Investigation of foamed polystyrene by positron annihilation lifetime spectroscopy

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Positron annihilation lifetime measurements obtained for foamed polystyrene samples of different density are presented. Two series of samples (exposed and not exposed to open air) were investigated. The dimensions of the pores were determined. The free volume was found to decrease from 137 to 104 Å^3 with increasing density of the material. The largest concentration of micropores (dimensions up to ~0.7 nm), represented by the intensity of the long-lived component, was obtained for a solid (not foamed) sample.

Foamed polystyrene / Positron annihilation / Micropores

Introduction

Polystyrene is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. Polystyrene is one of the most widely used kinds of plastic. Foamed polystyrene is used, for example, as packing material, for thermal insulation, and in foam drink cups. It is also used for non-weight-bearing architectural structures (such as ornamental pillars).

The low thermal conductivity characteristic for foamed polystyrene is the result of the highly porous structure of the material. The distribution of size of free volumes in polymers has been the subject of intensive scientific research for more than 40 years [1]. Recently several authors investigated the distribution of pore size, relaxation processes, transitions, electron beam and gamma irradiation effects for solid polystyrene [2-4]. But, although the porosity of foamed polystyrene is evident, our knowledge about pores of less than 2.0 nm (micropores) is not complete. The positron annihilation lifetime (PAL) method allows characterizing micropore sizes. In PAL spectroscopy the positron is used as a nuclear probe, which is repelled by the atom cores and preferentially localized in atomic size free volume holes. Therefore, the positron and positronium (Ps) annihilation signals are mainly contributing from free volume holes in the material. Ps has two spin states: para-positronium (p-Ps), having spin zero (lifetime in vacuum 125 ps) and ortho-positronium (o-Ps), having spin one (lifetime in vacuum 142 ns). The lifetime of o-Ps is reduced due to interaction of o-Ps with electrons from surrounding matter (pick-off annihilation) and decay into two gamma rays. Thus, three positron lifetimes (τ_1, τ_2, τ_3) are often found in polymers. These lifetimes, from shortest to longest, are believed to be due to the self-annihilation of p-Ps, the annihilation of free positrons, and the pick-off annihilation of o-Ps, respectively. The longest lived component is of particular importance to polymer studies, because the lifetime τ_3 is related to the average free volume hole size [5,6]. The relationship between τ_3 and the average radius R (nm) of free volume holes in the spherical approximation is given by the Tao-Eldrup model as:

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

where τ_3 and R (hole radius) are expressed in ns and Å, respectively. R_0 equals $R + \Delta R$, where ΔR (= 1.66 Å) is determined by fitting experimental values of τ_3 obtained for materials with known hole size. The micoropore volume V is given by $(4/3)\pi R^3$.

Experimental

A fast timing configuration of the "Ortec" positron lifetime system was used (Fig. 1). "Scionix" modules equipped with two XP 2020Q photomultiplier tubes optically coupled with cylindrical BaF$_2$ scintillators (⌀ 25.4 mm, 10 mm) functioned as the detectors of two different γ quanta attributed to start (1274.6 keV) and stop (511.0 keV) of a positron lifetime.
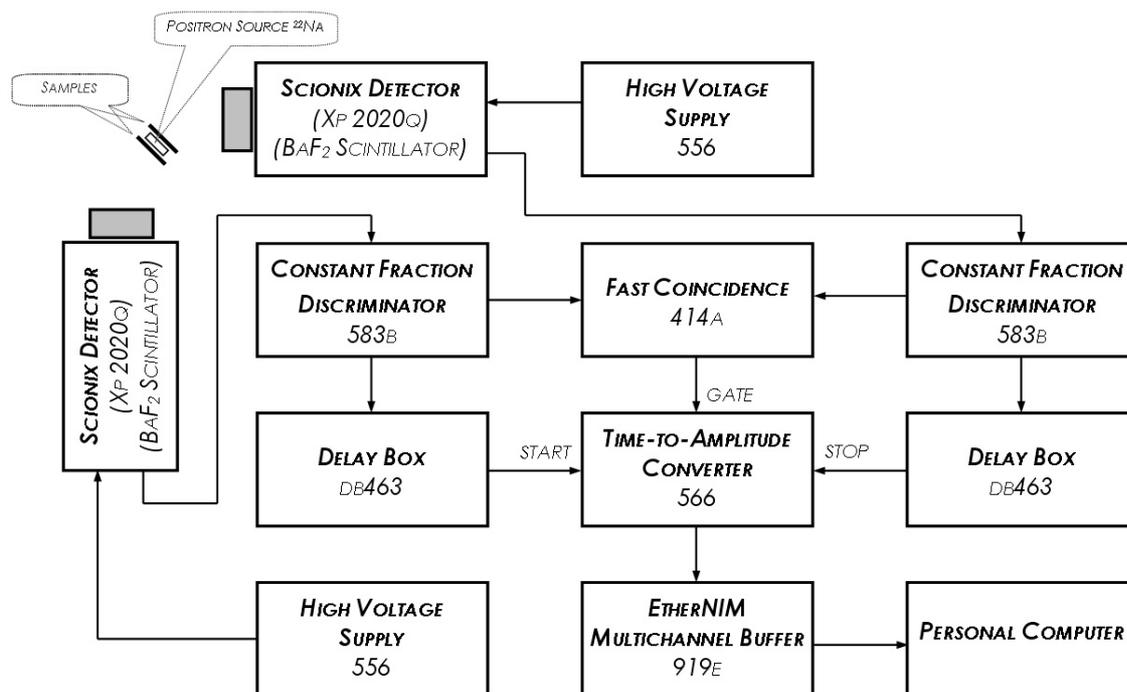
Fig. 1 Block diagram of the spectrometer.

A 0.4 MBq [22]Na positron source sealed by kapton foils (12.5 μm thickness) was placed between two plates of the same sample. The 90° geometry of the detectors was used to minimize the parasitic effects of simultaneous detection of both quanta (511 keV and 1275 keV) by one of the detectors (see Fig. 1).

The way of energy discrimination and the 90° geometry of the measurement influence the rate of recorded events (~13 coincidences per second). The time resolution of the device was determined to be 240 ps from the prompt curve of a ^{60}Co source.

Four polystyrene materials, ordinarily used as thermal insulators, of different density were investigated. The highest density polystyrene (0.96×10^3 kg/m^3), obtained by melting foamed polystyrene, is defined as HDPS. The low density foamed polystyrenes with densities of 10.9, 15.4, and 23.3 kg/m^3 are defined as LDPS1, LDPS2, and LDPS3, respectively.

Before the measurements, during two years of deposition, the samples LDPS1, LDPS2, and LDPS3 had not been influenced by weather conditions. A second group of samples, abbreviated as LDPSWC1, LDPSWC2, and LDPSWC3, was exposed to open air.

The analyses of the positron annihilation were performed using the LT program [7] without constraints imposed on the lifetime components and with no source correction. The timing response function was described by a superposition of two Gaussians differing from each other by their FWHMs and weights. Within this simple model one of the Gaussians turned out to be relatively narrow, representing usually about 98 % of the total area of the response function. The remaining, very weak Gaussian, originating from parasite pile-up events,

was found to be broad, typically with a FWHM of 600-700 ps. The relative positions of the Gaussians were fixed in zero position.

Results and discussion

The counting rate of a positron annihilation spectrometer is limited by the dimensions of the investigated samples. The larger the thickness of the samples, the greater is the distance between the detectors and the lower is the counting rate of the system. Taking into account the measurement geometry and the activity of the positron source, the thickness of the samples should not be larger than about 5 mm. For samples of very low density, like foamed polystyrenes, a thickness of about 5 mm would not be enough to stop all positrons inside the sample, therefore an estimation of the implantation depth of the positrons was made for the investigated samples. For polymers the implantation depth distribution of positrons with energy E (keV) is expressed by the Makhovian equation

$$P(z) = -\frac{d[\exp(-z/z_0)^2]}{dz} \qquad (2)$$

with

$$z_0 = \frac{80}{\sqrt{\pi}} \frac{E^{1.6}}{\rho} \qquad (3)$$

Here z (nm) and ρ (g/cm^3) are the positron implantation depth and sample density, respectively. The mean implantation depth z_m is given by:

$$z_m = \frac{\sqrt{\pi}}{2} z_0 \qquad (4)$$

The values of z_m for the average positron energy (150 keV) for a ^{22}Na source are listed in Table 1. The maximum value of z_m equals 11 mm. The preparation of samples with thickness 12 mm guaranteed the annihilation of nearly all the positrons inside the investigated material. This choice is a compromise between the counting rate of the system and the stopping power of the samples. Control measurements were made on samples with a thickness of 20 mm. No significant difference was observed between the results obtained for the samples of 12 mm and 20 mm thickness.

The positron lifetime spectra were analyzed in terms of three lifetime components. The example of a delayed-coincidence spectrum for the solid polystyrene sample (HDPS) (Fig. 2) shows the result of the deconvolution of the spectrum into lifetime components. Each lifetime corresponds to the average annihilation rate of a positron in a different state. The shortest lifetime ($\tau_1 = $ 231-269 ps and $I_1 = $ 34.5-63.1 %) corresponds to the annihilation of p-Ps atoms and free positrons, while the intermediate one ($\tau_2 = $ 487-603 ps and $I_2 = $ 23.5-41.5 %) arises from the annihilation of free positrons in the polystyrene matrix and of positrons inside the kapton foil surrounding the ^{22}Na source ($\tau_k = $ 386 ps). The longest-lived component ($\tau_3 = $ 2.076-2.458 ns and $I_3 = $ 7.08-24.0 %) is attributed to o-Ps atoms annihilating via a pick-off process in free volume of amorphous regions of the polystyrene. Using the relationship (1) between τ_3 and R, the hole radius (R) and the free volume hole size (V) were computed (Table 2).

Associated with the pick-off process, the lifetime τ_3 exhibits a decrease as a function of the density of the samples. The decrease in τ_3 is related to the change of the free volume resulting from the formation of new bonds or cross-linking. This decrease in τ_3 implies some shrinking of inner and inter chain of free volume holes [8]. The average free volume was found to decrease from 137 to 104 Å^3. The value obtained for solid polystyrene (104 Å^3) corresponds well to the data reported by [4] (102-105 Å^3). The intensity of the
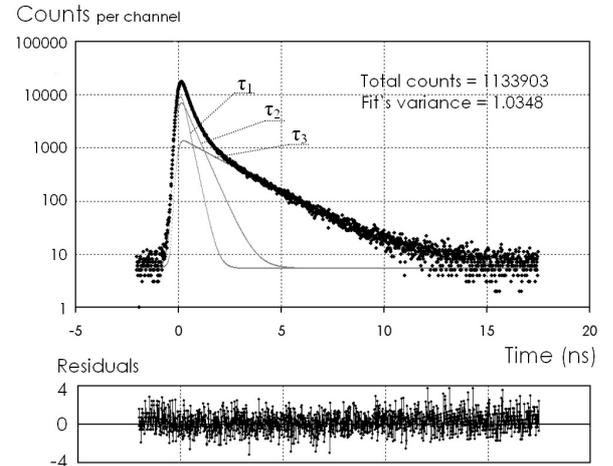
Fig. 2 Upper panel: delayed-coincidence spectrum obtained for solid polystyrene (HDPS). The result of the deconvolution of the spectrum into contributions of individual positron fractions to the annihilation process is shown. Lower panel: difference between the experimental spectrum and its fit expressed in units of standard deviation.

Table 1 The mean implantation depth z_m of positrons with energy $E = 150$ keV for polystyrenes of density ρ.

sample	ρ (kg/m^3)	z_m (mm)
LDPS1	10.9	11
LDPS2	15.4	7.9
LDPS3	23.3	5.2
HDPS	96·10^1	0.13

Table 2 The positron annihilation lifetime components (τ_1, τ_2, τ_3) and their intensities (I_1, I_2, I_3) for foamed polystyrenes (LDPS1,2,3), solid polystyrene (HDPS), and foamed polystyrenes exposed to open air (LDPSWC1,2,3). The radius R of the free volume was estimated using Eq. 1, the volume V was calculated from $(4/3)\pi R^3$.

sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	R (Å)	V (Å^3)
LDPS1	261.6 (5.7) [a]	62.6 (2.1)	522 (20)	29.9 (2.1)	2410 (32)	7.48 (0.33)	3.197	137
LDPS2	264.8 (6.6)	61.7 (2.3)	529 (23)	28.7 (2.4)	2304 (25)	9.56 (0.45)	3.112	126
LDPS3	268.4 (5.3)	62.8 (1.6)	590 (28)	23.5 (1.7)	2296 (22)	13.63 (0.48)	3.105	125
HDPS	231 (11)	34.5 (2.4)	487 (17)	41.5 (2.2)	2076 (14)	24.0 (1.1)	2.917	104
LDPSWC1	260.3 (5.4)	62.9 (1.9)	528 (18)	30.0 (1.9)	2458 (40)	7.08 (0.30)	3.235	142
LDPSWC2	262.2 (6.1)	60.8 (2.1)	533 (21)	30.1 (2.1)	2370 (32)	9.13 (0.41)	3.165	133
LDPSWC3	269.2 (3.9)	63.1 (1.2)	603 (23)	23.7 (1.3)	2308 (22)	13.18 (0.36)	3.115	127

[a] standard deviations are given in round brackets

long-lived component (I_3) exhibits an increase (from 7.48-24.0 %) with increasing density of the samples. The observed increase of I_3 with the maximum reached for the densest material (HDPS) may be surprising. One might suspect a rather low number of holes for a high-density material with low insulating properties. The obtained results do not contradict that opinion, but show the lack of a proportional relation between the number of micropores, represented by I_3, and the density of samples with pore dimensions of up to ~0.7 nm.

The lifetimes and intensities obtained for the samples exposed and not exposed to open air do not differ significantly, though, a small tendency to increasing of the free volume and decreasing of the micropore concentration, represented by I_3, is observed as a function of density. Assuming that small dimensions of micropores and large values of I_3 are characteristic for materials with relatively modest thermal properties, the tendencies observed for τ_3 and I_3 reflect the deterioration of the thermal properties of the samples by weather conditions.

References

[1] Y. Kobayashi, K. Ito, T. Oka, K. Hirata, *Radiat. Phys. Chem.* 76 (2007) 224-230.

[2] Y. Honda, M. Watanabe, M. Tashiro, Y. Terashima, K. Miyamoto, N. Kimura, S. Tagawa, *Radiat. Phys. Chem.* 68 (2003) 463-465.

[3] M. Ban, M. Kyoto, A. Uedono, T. Kawano, S. Tanigawa, *J. Radioanal. Nucl. Chem.* 210(2) (1996) 476-484.

[4] E.E. Abdel-Hady, H.M. Abdel-Hamid, Hamdy F.M. Mohamed, *Radiat. Meas.* 38 (2004) 211-216.

[5] S.J. Tao, *J. Chem. Phys.* 56 1972) 5499.

[6] M. Eldrup, D. Lighbody, J.N. Sherwood, *Chem. Phys.* 63 1981) 51.

[7] J. Kansy, *Nucl. Instrum. Methods Phys. Res., Sect. A* 374 (1996) 235.

[8] R. Kumar, R. Prasad, *Radiat. Meas.* 40 (2005) 750-753.