

SHAPES OF THE FREE VOLUME HOLES IN AMORPHOUS POLYMERS AS ESTIMATED BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY*

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Intermolecular spaces in polymer chains form the free volume, a useful concept to understand mechanical and transport properties of polymers. Quantification of the free volume can be obtained theoretically, using appropriate lattice models, as well as experimentally, through suitable probes. Among these, positronium (Ps) has become widespread due to the non-destructive character of the technique and the correlation between the Ps lifetime and the size of the holes. In most of the investigations, the cavity is approximated to a sphere. However, this may bias the evaluation of the free volume fraction. We show that by coupling results from Ps lifetime and specific volume measurement for amorphous polymers at equilibrium and the predictions of the Simha–Somcynsky equation of state, it is possible to shed light on dimensions of the holes as well as on their morphology.

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1. Introduction

The concept of free volume [1] turns out to be useful for explaining various properties of amorphous polymers such as diffusivity and ageing. The positron annihilation lifetime spectroscopy (PALS) [2] is a valuable technique to obtain information on the free volume due to its non-destructive character. Positronium, Ps, the unstable positron–electron bound system, localizes preferably in the open spaces of the host structure (*e.g.*, free volume holes in polymers), since it is repelled from the medium due to the exchange repulsion between the Ps electron and the surrounding electrons. Inside a hole ortho-Ps (o-Ps), the triplet ground state sub-level may annihilate with

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an external electron in a relative singlet spin state. This ‘pickoff’ process greatly reduces the lifetime of o-Ps as compared to its value in a vacuum (142 ns). The mechanism is the more efficient the smaller is the cavity, and it is possible to correlate the o-Ps lifetime to the typical size of the host hole by framing this last within a suitable geometry.

In order to get quantitative information on the (specific) free volume V_f

$$V_f = Nv_h, \quad (1)$$

or on the free volume fraction f

$$f = \frac{V_f}{V} = \frac{Nv_h}{Nv_h + V_{occ}} \quad (2)$$

(V is the specific volume, V_{occ} is the specific occupied volume, N is the number density of holes and v_h is the average volume of holes), we need to know N and V_{occ} . These quantities can be obtained by correlating specific volume measurements with the hole volumes from PALS. The guess about the hole geometry is, therefore, important in order to get — through the quantity v_h — the correct free volume fraction. Real holes are universally assumed to be spherical and we can ask ourselves if non-spherical geometries may better describe the holes [3]. In the following, we aim to show that a suitable comparison between f and the analogous quantity provided by the lattice-hole theory [4] may give us insights on the holes morphology.

2. Performed experiment

Specific volume measurements were performed by means of a capillary dilatometer containing the sample surrounded by mercury (purity > 99.999%, Fluka), used as the reference liquid. The temperature cooling runs were carried out by immersing the filled dilatometer in a thermostatic bath. Minimal stability of the temperature was within 0.5 K. The level reached by mercury into the capillary, determined by means of a cathetometer with digital reading, supplied the variations of specific volume. They were converted into absolute specific volume, V , by requiring that the value obtained at 298 K would coincide with that measured by buoyancy method in the same conditions.

PALS measurements were carried out on cylindrical samples. Their thickness (2 mm) was sufficient to stop all the injected positrons. The positron source (^{22}Na , activity 0.2 MBq) was enveloped between two Kapton[®] foils (thickness 7.6 μm each) and placed in a metallic sample holder, in direct contact with the heat exchanger of a liquid nitrogen cryostat (DN 1714 Oxford Instruments). Positron annihilation lifetime spectra were collected through a conventional fast-fast coincidence setup. Each spectrum, containing at least 2 Mcounts, was analyzed through the computer code LT [5].

3. Results and discussion

It is worth to give a very short introduction to the Simha–Somcynsky (S–S) equation of state [4]. It is obtained from the lattice–hole model: an amorphous polymer is considered as an assembly of chain molecules placed on the sites of a lattice. In order to simulate the molecular disorder, a fraction of vacancies is also considered, which represents a free volume quantity. The following S–S equation derived from the theory relates, at atmospheric pressure, specific volume and temperature of the polymer under investigation

$$\tilde{T} = 2y \left(y\tilde{V} \right)^{-2} \left\{ 1.2045 - 1.011 \left(y\tilde{V} \right)^{-2} \right\} \left\{ 1 - 2^{-1/6} y \left(y\tilde{V}^{-1/3} \right) \right\} . \quad (3)$$

These two quantities are expressed in terms of reduced thermodynamic coordinates $\tilde{T} = T/T^*$ and $\tilde{V} = V/V^*$. The requirement of equilibrium (minimization of the Helmholtz free energy) produces a second relationship between the two thermodynamic quantities

$$1 + y^{-1} \ln(1 - y) = \left(\frac{y}{6\tilde{T}} \right) \left(y\tilde{V} \right)^{-2} \left\{ 2.409 - 3.033 \left(y\tilde{V} \right)^{-2} \right\} + \left\{ 2^{-1/6} y \left(y\tilde{V} \right)^{-1/3} - 1/3 \right\} \left\{ 1 - 2^{-1/6} y \left(y\tilde{V} \right)^{-1/3} \right\}^{-1} . \quad (4)$$

Scaling parameters T^* and V^* depend on the specific investigated material and can be found by fitting the two above equations with the specific volume data.

In Eqs. (3), (4), y represents the volume fraction of occupied sites; consequently, $h = 1 - y$ plays the role of the calculated free volume fraction, which is adapted to the investigated polymer once the scaling parameters are known. The quantity h can be compared to the analogous quantity f as supplied from the experiment; this allows one to get some insight on the hole morphology. An example will clarify the adopted methodology.

Let us consider the results of an investigation carried out on two rubbers: a cis-polyisoprene (PIP) and a perfluoro rubber (PFR). They show a linear backbone, but PIP has an unsaturated carbon chain, contrarily to PFR. Furthermore, lateral groups in PFR mainly consist of $-\text{CF}_3$ instead of $-\text{CH}_3$.

Figure 1 shows the specific volume measurements carried out in the two rubbers.

These data are fitted by Eqs. (3) and (4) to obtain the scaling parameters T^* and V^* , which are essential to calculate h . It results in $V^* = 0.5163$ (3) $\text{cm}^3 \text{g}^{-1}$ and $T^* = 9161$ (26) K for PFR and $V^* = 1.0535$ (4) $\text{cm}^3 \text{g}^{-1}$; $T^* = 9547$ (29) K for PIP. Figure 2 shows the o-Ps decay rate as a function of the temperature in the two rubbers; it represents, within a very good approximation, the pickoff decay rate.

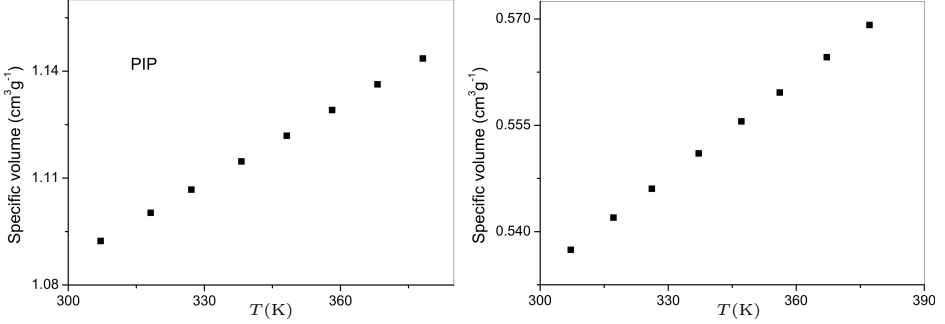


Fig. 1. Specific volume *versus* temperature in PIP (left) and in PFR (right).

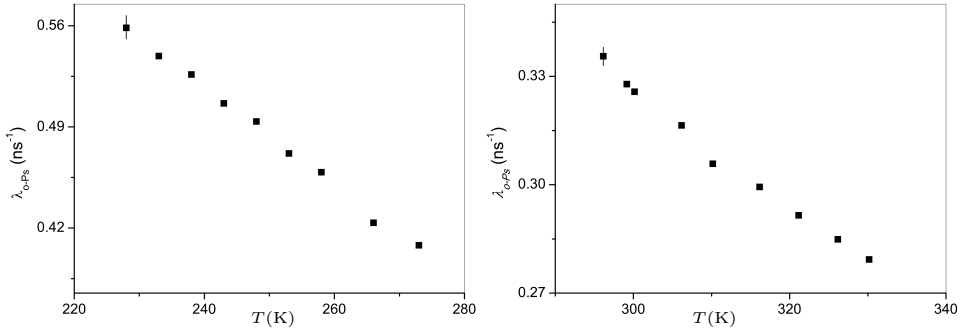


Fig. 2. o-Ps decay rate *versus* temperature in PIP (left) and in PFR (right).

We transform these rates into radii (R) of a spherical hole by using the Tao–Eldrup equation [6, 7]

$$\lambda_p = \lambda_0 \left[\frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(2\pi \frac{R}{R + \Delta R} \right) \right], \quad (5)$$

where $\lambda_0 = 2 \text{ ns}^{-1}$ and ΔR describes the penetration of the Ps wave function into the bulk. We now evaluate the specific volumes at the same temperature of the hole volumes and plot in Fig. 3 the specific volume *versus* the hole volume.

Since $V = Nv_h + V_{\text{occ}}$, it is concluded that, at least in the investigated ranges of temperatures, N and V_{occ} can be considered constant, since they represent slope and intercept of a straight line, respectively. Next, the free volume fraction f can be obtained, according to Eq. (2) and compared to the theoretical quantity h . The results, shown in Fig. 4, point out a systematic departure of f with respect to h .

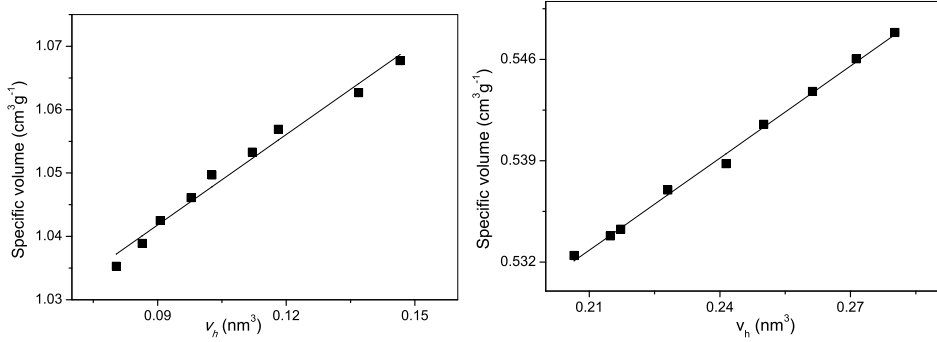


Fig. 3. Specific volume V versus the hole volume v_h (in spherical approximation) in PIP (left) and in PFR (right).

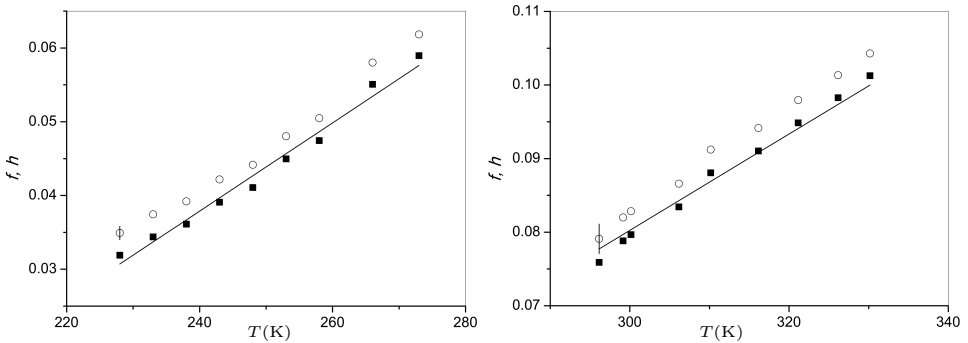


Fig. 4. Free volume fraction f assuming spherical holes (empty circles) or elongated cylinders (full squares) for PIP (left) and for PFR (right). Continuous line: theoretical free volume fraction h . Estimated uncertainties are shown for the data at the lowest temperature.

In order to solve the discrepancy, we make a different guess on the shape of the holes by assuming a cylindrical geometry: holes were approximated to finite cylinders with aspect ratio ξ between the height a and the radius R of the cylinder. The pertinent formula relating λ_p to R and a can be found in [8, 9].

The radius R is obtained numerically once the o-Ps lifetime is known. The hole volume becomes

$$v_h = \pi a R^2 = \pi \xi R^3. \quad (6)$$

The same procedure to obtain f starting from spherical holes was repeated, using ξ as a free parameter. The result, also shown in Fig. 4, is in a very good agreement between f and h for $\xi = 2.4$ and 4 for PIP and PFR, respectively. Physically, it means that elongated holes ($\xi > 1$) better represent

real holes with respect to spheres. We note that this result is in agreement with molecular dynamics simulations, indicating an elongated, rather than spherical, shape for holes in some stiff-chain polymers [10, 11].

4. Conclusions

PALS is a valuable technique to obtain typical sizes of the holes forming the free volumes in amorphous polymers. Nevertheless, in order to get the free volume fraction, it is needed to couple PALS to another technique, able to give the number density of holes. The amount of the free volume depends on the geometry assumed for the holes. The spherical assumption may not be the best choice for some classes of macromolecules. In this paper, we have shown how it is possible to combine PALS and dilatometry to obtain the relevant quantities (N and V_{occ}) to assess the free volume. The comparison between the two quantities f and h gives us the possibility to get insight on the shape of the holes.

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