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Positron Annihilation: A Unique Method for Studying Polymers

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Summary: Positron annihilation is a unique technique for studying the local free volume of polymers. Employing the positron annihilation lifetime spectroscopy (PALS) the size and size distribution of subnanometer size holes which constitute the excess free volume may be studied. In combination with macroscopic volume data the fractional free volume and the number density of holes may be estimated. After presenting the principles of the method, some examples typically for the investigation of the free volume in polymers will be given. Moreover, the study of interdiffusion in demixed polymer blends and further applications are shortly reviewed

Keywords: free volume; glass transition; interdiffusion; microstructure

Introduction

The free volume of polymers is generally defined by $V_f = V - V_{occ}$ where V is the total and V_{occ} the occupied volume. When identifying V_{occ} with the van der Waals volume V_W, $V_{occ} = V_W$, the value of V_f represents the total free volume which is known also in crystals and termed there as interstitial free volume. In amorphous polymers an additional or excess free volume appears due to the (static or dynamic) structural disorder. This excess free volume appears as many small holes and can be calculated assuming $V_{occ} = V_c$, $V_f = V - V_c$, where V_c is the specific volume of the corresponding crystal. Many properties of polymers are related to this type of free (excess or hole) volume, including the diffusion of small molecules through glassy polymers, the sorption of humidity and the dynamics of rubbery polymers. Modern theories of glass transition are more complex than the original free volume concepts but show also the close relation between mobility (dynamic heterogeneity) and free volume (structural heterogeneity).[1] Despite a great deal of interest in the investigation of free volume, there is still only limited information available about its structures: the hole dimensions, number

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densities and the size and shape distribution.

A unique tool to probe such holes is the positron annihilation lifetime spectroscopy (PALS).[2,3] In molecular substances a significant fraction of the injected positrons annihilates from the positronium (Ps) bound state. The Ps forms either in the para (p-Ps) or ortho (o-Ps) states with a relative abundance of 1:3. In vacuum, p-Ps has a lifetime of 125 ps and annihilates via 2 γ-photons while o-Ps lives 142 ns and annihilates via 3 γ-photons. In amorphous polymers Ps is trapped by the holes of the excess free volume (Anderson localisation). When within the holes, the 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 molecules of the surrounding material, a process generally known as the 'pick-off'. The result is a sharply reduced o-Ps lifetime depending on the frequency of collisions. The collision frequency of the Ps with the surrounding molecules will depend on the dimensions of the confining volume. This results in a highly sensitive correspondence of the o-Ps pick-off rate, and therefore the lifetime, to the free volume hole size[2-4]. In this paper we present a short introduction in the positron annihilation method and show typical examples for its applications for studying polymers.

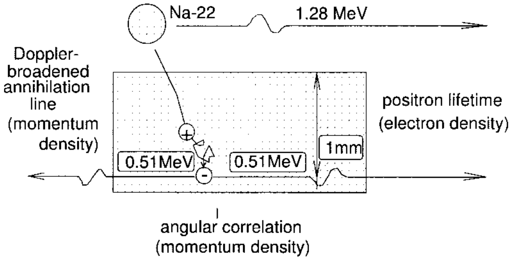

Figure 1. The positron experiments: Positron lifetime, 2γ-angular correlation and γ-spectroscopy.

The Positron Annihilation Techniques

Positrons are supplied by radioactive sources such as ^{22}Na with high kinetic energies (Figure 1).[2,3] If implanted into a solid the fast positrons slow down within a few ps due to ionisation and excitation of molecules. The implantation profile of positrons is an exponentially decreasing function $\exp(-\alpha x)$ where $\alpha = 42$ cm^{-1} is the positron absorption coefficient (in materials of density 1 g/cm^3) and x is the depth where the positron is stopped. 50, 90 and 99 %

of implanted positrons are stopped at depths of 0.17, 0.55 and 1.1 mm. Thin polymer foils may be stacked to obtain the required thickness of sample. The free (not Ps) positrons annihilate via emission of two (almost co-linear) γ-photons of 0.51 MeV energy. Simultaneously with the emission of the positron the ^{22}Na nucleus emits a 1.3 MeV photon. The time delay between the 1.3 MeV (start γ, positron birth) and the 0. 51 MeV photons (stop γ, positron annihilation), i. e. the lifetime of a positron, can be measured with a positron annihilation lifetime spectrometer (PALS) using two fast scintillation detectors. The momentum distribution of e^+-e^- pairs can be determined either by measuring the Doppler-broadening of the 0.51 MeV annihilation radiation (DBAR) using a Ge detector, or the 2γ angular correlation of annihilation radiation (ACAR, Figure 1).[2-4]

While the lifetime of an individual positron may vary between 0 and ∞, the lifetime spectrum of an ensemble of positrons annihilating from a solitary state is a single exponential $\exp(-t/\tau)$ where τ denotes the characteristic (mean) lifetime of positrons. As shown in Figure 2 for a CR39,[5] typically three lifetime components appear in amorphous polymers:

$$s(t) = \sum(I_i/\tau_i)\exp(-t/\tau_i), \qquad \sum I_i = 1, \qquad (i = 1...3). \qquad (1)$$

These lifetimes arise from annihilation of p-Ps (τ_1 = 125 - 200 ps), free positrons (τ_2 = 300 - 400 ps) and o-Ps pick-off (τ_3 = 1 - 5 ns). Only the third component (o-Ps) responds clearly to polymeric material properties: For CR39: τ_3 = 1640 ps (c = 0, T_g = 122 °C) and 2145 ps (content of comonomer c = 75 wt-%, $T_g \approx 0$ °C, Figure 2[5]). Typical specimens in PALS experiments are platelets of 8x8 mm^2 in area and 1.5 mm in thickness. For each experiment, two identical samples are sandwiched around a 5 MBq positron source (^{22}Na), prepared by evaporating carrier-free ^{22}NaCl solution on a Kapton foil of 8 µm thickness. One experiment lasts between 1 and 10 hours depending on the total counts accumulated.

Following convolution of $s(t)$ with the experimental resolution function and subtraction of background and source components the spectra can be analysed by a non-linear least squares fit of Equation (1) to the data points N_i. A continuous lifetime distribution may also be analysed using the Laplace-inversion routine CONTIN-PALS2 or the maximum entropy routine MELT. A relatively new analysis routine LT9.0 assumes a log-normal distribution of annihilation rates $\alpha(\lambda)$, $\lambda = 1/\tau$, for some, if not all, annihilation channels and calculates the mass centre and width of this distribution.[3,6]

The size of the free volume holes in which o-Ps annihilates can be estimated using a simple quantum mechanical model which assumes the Ps to be confined in a spherical potential well of radius $r = r_\mathrm{h} + \delta r$ and an infinite depth where r_h is the radius of the hole (see ref.[3,4] and references given therein). The Ps has a spatial overlap with molecules within a layer δr of the potential wall.

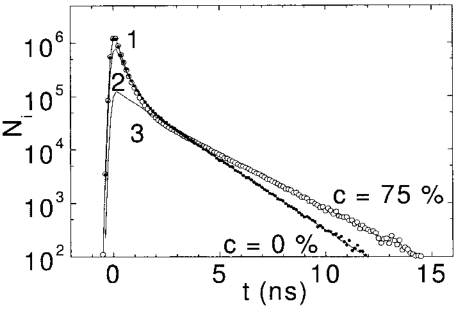

Figure 2. Positron lifetime spectra in CR39-copolymers with 0 and 75 % of comonomer.[6]

This provides a simple but very useful relationship between the o-Ps pick-off lifetime and the hole radius r_h:

$$\tau_{po} = 0.5ns\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r_h}{r_h + \delta r}\right)\right]^{-1} \qquad (2)$$

where 0.5 ns is the inverse of the spin averaged Ps annihilation rate in dense electron systems and δr is empirically derived to be 0.166 nm.[3,4] Similar formulas were derived for cylindrical or cubical holes.[3] Typically o-Ps lifetimes and holes sizes are $\tau_\mathrm{po} = \tau_3 = 1 - 5$ ns and $r_\mathrm{h} = 2 - 4$ Å ($v_\mathrm{h} = 4\pi r_\mathrm{h}^3/3 = 50 - 200$ Å^3). In polymer crystals Ps is sometimes formed in interstitial free volumes. In this case, the o-Ps pick-off lifetime reflects the packing coefficient C of the crystals ($C \approx 0.70$, $\tau_3 \approx 1$ ns). The Ps yield in crystals is usually lower than in the amorphous phase or can also be completely absent. Based on Equation (2) the mean size of the free-volume holes may be estimated as a function of temperature, pressure, the content of plasticizer, humidity, or the composition of copolymers and blends etc. The lower detection limit of the method is estimated to be $r_\mathrm{h} \approx 1.5$ Å ($v_\mathrm{h} \approx 20$ Å^3), while in mesoscopic systems τ_3 values of 100 ns corresponding to $r_\mathrm{h} \approx 10$ nm have been observed.[3]

Application of PALS as a probe of polymers

Characterisation of the free volume

PALS is able to deliver the mean size and size distribution of free volume holes.[3-5] As an example, we show in Figure 4 the mean hole volume, v_h, calculated from the o-Ps lifetime τ_3, for atactic polystyrene (PS) provided by the BASF AG, Germany (M_n = 175 kg/mol, M_n/M_w = 2.25, T_g = 104 °C). Together with $v_h(\tau_3)$, the boundaries $v_h(\tau_3 - \sigma_3)$ and $v_h(\tau_3 + \sigma_3)$ are shown where σ_3 is the dispersion (standard deviation) of the lifetime distribution. The mean volume v_h shows a strong increase in its expansivity at T_g. At low temperatures, o-Ps is trapped in local free volumes within the glassy matrix and τ_3, and hence v_h, show the mean size of static holes. The averaging occurs over the hole sizes and shapes. The slight increase of v_h with temperature mirrors the thermal expansion of free volume in the glass due to the anharmonicity of molecular vibrations and local motions in the vicinity of the holes. In the rubbery phase the molecular and segmental motions increase rapidly resulting in a steep rise in the hole size with temperature. Now v_h represents an average value of the local free volumes whose size and shape fluctuate in space and time. The o-Ps lifetime mirrors the mean geometrical hole size as long as the structural relaxation times do not reach the order of magnitude of this lifetime. This is probably the case above a temperature which we have denoted by T_k in Figure 4. The coefficients of thermal expansion of hole volume were estimated to be $\alpha_{hg} = (1.95 \pm 0.2) \times 10^{-3}$ K^{-1} ($T < T_g$) and $\alpha_{hr} = (9.5 \pm 0.08) \times 10^{-3}$ K^{-1} ($T > T_g$), the hole volume at T_g is $v_{hg} = (121 \pm 2)$ Å^3. The α_{hr} value is larger by a factor of ~15 than of the macroscopic coefficient of thermal expansion, α_r. The number density and volume fraction of holes can not be obtained from PALS alone, however, from a comparison of PALS with the macroscopic volume obtained from pressure-volume-temperature (PVT) experiments, in particular when these are analysed with the Simha-Somcynsky equation of

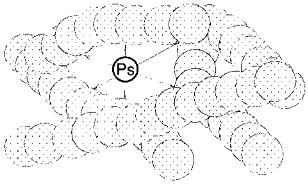

Figure 3. Ps localisation and annihilation in a hole of the (excess) free volume.

state (S-S eos) (see ref.[7] and references given therein). This theory assumes a lattice with an occupation y of less than 1. The hole fraction, $h = 1 - y = h(T/T^*, V/V^*, P/P^*)$, ($T^*$, V^* and P^* are scaling parameters) is calculated from an equation obtained from the pressure relation $P = -(\partial F/\partial V)_T$, where $F = F(V, T, h)$ is the (Helmholtz) configurational free energy. h can be identified with the fractional (excess) free volume defined by $f = V_f/V \equiv h$ where V and V_f are the specific total and free volumes.

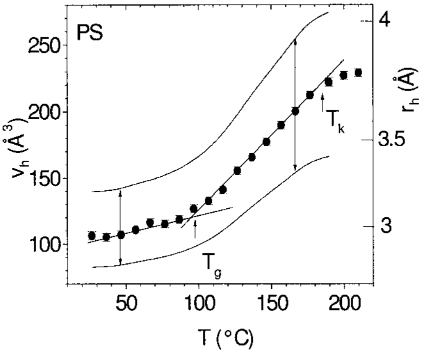

Figure 4. The mean volume $v_h(\tau_3)$ of excess free volume holes and its dispersion ($\pm\sigma$) of PS as a function of temperature T. Above T_k the o-Ps lifetime τ_3 and thus v_h does not anymore represent correctly the true hole volume.

We have determined the specific volume from PVT experiments using a fully automated GNOMIX high-pressure (mercury) dilatometer. Figure 5 shows the specific volume, V, and the specific occupied volume, $V_{occ} = (1 - h)V$, for PS together with the specific free volume, $V_f = hV = V - V_{occ}$ as example. V_{occ} includes the interstitial free volume, V_{if}, $V_{occ} = V_W + V_{fi}$, and has at T_g a value of $V_{occ} = 1.45V_W$ which corresponds well to a typical specific volume for crystalline polymers. The coefficient of thermal expansion of the occupied volume, changes at T_g from $\alpha_{occ,g} = 1.0\times10^{-4}$ K^{-1} ($T < T_g$) to $\alpha_{occ,r} = 0.2\times10^{-4}$ K^{-1} ($T > T_g$). This change seems to be unexpected, but is confirmed by the PALS data (Figure 6, behaviour of V below T_g). As can be observed in Figure 5, the specific volume shows an increase in its coefficient of thermal expansion at T_g from $\alpha_g = 2.25\times10^{-4}$ K^{-1} to $\alpha_r = 6.36\times10^{-4}$ K^{-1}. The corresponding increase for the free volume is from $\alpha_{fg} = 1.8\times10^{-3}$ K^{-1} to $\alpha_{fr} = 8.4\times10^{-3}$ K^{-1}. The fractional free volume at T_g amounts to $f \equiv h = 0.070$.

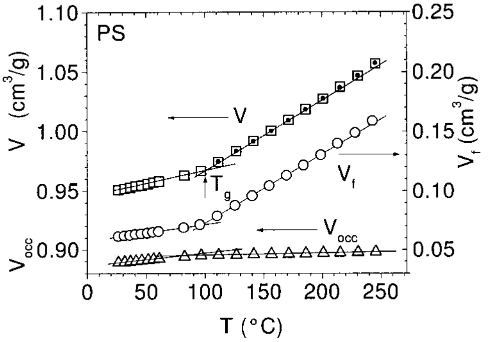

Figure 5. The specific total, V, free V_f, and occupied, V_{occ}, volume of polystyrene (PS) as a function of the temperature T at ambient pressure. Open symbols: experimental data, dots: Simha-Somcynsky equation of state fits in the temperature range $T > T_g$.

An accurate estimate of the mean number of holes per mass unit, N_h', may be obtained from one of the relations[6,8]

$$V_f = N_h' v_h \qquad (3) \qquad\qquad V = V_{occ} + N_h' v_h. \qquad (4)$$

Figure 6 shows the specific total volume, V, and specific free volume, $V_f = hV$, which were plotted vs. the hole volume v_h. One observes that both V and V_f are linear functions of v_h for data points above T_g with slopes of $N_h' = 0.55$ and $0.53(\pm 0.02)\times 10^{21}$ g^{-1}. The values correspond to a hole volume density of $N_h = 0.55$ nm^{-3}. There is almost complete agreement between the N_h' values estimated from both Equations (3) and (4).The constancy of the hole density, N_h', is a surprising and interesting result also confirmed by all other work in the literature[9] related to this question.

The intersection of the V_f vs. v_h lines with the abscissa does not show systematic deviations from zero and varies between -0.005 and 0.008 (±0.005). This shows that the (mean) o-Ps lifetime $\tau_{po} = \tau_3$ mirrors the true mean of the hole size distribution well although eq. (2) is based on a simple quantum mechanical model assuming spherical holes. From comparison of computer simulations of the hole size distribution with PALS results it has been concluded that o-Ps underestimates the hole size since non-spherical holes are detected as too small holes.[5] A possible preference to larger holes may, however, compensate this effect.[3] In the past we have employed PALS for the study of a variety of questions related to the free volume in polymers such as (i) the temperature dependence of the free volume in polyethylene and polytetrafluoroethylene,[10] plasticization and antiplasticization caused by humidity in polyimides[11] and polyamide 6[12], the relation between free volume, T_g, and branching in polyethylene[13] and propylene/α-olefine copolymers,[14] free volume in PA6-ABS blends,[15] ionic (Li^+, ClO_4^-) conduction and free volume in poly(ethylene oxide),[16] the estimation of the fraction of mobile and immobile amorphous phases in semicrystalline ethylene-octene copolymers,[17] and phase transitions in liquid crystals.[18]

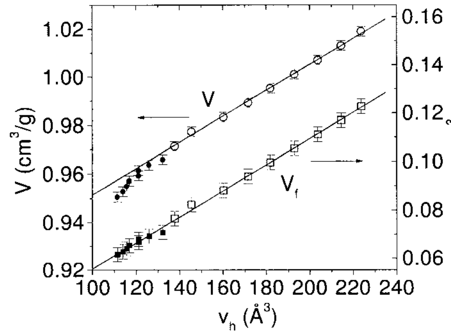

Figure 6. Plots of V and $V_f = hV$, vs. the mean hole volume v_h for PS. The lines are linear fits to the data above T_g and below T_k (open symbols). The filled symbols are data from below T_g.

Interdiffusion in polymer blends

Recently we have shown an interesting application of PALS which is not directly related to the free volume: the study of the interdiffusion in an originally demixed blend of two miscible polymers.[19,20] The blend was prepared as a particle-matrix system by mixing and pressing powders of the two polymers and annealing at a temperature between the T_g's of both. DSC experiments were used to characterise the state of the blend. Two systems were investigated: (i) styrene-maleic anhydride-copolymer containing 24 wt.-% maleic anhydride (SMA-24, particle) and poly(methyl methacrylate) (PMMA, matrix),[19] (ii) polyvinylchloride (PVC, particle) and poly (n-butyl methacrylate) (PnBMA, matrix).[20] We presented experimental evidence that the o-Ps intensity I_3 and the average positron lifetime τ_{av} respond on the interdiffusion process. The response is due to the diffusion of inhibitors for Ps formation from one phase into the other. Figure 7 shows that I_3 varies linearly with the weight fraction of the components when the blend is completely demixed. During the annealing diffusion of polymer molecules from the PVC particles into the PnBMA matrix and vice versa occurs which leads to a lowering of I_3. A core-shell model for the description of the PALS response to the local chemical inhomogeneity has been developed which makes use of a calculated concentration-distance profile. The comparison with the experiment allows the estimation of the interface width and of kinetic parameters, such as the exponent k of the time dependence of the interfacial width $\sigma =$ const. t_{ann}^{k} and the coefficient of mutual diffusion D.[20] When this model is applied to DSC experiments, kinetic parameters very similar to those derived from PALS are obtained.[21]

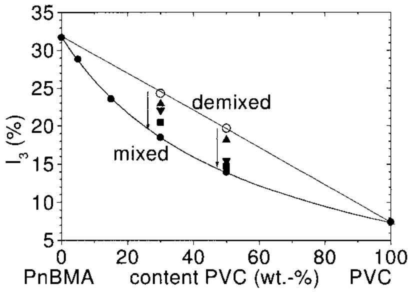

Figure 7. Variation of the o-Ps intensity I_3 as a function of the composition in molecularly mixed (filled symbols) and demixed (empty symbols) blends of PVC (particles) and PnBMA (matrix). The arrows show the change in I_3 due to interdiffusion (T_a = 110 °C, t_a = 3, 10, and 30 min).[20]

Outlook

We have attempted to point out the uniqueness of Positron Annihilation as a technique for polymer studies. The main application of the method lies in the study of the microstructure (hole size distribution) of the free volume. There are several further applications of the method such as the estimation of the chemical surroundings of holes sensed by DBAR[22] or the hole anisotropy in highly crystalline fibres detected by ACAR.[23] A particular interesting field is the study of surface and near-surface properties using a slow, monoenergetic positron beam.[3,24,25] This technique allows a variation of the energy of monoenergetic positrons from a few eV to about 40 KeV and thus the penetration depth of positrons into polymers from a few Å´s up to several µm´s. In past we have used this technique for the study of ion-irradiation effects in polyimides layers.[24] The study of interdiffusion in thin polymer bi-layers is now in progress. Further interesting applications are the study of glass transition at surfaces[25] and degradation of polymer coatings due to weathering.[26]

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