Anisotropic Nature of Open Volume "Defects" in Highly Crystalline Polymers

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ABSTRACT: We assess the size and shape of the free volume holes in crystalline polyethylene fibers (crystallinity ∼85%) via the measurements of confinement momenta of parapositronium trapped within these holes. The holes show considerable anisotropy and a shape that is compatible with those created by chain folds buried in the crystal lattice. We estimate their sizes to be ∼8 and 5 Å in two perpendicular directions. These are also compatible with those argued from the lattice parameter and other geometrical considerations.

Introduction

One of the important elements of polymer microstructure is the existence of sub-nanometer local free (empty) volume holes in amorphous polymer materials, which arises from their structural disorder.[1] Such holes (typically a few angstroms in "diameter") play a crucial role in determining a variety of polymer properties such as the permeation of gas and liquid through such materials, changes in their behavior under pressure or strain and under the influence of plasticizers, and changes in their general mechanical and rheological properties. In the past, the dimensions of these holes and their distributions have largely been derived from theoretical models. A number of experimental techniques have been applied to probe these hole sizes and their fractional volume. However, only limited information has been available due to the lack of a suitable probe of atomic scale.[1] The traditional techniques, e.g., small-angle X-ray and neutron scattering, used for the characterization of pores sizes and their distribution in porous materials are sensitive to pores of significantly greater dimensions. Although diffusion of gases through polymers is a more suitable probe, the pore size distribution can have a considerable tail, and a significant part of the holes may be smaller than the probing gas molecule. This may lead to an overestimation of the pore size and underestimation of their concentration. In recent years, positronium annihilation spectroscopy has provided a unique subatomic probe to study the dimensions of such cavities in polymers.[2]

The possible anisotropic shape of such holes or other possible defect types in stretched semicrystalline polymers is an additional important issue of the polymer microstructure. Such anisotropies may arise due to preparation process (e.g., melt-spinning of high-modulus fibers, buried chain folds in the crystal lattice) or through uniaxial or biaxial plastic stretching. These structural anisotropies may have important consequences on the material properties. For example, the permeability of a polymer membrane for a given gas can be varied via stretching (e.g., through reduction in one of the dimensions of the holes that allows permeation). The high-modulus fibers derive their tensile strength from fast cooling of their stretched structure. The relaxation behavior of the frozen structure is important for their durability and can be studied via the changes in the anisotropy of the holes where appropriate. In this paper, we evaluate the size and anisotropy of open defects due to buried chain folds and other anisotropic holes in highly crystalline polyethylene fibers using positron annihilation spectroscopy.

In polymers a substantial fraction of the injected positrons form and annihilate from a bound state called positronium (Ps) within the local free volumes. The Ps forms either in the so-called parapositronium (p-Ps: antiparallel electron and positron spins) or orthopositronium (o-Ps: parallel electron and positron spins) states with a relative abundance of 1:3. In a vacuum, a p-Ps has a lifetime $\tau^{\circ}_{p-Ps} \sim 125$ ps and annihilates via two γ-photons while an o-Ps lives ∼140 ns and annihilates via $3-\gamma$. Confined within the free volume in polymers, the long-lived o-Ps has a finite probability of annihilating with an electron other than its bound partner (and of opposite spin) during the numerous collisions that it undergoes with the surrounding molecules, a process generally termed as "pick-off". The result is a drastically reduced o-Ps lifetime, which can be related to the size of the hole that confines the o-Ps.

The predominant mode of decay for the p-Ps is self-annihilation. The p-Ps is thermalized prior to annihilation, but it possesses momentum due to its confinement within the free volume holes. This momentum can be measured via the so-called 2-dimensional angular correlation of the $2-\gamma$ electron−positron annihilation radiation (2DACAR).[3] The 2DACAR technique measures a two-dimensional projection[3]

$$N(\vartheta,\varphi) \equiv N(p_x,p_y) \equiv \int \rho(\mathbf{p})\, \mathrm{d}p_z \qquad (1)$$

of the underlying 3-dimensional momentum density $\rho(\mathbf{p})$ along p_z, where (ϑ, φ) are angles between the two photons and p_x, p_y define the projection plane. The full momentum density curve is a superposition of a narrow (approximately Gaussian) component due to the self-annihilation of p-Ps and much broader distributions (also approximately Gaussians) arising from the annihilation of free positrons and the o-Ps pick-off process. The narrow component reflects the confinement momentum of the p-Ps due to its localization within the holes. In a simple quantum-mechanical model, it is

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assumed that the Ps is confined in a spherical potential well of radius r and an infinite depth with a spatial overlap of the Ps with molecules within a layer δr of the potential wall. This provides a relationship between the full width at half-maximum (fwhm) of the narrow component and the radius of the hole in a given momentum direction[4]

$$r = \frac{1.66}{\text{fwhm}} - \delta r \qquad (2)$$

Here, the fwhm is in mrad, r is in nm, and δr is empirically derived to be 0.166 nm. The directional dependence of the confinement momentum allows directional probing of the extent of the confining volume and therefore its shape.

The success of such measurements and the evaluation of the size and shape of the volume that confines the positronium depends on accurate separation of the p-Ps narrow component from the other contributions to the 2DACAR spectrum. Previous authors[5] have used the 2DACAR technique to look at the effect of stretching on the orientation of free volume holes in PEEK. In their work, they separated the p-Ps component by fitting a three-component Gaussian model to one-dimensional spectra obtained from the measured two-dimensional momentum distributions. These one-dimensional spectra were obtained by integrating across the 2D array along various axes through the data. The advantage of such an integration across the other dimension is an increase in statistics. However, this technique must be used with caution. By analyzing model anisotropic data, we have shown that this procedure can seriously distort the true shape of the p-Ps component, introducing an anisotropy that is purely a result of this integration procedure. If sufficient counts are accumulated, an alternative way to obtain one-dimensional spectra is to look at sections through the two-dimensional distribution along various directions. Analysis of model data in this way shows that this procedure does not introduce extra anisotropy into the results. Therefore, despite the reduced statistical accuracy, we use only sectioned spectra in our subsequent analysis.

Morphology of the Polyethylene Fibers

The polymer samples were highly crystalline (~85%), highly oriented polyethylene fibers produced via the gel-spinning technique.[6] The schematic structure of these gel-spun fibers is shown in Figure 1.[7] The polymer chains form elongated crystals that are connected by fringelike amorphous regions. The chains that emerge from these amorphous regions may fold back on themselves in a manner similar to that found in a "shish-kebab" structure. The bulk fiber consists of bundles of these extremely fine fiber structures twisted together.

The nature of the free volume in these fibers is likely to be relatively complex. In the crystalline regions, there will be free volume between the crystal planes. As shown in Figure 1, there are also defects in the crystalline fiber cores. Order is broken occasionally in this region by the chains folding back on themselves. Another chain also reverses direction further down the backbone, leaving a void. The size of these holes have been estimated from considerations of the crystal structures. Their width perpendicular to the polymer chains is set by the lattice parameters of the polyethylene crystal, and in the y-direction they can be no longer than

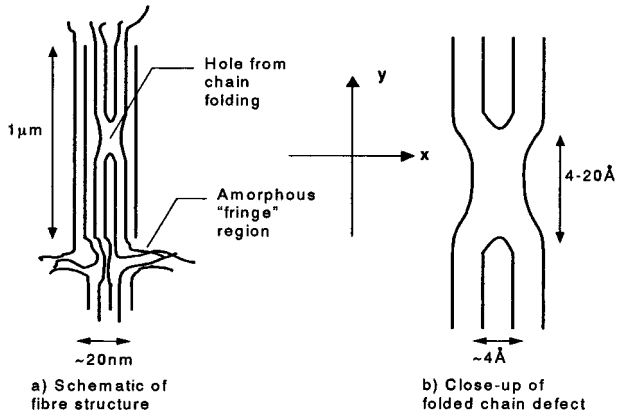

Figure 1. A possible schematic diagram of an anisotropic defect in the highly crystalline polyethylene due to buried chain fold within the crystal. The coordinate system relates to the crystallographic axes discussed in the text.

~20 Å; otherwise, the hole is likely to be filled by a fold in a neighboring chain. At the junction between the crystalline and amorphous regions, there are "fringes" where many of the chains cross over or leave the backbone before another crystalline region begins. These fringes, although still having a high degree of order, contain a greater density of similar voids since most of the disorder is forced into these short regions by the drawing process. Many such backbones are linked and wound together to form the bulk of the fiber. The structure of the amorphous fringe regions is complicated, but it does contain free volume holes. As these regions are also highly oriented, the shape of the free volume in these regions should reflect this.

Experimental Details

The polymer samples obtained were in the form of fibers of ~25 μm in diameter. To provide adequate surface area for our experiments, a specimen (1 cm × 1 cm × 2 mm) was prepared by carefully winding the fiber around a wire former, ensuring that each turn was vertical. Two 2DACAR spectra were obtained using the University of Bristol spectrometer[3] at a sample temperature of ~70 K. In the first experiment, the fibers were aligned along the y-axis of the spectrometer as shown in Figure 1. The second spectrum was collected with the fibers aligned at 45° to the spectrometer y-axis in the $y-z$ plane. Following the standard correction of the spectra to account for the detection geometry,[3] the spectra were folded along the x- and y-axis to improve the statistical precision. The spectra (accumulated in 512 × 512 arrays with bin widths of 0.098 mrad of momentum) contained a total of ~400 × 10^6 effective counts with the fibers along the y-axis and ~300 × 10^6 effective counts with the sample tilted at 45°.

Results and Discussion

To assess any anisotropy in the measured two 2DACAR spectra, we first inspect the radial anisotropy of the distributions. The radial anisotropy is calculated by subtracting the cylindrical average of the distribution from itself $N(p_x,p_y) - N(\sqrt{p_x^2+p_y^2})$. In the case where the fibers are aligned along the y-axis, we observe substantial anisotropy which is shown in Figure 2.

This anisotropy can have a number of origins: (i) p-Ps confinement in a combination of the anisotropic defects created by the chain folding shown in Figure 1 and the possible "anisotropic" free volume "holes" present in the fringe regions where the crystalline and amorphous regimes of the polymer form interfaces; (ii) due to the crystalline anisotropy itself. The origin of any crystalline

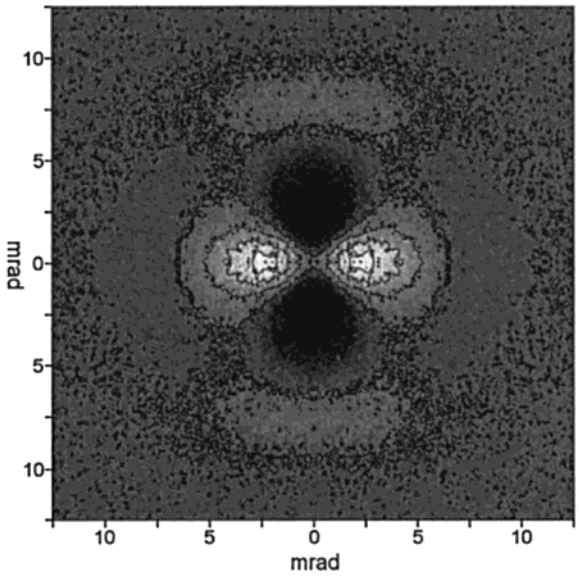

Figure 2. Radial anisotropy in the measured positron/positronium momentum density with the fibers orientated along the *y*-axis.

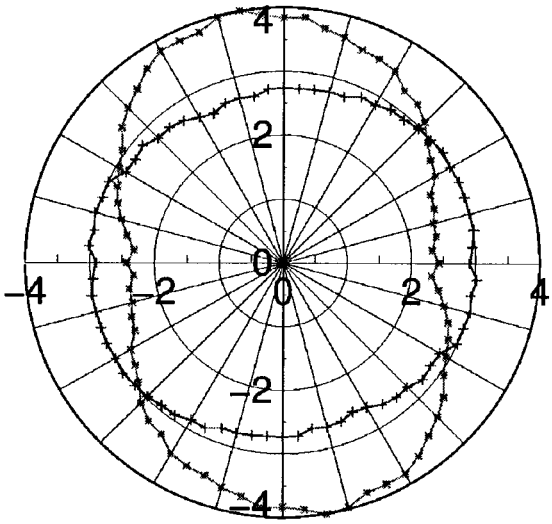

Figure 3. Size and shape of the free volume holes in crystalline polyethylene fibers determined experimentally via directional dependent parapositronium momentum displayed as polar diagrams. The grid rings are 1 Å apart. The curve elongated along the vertical direction represents a projection of the hole on to the $x-y$ plane of Figure 1. The roughly circular curve is the cross section of this defect viewed from an angle of 45° to the vertical.

anisotropy would be due to the anisotropic electronic momentum density in the underlying crystal lattice. In a metallic system, this may be a combination of the anisotropy of the conduction electron momentum density (Fermi surface anisotropy) and any anisotropy associated with more tightly bound electrons as seen by the propagating positron. In an insulating system, as is the case here, the anisotropy would be entirely due to the latter. In either case, if the sample is rotated in the spectrometer with respect to the integration axis p_z, the measured spectrum would contain the underlying anisotropy of the same magnitude but projected along a line at a different angle. However, in our experiment, the spectrum where the fibers were orientated at 45° to the *y*-axis shows very little radial anisotropy (not shown to save space), indicating that the electron momentum density associated with the crystallinity is essentially isotropic. This we also take to be the sign that the anisotropy seen in Figure 2 has its origin in the p-Ps confinement in anisotropic defects. The largely isotropic nature of the spectra for the sample in 45° rotation can then be explained in terms of the projection of the defect as a fairly circular cross section of the free volumes in this orientation.

To obtain a quantitative evaluation of the shape and size of these defects, 1-dimensional sections were taken through the center of the measured 2-dimensional momentum density at 5° intervals and three superposing Gaussians were fitted to these sections. The size of the confining volume in the appropriate direction was calculated from the fwhm of the narrowest Gaussian using the model above (eq 2) and subsequent deconvolution of the contribution of the finite spectrometer resolution. The results derived from the two momentum density spectra are presented in Figure 3 as a polar plot.

The individual points are linked together with line segments only to guide the eye. The "pinched rectangular" shaped curve elongated along the *y*-axis derived from analysis procedure represents the average shape of a possible confining volume for a p-Ps in the measurement geometry with the fibers orientated along the *y*-axis (see Figure 1). Via experiments in stretched and unstretched semicrystalline (crystallinity ∼20%) polymer PEEK, Jean and co-workers[5] found that the shape of the free volume holes in the stretched polymer was ellipsoidal while those in the unstretched samples were fairly spherical. The measured average shape in our experiment must also contain such an ellipsoidal (and even some spherical) contribution arising from holes within the amorphous or in the fringe regions. However, the remarkable resemblance of this figure to the schematic drawing of the defect (see Figure 1) due to faulty chain folding in the crystalline regions suggests that the dominant type of open volumes are of this kind. It is also interesting to note that the average dimensions of this confining volume of ∼8 Å along *y* and ∼5 Å along *x* are well within the expected range derived from geometrical considerations shown in Figure 1. Given the high crystallinity of the specimens, this is perhaps not surprising. It has to be noted that, given the nature of eq 2, as the fwhm becomes large, the subtraction of a constant δr can lead to the pinching effect observed along the *x*-axis in Figure 2. However, our analysis without subtracting the constant in eq 2 still produces the pinched shape, confirming that it is contained in the momentum density although the subtraction process can itself produce some uncertainty in its magnitude.

When the sample is orientated with the fibers at 45° to the *y*-axis, one would expect to project a fairly circular cross section across the belly of the anisotropic defect with small anisotropy. Our observation, as shown in Figure 3, is compatible with this expectation. The average diameter of this projection is ∼6 Å, which is also compatible with the expected projection of the belly region being longer than the diameter of the belly itself.

Conclusions

Via the measurement of the 2-dimensional momentum densities of parapositronium confined in free volume holes and other defects in highly crystalline polyethylene fibers, we show that the predominant defects are those arising from buried chain folds. The

observed shape of these defects is highly anisotropic and compatible with predicted models. Their observed dimensions are also within the expected ranges.

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