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Application of Positron Annihilation Lifetime Spectroscopy in Studies of Polymer Composites

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A brief review of the concept of the free volume and its fraction in polymer composites is presented. The experimental results obtained using positron lifetime spectroscopy for the detection of these volumes in two composites of poly(glycolide-co-L-lactide) with bioactive glasses and mixes of ethylene propylene diene monomer and surface-modified precipitated silica are discussed in more detail. It is demonstrated that the free volume fraction exhibits a linear relationship with the bioactive glass content in the first composite. However, in general, deviations from linearity can be induced by the presence of the interfacial regions between the filler and the polymer matrix. Additionally, the Psc_12 computer program, which calculates radii of free volume holes, pores, and capillaries from the values of the ortho-positronium pick-off annihilation lifetime, is described in detail.

topics: polymer composites, positron annihilation lifetime spectroscopy, free volume

1. Introduction

The concept of free volume is widely used to explain various phenomena and properties related to polymers. It was originally introduced for liquids [1] and was then developed for amorphous polymers. Free volume is defined as the difference between the total volume and the occupied volume [2]. The free volume defined in this way comprises two contributions, depending on the temperature. First is the so-called vibrational free volume, i.e., the volume surrounding the "hard core" occupied volume that encompasses the vibrational movements of polymer segments. Second is the so-called excess free volume, i.e., the additional free volume required to reach the overall total volume, which allows for the random movement of polymer segments [3]. In polymers, the excess free volume includes free spaces between polymer chains. These spaces occur between imperfectly packed polymer chains and even between perfectly aligned polymer chains. Free volume influences various utility properties, including molecular mobility, diffusion of small molecules, mechanical relaxation, thermal behavior, and longevity, as well as interfacial degradation and moisture ingress.

One method for obtaining materials with new properties that meet the needs of various applications is to create a dispersion of inorganic or metallic particles in a polymer matrix. Such materials are referred to as polymer composites or nanocomposites [4]. It is often associated with changes in the free volume properties of the material resulting from the creation of an interface between the filler and the polymer matrix. Controlling the free volume (i.e., its fraction, average size, and distribution) is therefore important for practical reasons, especially in demanding applications. Various experimental methods are used to characterize free volume in polymers, either directly or indirectly [5]. Among these methods, positron annihilation lifetime spectroscopy (PALS) is most often used. It is worth mentioning that PALS also creates opportunities to study more complex systems, such as biological objects [6, 7]. This brief review provides examples of applying PALS to characterize free volume in polymer composites. It also describes a new software tool that calculates free volume hole sizes from PALS data.

2. Positron annihilation lifetime spectroscopy

When an energetic positron from a radioactive source (usually ^{22}Na) enters the polymer, it slows down by interacting with atoms and electrons, and creates an ionization track (spur) [8, 9]. According to the spur model, a blob is created at the end of the

spur, i.e., an area containing ion-electron pairs. The thermalized positron can form a localized positronium (Ps) atom, i.e., a bound state positron-electron, with a secondary electron created through ionization. Ps can be formed in a single or triplet spin state, which are called para-positronium (p-Ps) and ortho-positronium (o-Ps), respectively. The lifetime of p-Ps is 125 ps in vacuum, and o-Ps can survive a long time, i.e., 142 ns in vacuum. However, in polymers, when o-Ps is localized in regions of low electron density (free volume holes), the bound positron can annihilate with another electron from the environment, e.g., a wall of the free volume in the so-called pick-off process. Hence, the o-Ps lifetime is significantly shortened to a few nanoseconds. In a typical PALS spectrum for polymers, there are usually three components: the short-lived p-Ps component with lifetime τ_1 close to 125 ps and intensity I_1, the intermediate one, coming from annihilation of free positrons with lifetime τ_2 and intensity I_2, and the o-Ps component with lifetime τ_3 and intensity I_3.

Based on quantum mechanics, assuming that o-Ps is in the ground state in the infinite square well of spherical shape, Tao [10] and Eldrup [11] obtained the well-known formula which links the measured long positron lifetime τ_3 with the free volume radius R as follows

$$\tau_3\ [\mathrm{ns}] = 0.5\left[1 - \frac{\mathrm{R}}{\mathrm{R}+\Delta} + \frac{1}{2\pi}\sin\left(\frac{2\pi\mathrm{R}}{\mathrm{R}+\Delta}\right)\right]^{-1}. \quad (1)$$

The infinitely deep well is broadened by a layer of thickness Δ, where the bounded positron can penetrate and find an outer electron. Its thickness was established experimentally and is equal to 0.1656 nm. The Tao–Eldrup formula (1) is successfully applied to free volume holes in polymers or bubbles forced by Ps in liquids at low temperatures, where the radius range is $\simeq$ 0.2–0.4 nm. This formula was incorporated into the Psc_12 computer program, which is available for download from the website [12]. Other options of the Psc_12 program useful for positron porosimetry are described in the Appendix.

Interpreting the meaning of o-Ps intensity I_3, obtained from the deconvolution of the measured PALS spectrum, is more complicated. Kobayashi et al. [13] proposed that I_3 corresponds to the number density of free volume holes in the polymer amorphous phase. However, some processes can also influence the formation and annihilation of o-Ps. For example, I_3 may decrease due to the inhibition of o-Ps formation in certain polymers caused by the build-up of species in the ionization spur during irradiation by the positron source. These species compete with Ps formation [9].

However, assuming that I_3 is proportional to the number density of free volume holes, the fractional free volume (FFV) is given by

$$\mathrm{FFV} = C\, I_3\, \langle v_h \rangle\,, \quad (2)$$

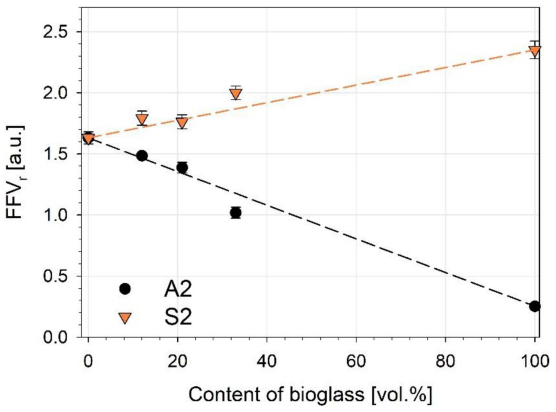

Fig. 1. The dependence of the relative FFV on the bioactive glass content for the PGLA/bioactive glass composites with two different bioactive glasses denoted as A2 and S2. Based on data from [15].

where C is a constant and $\langle v_h \rangle = 4\pi R^3/3$, where R is the mean free volume hole radius obtained from (1). The constant was estimated to be 0.0018 for many polymers [14]. Due to chemical differences between polymers, it may be more appropriate to use the relative FFV with $C = 1$, denoted as FFV$_r$. However, (2) should be used with caution because the presence of certain chemical groups in the studied material may cause not only changes in I_3 but also in τ_3 value, e.g., due to chemical quenching [8].

3. Free volume in polymer composites probed by PALS

In polymer composites, filler particles dispersed in the polymer matrix influence the free volume. This is especially the case for nanocomposites. The interaction between the surface of the filler particles and the polymer matrix gives rise to the formation of an interfacial layer of the polymer, which has distinct properties that differ from those of the bulk matrix. Figure 1 shows the dependence of the relative FFV (FFV$_r$) on filler content for two composites of poly(glycolide-co-L-lactide) (PGLA) with bioactive glasses [15]. As in the case of the free volume hole size and I_3 dependencies, deviations of FFV$_r$ from linear additivity are small. This is understandable for a microcomposite in which the filler particle surfaces were not functionalized.

In many cases, deviations from the linear additivity of these parameters were found for nanocomposites [16]. This has been explained as a result of the agglomeration of filler particles, which causes a reduction of interfacial regions. To describe the deviation from linear additivity of FFV, the so-called β interaction parameter, originally proposed for polymer blends, was adopted [17], defined by

$$f = f_1\Phi_1 + f_2\Phi_2 + \beta f_1 f_2 \Phi_1 \Phi_2, \quad (3)$$

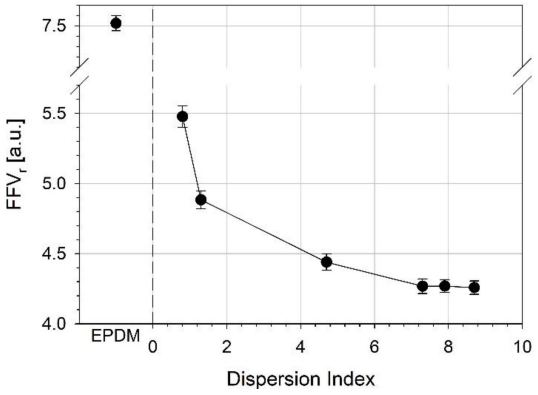

Fig. 2. The dependence of the relative FFV on the dispersion index value for the EPDM/silica mixes with the same silica content. Based on data from [19].

where f, f_1, and f_2 are FFVs of the composite, the matrix, and the filler, respectively; Φ_1 and Φ_2 are specific volume fractions of the matrix and the filler, respectively. An analogous parameter was also defined to describe the deviation from linear additivity of the intensity of the intermediate positron lifetime component I_2 (see, e.g., [18]).

This influence of filler dispersion on the free volume was directly verified for a series of mixes of ethylene propylene diene monomer (EPDM) and surface-modified precipitated silica, with the same filler content, prepared in such a way that they differed in filler dispersion [19]. As an example, Fig. 2 shows the dependence of the relative FFV of the mixes and pure EPDM on the dispersion index. The better the filler dispersion, the higher the dispersion index. Due to chemical binding between the silica surface and the polymer matrix, a dense interfacial layer is created, for which the o-Ps formation probability is reduced. Agglomeration of filler particles in the poorly dispersed mixtures, as confirmed by atomic force microscopy (AFM), resulted in a reduction of the interfacial layer [19].

The interfacial layer helps the stress transfer between the nanoparticles and the matrix. It was found that FFV$_r$ is correlated with the mechanical properties of carbon-fiber-reinforced polymers [20]. Better filler dispersion and stronger interfacial interactions also improve other properties of the composites, such as thermal resistance [18].

PALS studies have shown that tensile deformation changes the free volume structure in fiber-reinforced polymers [21]. After the tensile test, larger free volume holes were created at the fracture points in the carbon-fiber-reinforced polymer. They resulted from the agglomeration of the intrinsic free volume holes in the polymer matrix due to breaks in polymer chains upon fracture [22].

In some cases, the nanofiller addition to a polymer matrix can lead to an increase in free volume with increasing nanofiller concentration, indicating the creation of larger free volume holes when the interaction between the matrix and the filler is weak [23]. For polymer clay nanocomposites, the interstitial cavities in filler agglomerates can also increase free volume [24].

Free volume in polymer composites influences their transport properties. The results of the composite membrane studies using a slow positron beam correlate with the permeability and selectivity of the membranes, which are connected to their applications in pervaporation, nanofiltration, microfiltration, ultrafiltration, and gas separation [25].

A thorough review of PALS studies in nanocomposites can be found in [16].

4. Conclusions

Positron annihilation lifetime spectroscopy has been demonstrated to be a useful tool for determining the size and size distribution of free volume holes, and to some degree, their density in polymer composites, which are modified in relation to the pure polymer by the presence of the filler. This has significant practical implications, as the free volume influences many properties of polymers and polymer composites.

Appendix

In addition to calculating the size of free volumes according to the Tao–Eldrup model [10, 11], the PSC_12 program also offers the possibility of carrying out calculations according to the extended Tao–Eldrup (ETE) model.

When the radius of a pore is larger, o-Ps can occupy excited states in the well, so more levels can be significantly populated, and (1) becomes more complex. It is the case of pores or cavities with a radius larger than 1 nm. Then, the probability of finding o-Ps being in the exited state with quantum numbers nl in the spherical well surrounded by the layer of thickness Δ can be defined as follows

$$p_{nl} = \left[\int_{X_{nl}\frac{R}{R+\Delta}}^{X_{nl}} \mathrm{d}r\; r^2 j_{nl}(r)^2\right]\left[\int_{0}^{X_{nl}} \mathrm{d}r\; r^2 j_{nl}(r)^2\right]^{-1}, \tag{4}$$

where j_{nl}(r) are the spherical Bessel functions, and X_{nl} are the n-th node of these functions. The annihilation rate, i.e., the reciprocal value of lifetime for o-Ps in the exited state, is then equal to

$$\lambda_{nl} = \left(\frac{\lambda_\mathrm{S}}{4} + \frac{3\lambda_\mathrm{T}}{4}\right) p_{nl} + \lambda_\mathrm{T}(1 - p_{nl}), \tag{5}$$

where $\lambda_\mathrm{S} = 7.9895\ \mathrm{ns}^{-1}$ and $\lambda_\mathrm{T} = 7.04 \times 10^{-3}\ \mathrm{ns}^{-1}$. These values correspond to the annihilation rate of Ps in the singlet and triplet states, respectively. Note that for $n = 1$ and $l = 0$, (5) reduces to (1). However, when the temperature increases, higher

excited levels can be occupied with a certain population. Thus, to obtain the positron lifetime value, the sum of all annihilation rates λ_{nl} up to $n_{\max}$ and $l_{\max}$ with the population of energy levels of o-Ps given by the Boltzmann distribution has to be calculated. After normalizing the obtained value and inverting it, the lifetime of o-Ps annihilating in the pick-off process can be expressed as follows [26, 27]

$$\tau_3\,[\mathrm{ns}] = \left[\sum_{n=1}^{n_{\max}}\sum_{l=0}^{l_{\max}}(2l{+}1)\exp\left(\frac{-h^2X_{nl}^2}{16\pi^2 m_e(R{+}\Delta)^2 k_{\mathrm{B}}T}\right)\right]\left[\sum_{n=1}^{n_{\max}}\sum_{l=0}^{l_{\max}}(2l{+}1)\lambda_{nl}\exp\left(\frac{-h^2X_{nl}^2}{16\pi^2 m_e(R{+}\Delta)^2 k_{\mathrm{B}}T}\right)\right]^{-1}, \tag{6}$$

where m_e is the electron mass at rest, k_{B} is the Boltzmann constant, h is the Planck constant, and T is the absolute temperature.

The Psc_12 program has been written to accommodate these complex calculations. The values of the longest lifetime component τ_3 and its uncertainty should be entered in the Input section. To obtain the free volume radius, the button labeled "Calculate" in the section below should be selected. When employing the ETE model for large pores, it is possible to input the maximal values of the energy level, i.e., $n_{\max}$ and $l_{\max}$. The default values for these variables are set to 10. The value of the absolute temperature must also be entered. The calculations are performed for the spherical shape of the pore; however, in many cases, the pores are in the shape of capillaries. In such a case, the infinitely long cylinder must be used in the calculations. The above equation needs to be slightly modified, see [28]. One can obtain the radius of the capillary within the ETE model using the lowest section of the Psc_12 window. In many cases, the capillary wall can be covered by gas, e.g., air. Zaleski and Sokół [29] proposed to modify the positron lifetime obtained from the extended model (4), introducing the annihilation rate in the gas as follows

$$\tau_3^{-1} = \tau_{\mathrm{ETE}}^{-1} + \lambda_{\mathrm{gas(1\ atm)}} + \frac{4.5}{D\,\lambda_{\mathrm{gas(1\ atm)}}}, \tag{7}$$

where D is the diameter of the capillary, τ_{ETE} is the τ_3 value obtained from (6), and $\lambda_{\mathrm{gas(1\ atm)}} = 4.6\ \mu\mathrm{s}^{-1}$ is the annihilation rate of o-Ps in the adsorbed gas.

In the presented models, there are several parameters: Δ, λ_{S}, λ_{T}, and $\lambda_{\mathrm{gas(1\ atm)}}$. Their values can be changed if necessary after opening an additional window by selecting the "Parameters" button.

The usefulness of (1), (6), and (7) has been confirmed experimentally in many studies, see, e.g., [29]. The Psc_12 program can be used to calculate radii of free volume in polymers, molecular solids, and porous materials.

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