free-volume sizes in HDPE stressed by 450 kV/cm as a function of temperature: (●) heating cycle; (□) cooling cycle.

$$\frac{[V(100^{\circ}\text{C}) - V(20^{\circ}\text{C})]}{[V(20^{\circ}\text{C}) \cdot (100^{\circ}\text{C} - 20^{\circ}\text{C})]}$$

is estimated to be  $7.53 \times 10^{-3}/^{\circ}\text{C}$ , which is eight times as high as that deduced from specific measurements. This would be expected, since the coefficient deduced from the free volumes represents expansion of the amorphous region where the density is lower and the configuration is more flexible than in the crystalline region.

The authors would like to thank Dr. Amin Ali Rasmi, Faculty of Engineering, Canal Suez University, for valuable discussions, helpful comments, and carrying the high-voltage stress to the specimens.

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Received October 15, 1992

Accepted May 4, 1993