

Presented at the *Interdisciplinary Conference on Dielectrics: Properties, Characterisation, and Applications*, Paris, France, March 1992

PROBING ATOMIC-SIZE DEFECTS AND FREE VOLUMES WITH POSITRON AND POSITRONIUM

Guo-Huan Dai¹, Jean-Yves Dolveck², and Pierre Moser²

¹ Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA

² Département de Recherche Fondamentale sur la Matière Condensée, Centre d'Études Nucléaires de Grenoble, 85X, 38041 Grenoble Cédex, France

Abstract

The lifetime measurement of positrons injected in a metal allows to investigate defects of atomic dimension. Many crucial problems in metallurgy have found their solutions by the positron annihilation (PA) techniques for about three decades. Application to semiconductors research has been developed in recent years. Specific theory and analysing method can be used in the studies of the free-volume hole in polymers, the size of the empty spaces being between 0.3 and 1.5 nanometers. In many insulating materials, the diffusing positron can trap an electron and form a metastable positronium (Ps). Like a gas bubble, the Ps atom may diffuse and get trapped by the free-volume hole. Its lifetime, 140 nanoseconds in vacuum, is drastically reduced if the positronium hits the wall of the hole. When this mechanism is governing, lifetimes over the range of 1-10 ns are well observable and a correspondence exists between the positronium lifetime and minimum diameter of the trapping open space. Example of application is given in a study of polyimide membranes used for gas separation. A good correlation is revealed between the Ps lifetime and H₂ and/or CH₄ permeabilities. Recent progress in polymers research is also reviewed.

1. Positron and positronium

In 1930, Dirac predicted the antiparticle of electron, positron, which was observed experimentally by Anderson (1932, 1933) two years later. The two particles have identical properties except that they have opposite electric charges. When a positron encounters an electron, they are annihilated, and their mass is converted into pure energy in the form of mostly two γ -rays, each with energy about 0.511 MeV. The process is a direct demonstration of the fundamental laws of energy, charge, spin and momentum conservations of modern physics. Since certain characteristics of the process can be influenced if the particles meet in an atomic environment, positrons can be used as a probe for exploring the nature of matter. It has turned out that the probe is remarkably sensitive and revealing.

The annihilation cross section, calculated by Dirac (1930) in the non-relativistic limit, between a positron with velocity v and an electron at rest is

$$\sigma = \pi r_0^2 c / v, \quad v \ll c, \quad (1)$$

where r_0 is the classical electron radius. As a consequence, for a positron embedded in a sea of electrons with a density n , one obtains the decay rate,

$$\lambda = \pi r_0^2 c n. \quad (2)$$

The positron-electron pair can also form a quasi-stationary state called positronium (Ps). Apart from the effects due to annihilation, Ps is an analogue of the hydrogen atom. Positronium, therefore, is found either in the para state ($S = 0$, spins anti-parallel) or in the triply degenerate ortho state ($S = 1$, spins parallel). Owing to conservation of spin momentum, in vacuum the para Ps (p -Ps) will decay by 2γ emission with a rate of $1/(125 \text{ ps})$, and the ortho Ps (o -Ps) by 3γ emission at a rate of $1/(140 \text{ ns})$. In dense matter, however, the Ps atom undergoes many collisions during its lifetime. Surrounding electrons compete with the original electron for the positron. The process, referred to as *pickoff*, has a rate $\sim 1/(1 \text{ ns})$, which is substantially faster than the vacuum decay rate of o -Ps. The pickoff process results in emission of two γ -photons, as does the annihilation of the p -Ps. Pickoff will be less important for p -Ps because of its much higher decay rate. Ps is generally not found in metals, but is found in metal oxides, molecular solids, liquids, and gases.

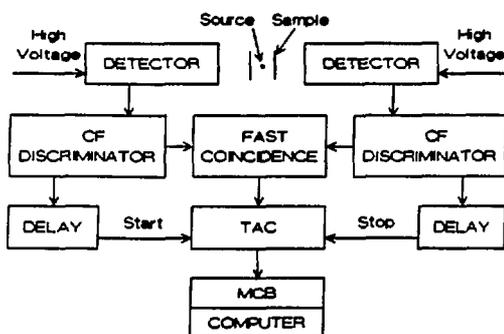


Fig. 1 A typical lifetime spectrometer. The positron source is sandwiched by two pieces of samples. The start and stop detectors/electronics select signals resulting from 1.28 and 0.511-MeV γ -rays, respectively.

1970) and experimental observations (see, e.g., Kubica and Stewart 1975). The positronium is normally formed during the slowing-down process and at nearly thermalised stage of the positron which may pick up an electron from the environmental molecules. The rate of their subsequent annihilation, λ is proportional to the electron density at the site of the annihilation (Eq. 2). That rate is determined by measuring the mean lifetime, τ , of the positron ($\lambda = 1/\tau$), i.e., the average value of many measurements of the time interval between the moment when the 1.28-MeV γ -ray signifying the birth of the positron is detected, and the moment when one of the 0.511-MeV γ -rays from the annihilation of the positron is detected. Positrons typically live a few hundred ps. The state-of-the art electronics renders powerful means to resolve differences of only a few ps between the mean lifetimes of positrons annihilated in different electronic milieu. A typical fast-fast positron lifetime spectrometer is schematically shown in Fig. 1.

In practice, a lifetime spectrum can be expressed as the sum of several decaying exponentials,

$$S(t) = -\frac{dN(t)}{dt} = \sum_{i=1}^n I_i \lambda_i e^{-\lambda_i t}, \quad (3)$$

where n is the number of exponential terms, I_i and λ_i represent the number of positrons present at the i th state and the decay rate of positrons from that state. As mentioned above, positron lifetimes are the reciprocals of the decay rates, i.e., $\tau_i = 1/\lambda_i$. Based on our understanding of the positron/Ps states in various materials and restricted by the difficulties raised in the numerical analysis of the multi-exponentially-decaying curve convoluted with the instrumental resolution function, lifetime spectra are usually resolved into $n = 3$ exponential components employing the standard computer program package PATFIT (Kirkegaard *et al.* 1981).

2.2. Angular correlation of annihilation radiation (ACAR)

The momentum distribution of the electrons in the material can be determined by observing the two 0.511-MeV γ -rays that result from the annihilation ending the positron's life. The γ -rays emerge exactly 180 degrees apart in the frame of reference where the annihilating positron-electron pair is at rest, i.e., in the center-of-mass frame. The electrons inside the sample are moving, however, their momenta must be carried away by the γ photons in order to conserve the total momentum of the system. Consequently, in the laboratory frame of reference the γ -rays actually emerge at an angle that deviates slightly from 180 degrees. The amount of the deviation can be measured by having two detectors register the arrival of the γ -rays in coincidence. In spite of the very slight deviation from 180 degrees, which is of the order of 0.1 degree, refined techniques of detection and computation have been developed for measuring the angle precisely. The mean angular deviation indicates the average momenta of the electrons encountered by the positrons injected into the sample. Moreover, the shape of the angular deviation reveals details of the electronic structure in the substance where positrons are annihilated.

2.3. Doppler broadening spectroscopy

The positron method can also yield directly the kinetic energy distribution of the electrons within the sample. Since electrons in motion have a kinetic energy that is conserved in the annihilation process, the outgoing γ -rays carry energies slightly deviated from the exact value of 0.511 MeV (the rest mass of the electron), corresponding to the case of momentum mentioned above. The variations in the energy are

2. Positron annihilation techniques

Beginning with the pioneering work of De Benedetti (1950), investigators began to develop an intriguing new tool for materials research: the positron annihilation (PA) method. Positrons are most commonly obtained from radioactive nuclei such as ^{22}Na , ^{58}Co , and ^{64}Cu , etc. In the course of its decay, a ^{22}Na in most cases emits a positron accompanied by the emission of a γ -ray with an energy of 1.28 MeV. The γ -photon can be detected and can trigger the measurement system to signify the birth of the positron.

2.1. Lifetime spectroscopy

When the positron is injected into a solid, it is thermalised within a few picoseconds, according to both the theoretical estimates (Perkins and Carbotte

essentially a measurement of the Doppler shift of the γ -rays that result from positrons being annihilated in encounters with moving electrons.

Therefore, positron experiments fall into two major categories (For details about the techniques, the reader is referred to Hautojärvi 1979, Brandt and Dupasquier 1983): lifetime and momentum measurements. Lifetime method involves only a determination of the lifetime of the positron in the material under study. Momentum measurements are useful in exploring the electronic structure of solid matter. However, the PA techniques are confronted with the inherent difficulty that the positive charge of the positrons distorts the configuration of the electrons in their vicinity. Thus the electron density is enhanced around the positron, resulting in a substantial increase in the decay rate. Considerable effort has gone into the theoretical understanding of the interactions between the positron and the electrons.

3. Atomic-size defects in solids

Since mid 1960s, however, the research has entered a new phase as a result of the discovery that the positron is extremely sensitive to structural imperfections in solids. Immediately after thermalisation, the positron is in the free or untrapped state, which is commonly described as a superposition of Bloch waves such that the positron has zero probability of being near the positive ion cores and maximum probability of being in the interstices. This is due to the strong repulsive potential between the ion cores and the positively charged positron or highly polarisable Ps and due to the gain of 6.8 eV of Ps binding energy for Ps; The work function has been found to be negative for Ps in solids and for the positron in many solids. Consequently, both the positron and Ps are energetically less stable in the material bulk than in vacuum, and thereby they are squeezed to and then localised in any open spaces of atomic dimension such as vacancy-like defects for the positron and free-volume holes (Doolittle 1951, Brandt *et al.* 1960) in molecular materials for Ps. In the localised or trapped state, which has an energy below that of the free state, the positron probability density is non-zero only in the vicinity of the defect in which the positron is trapped. The basic theoretical tool in interpreting positron data is the trapping model, which was first introduced by Brandt (1967), Bergersen and Stott (1969), and Connors and West (1969). From then on, various more complicated considerations have been contributed to approach the reality in materials (see, *e.g.*, Pagh *et al.* 1984, Frieze *et al.* 1985, Dannefaer *et al.* 1991).

Metallurgy has been one of the fields considerably profited from the positron method. About three decades ago, it was found (Dekhtyar *et al.* 1964) that the cold-working of metals and alloys has the effect of narrowing the width of the angular deviation in the annihilation γ -rays, which was interpreted as positron trapping in dislocations produced during the working of the materials (Berko and Erskine 1967). The field sprang to life and attracted wide interest outside the small community of positron physicists when MacKenzie (1967) and his colleagues reported that the lifetime of positrons in a metal increases when the metal is heated to temperatures of only a few hundred degrees C, in clear contrast to the fact that conventional methods for detecting defects in a metal work only at temperatures near its melting point. The average positron lifetime changes when there is less than one vacancy per million atoms in the crystal, a concentration rarely before accessible to experimental scrutiny. The technique has since been widely applied to thermal-equilibrium measurements of the vacancy formation energy in metals.

Another successful example of application of the PA techniques to metallurgical problems has been the annealing experiment performed on hyper-pure α -iron by Hautojärvi *et al.* (1979), which decisively ended the notoriously long-time dispute between one and two interstitial models. When comparing positron annihilation to, for instance, resistivity measurements, one notes that the positron is trapped only by vacancy-like defects although electrons are scattered by both interstitial and vacancy-type defects. In this sense the positron is vacancy-like defect specific. As a consequence, the experiment revealed single-vacancy migration and clustering beginning at temperatures as low as about 200 K; the abrupt

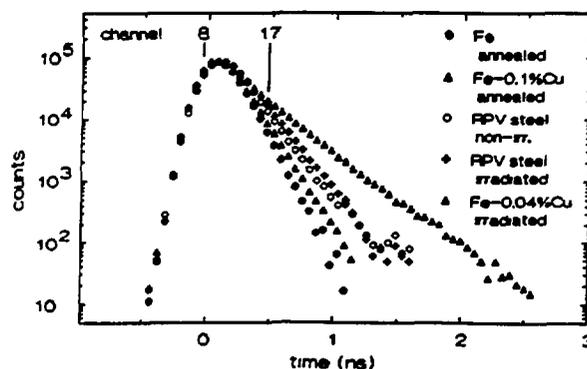


Fig. 2 Lifetime spectra for RPV steels neutron-irradiated for 13 years (no voids) and electron-irradiated/352 K-annealed Fe-0.04%Cu for which the long tail (0.29 ns, 67 %) indicate vacancy clusters (Dai *et al.* 1992)

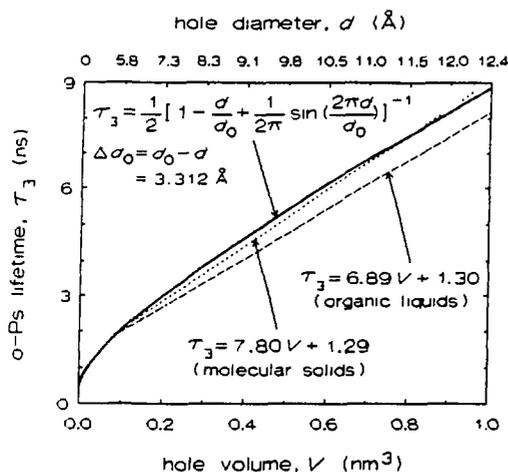


Fig. 3 Relationship between o -Ps lifetime in a cavity and the volume and diameter of the cavity, V and d . Redrawn from Eldrup (1982), Jean *et al.* (1986), and Nakanishi and Jean (1988)

In the studies of molecular materials where Ps atoms may form, the shortest-lived lifetime component, $\tau_1 = 0.13 \pm 0.03$ ns, is attributed to annihilation of p -Ps and Ps-molecular species; the intermediate-lived component, with $\tau_2 = 0.3$ - 0.5 ns, is assigned to direct annihilation of positrons and positron-molecular species; and the longest-lived one, with lifetime $\tau_3 = 0.5$ - 10 ns, is o -Ps pickoff annihilation in free-volume holes. It is the o -Ps lifetime that directly correlates to the free-volume hole size. Its corresponding intensity, I_3 , contains information about the free-volume concentration.

The o -Ps lifetime dependence of the hole volume in various molecular crystals and liquids was first summarised by Eldrup (1982). As shown in Fig. 3, the experimental data points (not depicted) beyond $V \approx 0.1$ nm^3 can be well fitted to the straight (dotted and dashed) lines (Jean *et al.* 1986). A simple equation,

$$\tau_3 = \frac{1}{2} \left[1 - \frac{d}{d_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi d}{d_0}\right) \right]^{-1}, \quad (4)$$

corresponding to the solid curve in Fig. 3, has been obtained (Nakanishi and Jean 1988) quantum mechanically by solving the Schrödinger equation with a finite spherical potential of diameter d_0 having an electron layer of thickness $\Delta R_0 = \Delta d_0 / 2$, suggested by Tao (1972) and Eldrup *et al.* (1981) on the basis of the bubble model (Ferrell 1957).¹ Eq. 4 is semi-empirical since the thickness of the electron layer is found by fitting the equation to the experimentally measured o -Ps lifetimes. An analogue curve for liquids, corresponding to the dashed line in Fig. 3, is also readily available with a different semi-empirical parameter $\Delta d_0 = 3.66$ Å. Several tens of molecular solids and liquids including hexane, sulfur hexafluoride, neopentane, and zeolites, *etc.* have been characterised and the results are found to fall very closely around the curves.

4.1. Positronium formation vs. crystallinity

The probability of Ps formation, on the other hand, can be determined experimentally from the intensity of the o -Ps component, I_3 , that is, $4I_3/3$. A typical amorphous polymer contains about 95% of bulk (excluded volume) and 5% of free volume. However, the free volume does not exist in a crystalline molecular material. Despite a great deal of research effort expended for more than three decades, the question of whether Ps is solely formed in free volume has not yet been unambiguously answered until a recent PA lifetime study on semicrystalline poly-arylether-ether-ketone (PEEK) as a function of the degree of crystallinity, X_c (Nakanishi *et al.* 1989). It was observed that τ_3 does not vary with respect to X_c , and thus the free-volume hole diameter and the average free volume equal 5.3 ± 0.3 Å and 78 Å³ according to Eq. 4. On the other

increase of the positron lifetime at around 220 K directly indicates the agglomeration process of vacancies (Hautojärvi *et al.* 1979).

The positron lifetime spectroscopy has also been applied to the study of voids in metals and alloys that form after long exposure to radiation in nuclear reactors, a study that has important implications for nuclear engineering. Recently, it has been shown (Fig. 2) that there are no large voids (> 20 single vacancies) present in stainless steel materials taken from the surveillance program of the reactor pressure vessels (RPV) in a nuclear power plant, which have been irradiated for such a long time as up to 13 years (high dose, but low dose rate); similar results have also been obtained on other types of RPV steels (Dai *et al.* 1992 and references therein). Such information is uniquely furnished by the positron probe, which is difficult to obtain by utilising conventional methods.

4. Free volumes in polymers

¹ This model was first proposed to account for the long lifetime of o -Ps in liquid helium in which Ps is self-trapped and creates a cavity, called "bubble." The formation of the bubble is due to a strong repulsive force between the electron of the Ps and the surrounding electrons of the medium. The o -Ps lifetime is thus substantially prolonged in the bubble in comparison with the bulk since there are virtually no molecular electrons inside the bubble.

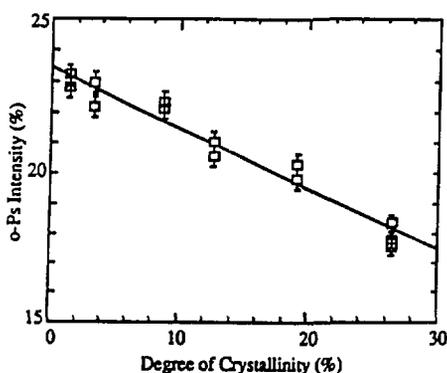


Fig. 4 The *o*-Ps intensities in semicrystalline PEEK as a function of crystallinity. The solid line is a least-squares fit to the data (Nakanishi *et al.* 1989)

hand, I_3 decreases linearly with increasing X_c (Fig. 4). The linearity seems much better than that observed in poly-tetra-fluoro-ethylene (PTFE), and polyethylene (Stevens and Edwards 1970, Brandt and Wilkenfeld 1975). A straight line was fitted to the data points, which could be extrapolated to $X_c = 100\%$, yielding 0% of Ps formation. This result strongly supports the assumption that Ps only forms in the amorphous region, that is, at free volume sites. The free-volume concentration could thus be determined from the observed *o*-Ps lifetime and intensity.

4.2. Temperature and pressure effects on free volumes

The free volume properties are affected by the sample's environmental temperature and external pressure exerted on the material under study, since temperature and pressure have considerable effects on the mobility of molecules and the relaxation rate of the local motion of molecular chains. The dependence of viscoelastic behaviour on temperature and pressure can be monitored by positron lifetime measurements. It was discovered a long time ago (see, *e.g.*, the review by Stevens, 1980) that the positron lifetime undergoes a dramatic change at the glass transition temperature, T_g . In recent years, Jean and colleagues have performed systematic investigations on DGEBA/DDH/DAB epoxy polymers; the positron lifetime as a function of temperature (Fig. 5) and of pressure has been measured, rendering fruitful results (Jean *et al.* 1986, Wang *et al.* 1990, Jean 1990). The T_g 's of the epoxy polymers, carefully determined by differentiating the *o*-ps lifetime with respect to temperature (Fig. 6), were found in perfect agreement with those given by the differential scanning calorimetry (DSC). The *o*-ps lifetime and hence the free-volume size are observed to increase linearly as a function of temperature with apparent discontinuities at various transition temperatures including T_g , but to decrease with increasing pressure. The free-volume compressibility, β_f , can then be calculated as a function of pressure and T_g is found to shift to higher temperatures with pressure. The viscoelastic properties of polymers, related to the parameter $\zeta = (\partial T / \partial p)_f = \beta_f \alpha_f$, are thus followed with the aid of the deduced $\beta_f(p, T)$ and the thermal expansion coefficient, $\alpha_f(p, T) = \alpha_f(p)$. This ζ parameter is, however, nearly independent of p and T , which is expected to find application in characterising polymeric materials (Jean 1990).

4.3. Sub- T_g physical aging

When a polymer is heated above its T_g

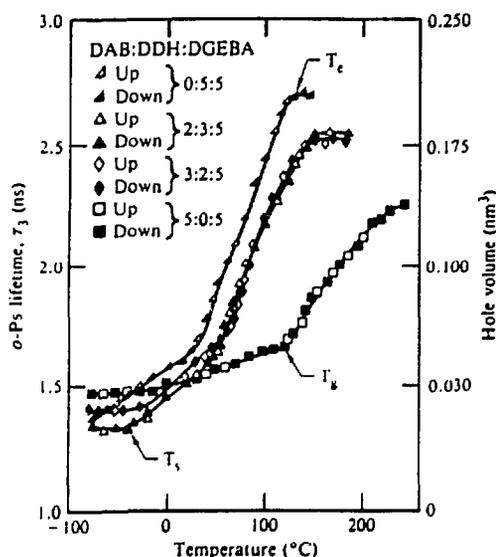


Fig. 5 Variation of *o*-Ps lifetime vs. temperature in epoxy polymers. Open and closed symbols are for increasing and decreasing temperature, respectively (Jean *et al.* 1986)

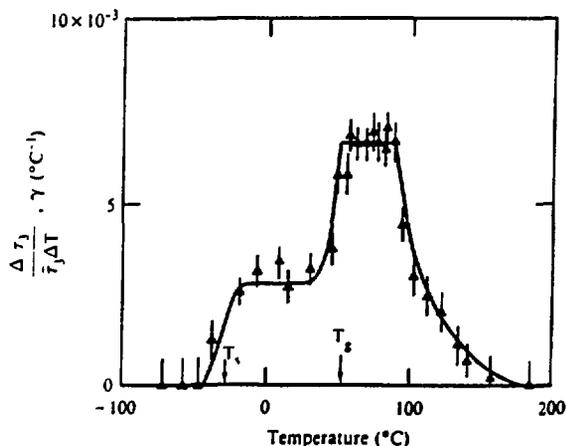


Fig. 6 Differential *o*-Ps lifetime vs. temperature in an epoxy polymer DGEBA/DDH/DAB (5:2:3). Taken from Jean *et al.* (1986)

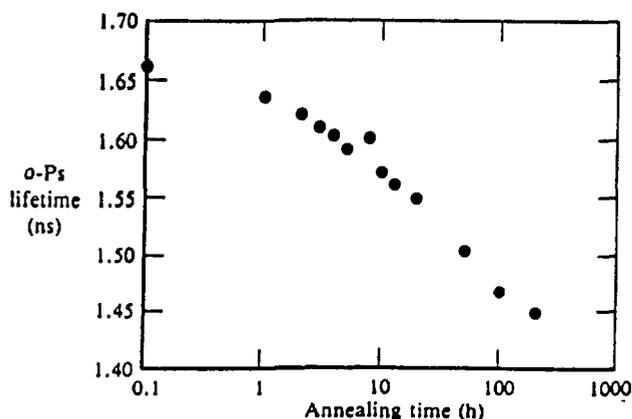


Fig. 7 *o*-Ps lifetime, τ_3 , in a DGEBA/DAB epoxy polymer as a function of log annealing time at ($T_g - 25$ K). From Sandreczki *et al.* (1988)

lifetimes decreased almost linearly with the logarithm of aging time (Fig. 7), which could be accounted for by the one-parameter model (Doolittle 1951) often applied to total-volume or free-volume relaxation. Another recent aging study of poly-vinyl-acetate also shows the sensitivity of the PA method to monitor the free volume changes (Kobayashi *et al.* 1989).

4.4. Polyimide membranes for gas separation

We have recently studied polyimide membranes by comparative measurements of gas permeabilities, and free-volume dimensions by *o*-Ps annihilation (Dolveck *et al.* 1992). The industrial interest of the membrane is that it may be utilised for gas separation. For instance, H_2 and CH_4 gases can be separated simply because of their different mobilities dependent on the free-volume holes (pipe-like empty spaces) in the polyimides and rotation ability of the polymeric chains and segments. In deducing the hole sizes in the polyimides, a difficulty arose: both the scaling curve in Fig. 3 and Eq. 4 were obtained with the assumption that the cavities in the materials are spherical, which seems not the case in the polyimides. We have evaluated the free-volume size by simply supposing that the holes are cubic, *i.e.*, $d = V_{1/3}$, which is smaller than the calculated diameter of a spherical void. This is because the *o*-Ps lifetime is generally associated with the minimum diameter in the pinhole-shaped free volume. Experiments showed that the presence of moisture in the membranes suppresses I_3 so strongly that sometimes the *o*-Ps signals are even missing. Thus, sufficiently drying the sample *in situ* before the lifetime measurements turns out extremely important as the polyimides absorb moisture in air very efficiently (Fig. 8). On the other hand, moisture has little influence on permeability measurements since presumably it will be driven throughout by passing gas molecules. It was also observed that the hole size can be enlarged either by quenching the specimen from above T_g or by chemical methylation of the polyimides. The change of the hole size and concentration monitored by the positron probe is consistent with that of the measured gas permeabilities (Figs. 9 and 10). After thermal aging at temperatures below T_g , the positron parameters are hardly changed, indicating that both chemically and physically modified structures in the polymer are highly heat-resistant, which ensures its industrial application for gas separation.

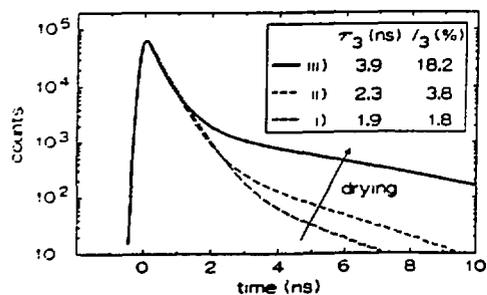


Fig. 8 Lifetime spectra of tri-methylated polyimide at various stages of drying: i) as received, ii) pumped 12 h till 10^{-4} torr, iii) dried *in situ* 12 h, 400 K (Dolveck *et al.* 1992)

and rapidly quenched to a temperature below T_g , excess free volume is retained in the sample, which allows molecular segments to diffuse and imparts toughness to the polymer. If the polymer is subsequently annealed, that is, aged at a temperature near but below T_g , its free volume relaxes as the polymeric molecules slowly approach their equilibrium conformation, resulting in a change in the toughness of the material. The PA techniques are particularly suitable for sub- T_g annealing studies on polymers because τ_3 varies significantly even at temperatures below T_g . It was found (Sandreczki *et al.* 1988) that in the DGEBA/DDH/DAB epoxy polymers the *o*-Ps

4.5. Anisotropy of free-volume-hole dimensions

In reality, the free-volume holes in many polymers are not ideally spherical, but have certain three-dimensional structure. The polyimides described above are merely one example of many types of existent non-spherical free-volume holes, for which Eq. 4 and Fig. 3 cannot be applied directly if good precision is required. Fortunately, it is possible for us to map out the structure of free-volume holes in polymers by measuring ACAR (see Sect. 2.2) spectra as a function of sample orientation. For instance, samples of PEEK and PMMA (poly-methyl-methacrylate) were intentionally stretched uniaxially and biaxially, respectively,

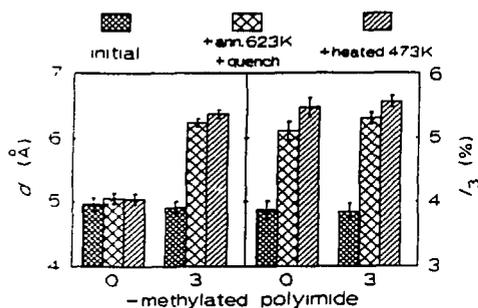


Fig. 9 Void diameters deduced from τ_3 and I_3 for un- and tri-methylated polyimides undergone various physical treatments (Dolveck *et al.* 1992)

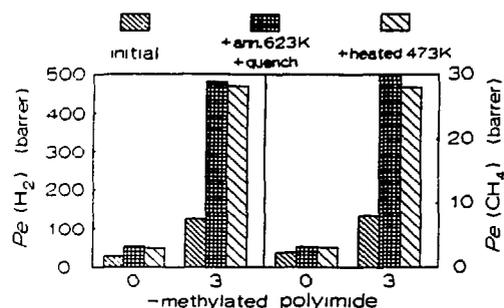


Fig. 10 CH_4 and H_2 permeabilities of the polyimides treated by various chemical and physical means, corresponding to figure 9 (Dolveck *et al.* 1992)

and one-dimensional ACAR experiments were performed at room temperature (Jean *et al.* 1990). The long and short axes were determined and the cylindrical and ellipsoidal shapes of the free-volume holes were revealed together with their anisotropies (*i.e.*, the ratio of the long axis over the short one) of 2.6 ± 0.2 and 1.7 ± 0.2 for PEEK and PMMA, respectively, which are found consistent with the ratios of stretched dimensions in macroscopic measurements.

5. Concluding remarks

In summary, we have described our probes, positron and positronium, and the positron annihilation techniques (including lifetime, ACAR, and Doppler broadening spectroscopies) as valuable tools for the characterisation of atomic-size defects and free-volume structures. The positron has greatly contributed to our knowledge in various fields such as metallurgy, semiconductors, and superconductors, *etc.* The unique properties of Ps localisation in free-volume holes in polymers make it possible for us to determine the size, shape, and concentration of free volumes. Present results have built solid foundation for further advances and lots of exciting developments are forthcoming: (1) Rather than the "conventional" discrete lifetime values, continuous lifetime/free-volume-hole size distribution is being resolved by applying a Laplace inversion algorithm (Gregory and Zhu 1990, Deng *et al.* 1992). (2) Two-dimensional ACAR is expected to be used in polymer research, which is capable of yielding detailed 3D hole structure. (3) Mono-energetic slow positron beam could be directly applied to characterise thin film polymers.

Acknowledgements

GHD would like to thank Prof. Y.C. Jean for encouragement. Collaboration of Dr. M. Pineri and Dr. M. Escoubes are gratefully appreciated.

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