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A Review of Studies of Polymeric Membranes by Positron Annihilation Lifetime Spectroscopy^{*}

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Abstract A review is presented of studies of polymeric membranes by applying positron annihilation lifetime spectroscopy (PALS). PALS has been used to study subnanometer-sized holes, to determine their size distribution and free-volume fractions, and to probe molecular-sized vacancies in glassy polymers. At present, PALS is believed to be a highly effective physical method for the examination of polymeric membranes.

Keywords: polymeric membrane, applying positron annihilation lifetime spectroscopy (PALS), nuclear track, desalination, permeability, reverse osmosis, supermolecular structure

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1 Introduction

Membrane systems have been used in industrial applications such as coating and gas separation. PALS is one of the most sensitive methods for probing the variation of the average size and concentration of freevolume holes. This technique has been developed to directly examine the free-volume properties in polymeric material. Therefore, it is widely used for studies of polymeric membranes in recent years.

This technique allows mono-energetic positrons (kinetic energy of up to 0.54 MeV) emitted from a radioactive source to penetrate the polymer sample, where the positrons quickly lose their energy in about 10 ps before being thermalised. A positron can be directly annihilated as a free positron together with a surrounding electron into two γ -rays or combined with the electron in ~ 0.4 ns to form a metastable state known as a positronium (Ps) atom with a vacuum binding energy of ~ 6.8 eV. Depending on the spins of the positron and the electron, para-Ps or ortho-Ps may be formed. If the spins are antiparallel, the total spin is S = 0 ($m_s = 0$), the singlet ${}^{1}S_{0}$ state (p-Ps) has an intrinsic lifetime (τ_{p-Ps}) of approximately 0.125 ns and decays predominantly into two γ -rays of 511 keV energy. When the spins are parallel, the total spin is S = 1 ($m_s = 0, \pm 1$), the triplet ${}^{3}S_{1}$ state (o-Ps) has a mean lifetime (τ_{0-Ps}) of about 142 ns and o-Ps decays into three or more γ -rays in vacuum. The lifetime τ_{o-Ps} in polymers is found to be 1 ns \sim 5 ns because the positron can pick off one of the surrounding electrons with opposite spin and be annihilated with it. Because of the positively charged nature of the positron, the positron and Ps are repelled by the core electrons, the open spaces such as holes, voids, and free volume are found. The annihilated photons mostly come from these spaces. By a simple model, the measured o-Ps lifetime, τ_{o-Ps} , depends on the radius of the free volume hole R according to the semi-empirical relation $^{[1,2]}$:

$$\tau_{\rm o-Ps} = [\lambda (1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R})]^{-1}, \quad (1)$$

where $\lambda = 2 \text{ ns}^{-1}$ is the spin averaged Ps annihilation

rate and $\Delta R = 1.656 \text{ Å}^{[3]}$ is the thickness of the homogeneous electron layer whose value is valid for polymers and containing simple covalent bonds. In this model the free-volume holes are assumed infinite spherical potential wells of the radius $R_0 = R + \Delta R$.

The volume of the free-volume hole $V_{\rm F}$ (in Å³), for a spherical hole can be calculated

$$V_{\rm F} = \frac{4\pi R^3}{3},\tag{2}$$

where R can be calculated from Eq. (1). The relative fractional free-volume (%) is expressed as ^[4],

$$f = bV_{\rm F}I_3,\tag{3}$$

where $V_{\rm F}$ is the free-volume of the membrane and I_3 is the intensity corresponding to τ_3 . The scaling factor b is obtained from a variation of the free-volume with temperature.

Because Ps has a relative small size (~ 1.59 Å) and small scale of probe lifetime (~ ns), PALS is very sensitive in measuring small holes and free-volumes in a size (1 Å ~ 20 Å) and at a time of molecular motion from 10^{-10} s and longer. The positrons and Ps are localized in preexisting holes and free-volumes in polymers. Therefore the measurements depend on a function of the temperature, pressure, degree of crystallinity and time of aging.

2 Results and discussion

The PAL technique has been applied in polymeric membranes to control the gas flow ^[5], for the application of field-assisted positron moderation ^[6], to alter the structural conformation of a polymeric chain ^[7], to observe hydrophilic / hydrophobic characteristics ^[8], to study vacancy profiles associated with salt selectivity ^[9,10], and to measure the relationship between the gas permeability and the free-volume ^[11~16].

The effect of swift heavy ions (SHI) irradiation in polycarbonate (PC) polymeric membranes is the creation of nuclear tracks of permanent nature. The value of τ_{o-Ps} is found to vary with the irradiation dose and

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Fig.1 (a) Mean lifetime; (b) deduced bulk lifetime using the standard two-state trapping madel, as a function of incident positron energy at room temperature

gives the estimate of the size of the track free-volume in the order of 0.25 nm. The gas permeation increases with the increase in free-volume of latent tracks produced by the ions. The flow rate, very small in a dense membrane, can be controlled by generating nuclear tracks ^[5].

Three diamond membranes, a thin film on a Si substrate (P015 and P017), a free-standing membrane (P002) and a type II a single crystal diamond have been used in this work. The average grain size is about $t (\mu m) \times 1 \mu m \times 1 \mu m$, t ~ $2 \mu m$ thickness for P015 and P017, and $3.5 \mu m$ for P002. Two free lifetimes were fitted with a modified version of POSITRONFIT. Positrons can annihilate with electrons either in individual grains or in grain boundaries in a diamond membrane.

In Fig. 1, the trapping of positrons to surface states is involved at a low energy (< 5 keV), and at a high energy (> 12 keV). The trapping of positrons to the interface between the membrane and the Si substrate starts to be activated for P015 and P017. P002 and P017 have the same type of defects because of nearly the same bulk lifetimes, but the trapping rate to defects of P002 is larger than that of P017. Both lifetimes of P015 have smaller values and P015 has a better quality. The results show that the trapping process in the insulator and diamond membranes has sufficient quality to be used as the main body of field-assisted moderators ^[6].

The pure form polydimethylphosphazene (PDMP), sample P and the catalyst Ru-doped PDMP, in both the virgin and hydrogenated forms, samples A and B, have been studied for the molecular packing of the system related to the effect of doping and hydrogenation. The values of τ_3 and I_3 yield a measure of the average size of the inter-and intra-chain spacings, and the number of density of these sites as shown in Table 1.

Table 1 shows the result of a decrease in the size of the inter- and intra-chain spacing because of Ru-doping. The values of τ_3 and I_3 , of sample A are less than that of sample B and P. Sample A inhibits o-Ps formations. Therefore the Ru ion not only fills the nanospace but also induces structural compacting ^[7].

Table 1. Orthopositronium lifetime and intensity data for PDMP representing the size and population of internal nano-voids

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Specimen	$\overline{\tau_3}$ (ns)	I_3 (%)
В	2.16 ± 0.02	14.02 ± 0.14
А	2.05 ± 0.02	5.89 ± 0.11
Р	2.43 ± 0.03	22.32 ± 0.27

 Table 2.
 Free volume parameters of EC and MEC4 membrane

Membran	$\mathrm{e} \tau_3 \ \mathrm{(ns)}$	I_3 (%)	$r(\mathrm{nm})$	$V_{\rm f} ({\rm nm}^3)$) <i>f</i>
EC	2.63 ± 0.01	26.0 ± 0.2	2 0.337	0.160	0.042
MEC4	2.26 ± 0.01	17.5 ± 0.2	2 0.308	0.121	0.021

 Table 3.
 Pick-off lifetime parameters and estimated radii

 of the cavities in the polyamide samples

<u> </u>		7 (07)	D 7
Sample	$\tau_3 (ns)$	$I_3(\%)$	R(nm)
PA-1	1.64	8.86	0.249
PA-2	1.58	8.93	0.243
PA-3	1.49	9.98	0.223
Before irradiation			
Polymer 1	1.44 ± 0.03	7.66 ± 0.27	0.228
Polymer 2	1.45 ± 0.02	13.54 ± 0.34	0.229
Polymer 3	1.38 ± 0.03	5.77 ± 0.26	0.220
After irradiation			
Polymer 1	1.45 ± 0.02	10.71 ± 0.21	0.229
Polymer 2	1.42 ± 0.01	19.33 ± 0.29	0.226
Polymer 3	1.47 ± 0.01	11.37 ± 0.21	0.238

Modifications by reacting ethyl cellulose (EC) polymer with varying amounts of phenyl isocyanate were carried out to alter its characteristic from hydrophilic to hydrophobic. A modified membrane MEC4 (4.0 ml phenyl isocyanate in 100 g of polymer solution) was obtained with a smaller free-volume in comparison to the unmodified form of EC, shown in Table 2 ^[8].

Dense aromatic polyamides (PA-1, 2, 3) were synthesized from 1, 3-phenylenediamine and 1, 3, 5-benzenetricarbonyltrichloride ^[9] and the effect of ionizing radiation (⁶⁰Co γ -rays, ~ 110 kGy) on the polyamide was obtained to have a significant increase in the relative population of the voids ^[10], to be used for the separation of fresh water from sea or brackish water.

As indicated in Table 3, after receiving a high irradiation dose, although the intensities are appreciably changed, the pick-off lifetimes are least affected. This means that the relative concentration increases are likely to increase the flow rate of the solvent in the reverse osmosis process. All the pore sizes are smaller than the size of hydrated Na⁺ and Cl⁻ ions (together ~ 4.75 Å), and a result of effective desalination can be achieved. Thus aromatic polyamide membranes can be utilized for high salt rejection.

Poly(1-trimethylsilyl-1-propine) (PTMSP) is a well known polymer with the highest permeability to gases. After chlorination the number of chain ends increases due to the chain breaking and the loss of the bulky-Si (CH₃)₃ groups. The strong decrease in the total o-Ps density $(I_3 + I_4)$ in the chlorinated membrane (PTM-SPCL) with respect to that in PTMSP is reasonable in that chlorine inhibits Ps formation. This agrees with the finding that the smaller dimensions of channel-like hole radii (R_3) appear and densities increase in aged PTMSPCL ^[11].

In Table 4, the PTMSP membrane cast from tetrahydrofuran (THF) has lower values of lifetime τ_4 , o-Ps intensity I_4 and permeability of oxygen, nitrogen, carbondioxide than the membrane cast from toluene, cy-

Table 4.	Results of PTMSP	membranes ca	st from di	fferent solvents

Solvents	$ au_4$ (ns) .	$I_4 (\%)$	$P_{\mathrm{O}_2} imes 10^{6a}$	$P_{ m N_2} imes 10^6$	$P_{\rm CO_2} \times 10^6$
Cyclohexane	12.54 ± 0.04	20.2 ± 0.1	2.34	1.56	7.02
Toluene	12.20 ± 0.01	22.0 ± 0.1	1.46	1.03	3.81
THF	11.63 ± 0.03	20.2 ± 0.1	0.446	0.299	2.08
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^a In the unit of cm^3 (STP) $cm / cm^2 s cm$ Hg.



Fig.2 Fractional free-volume vs. hard segment content

clohexane. Free-volume and free-volume fraction are directly related to permeability of the membrane because of its packing structure. PALS is useful for gas separation in order to study the suitable microstructure of polymers ^[12].

Correlations between gas permeation and freevolume hole properties of polyurethane (PU) membranes based on hard segments consisting of toluene diisocyanate and 1,4-butanediol and different soft segments consisting of hydroxyl terminated polybutadiene (HTPB), hydroxyl terminated polybutadiene/styrene (HTBS) and hydroxyl terminated polybutadiene/acrylonitrile (HTBN) were described. The permeability, free-volume hole size (R) and fractional freevolume decrease with the increase of hard segment content. These are due to the enlargement of the hard segment of the cluster aggregate and the restriction of the movement of the soft segment. In HTPB-PU, the hydrogen bond cannot be formed between soft segments and hard segments, although in HTBS-PU, rigid benzene rings increase the stiffness of the polymer chain and restrict the chain mobility. In HTBN-PU, -CN of acrylonitrile in HTBN can form a hydrogen bond with -NH of the hard segments. In Fig. 2, HTBN-PU with the increase of hard segment content has the lowest fractional free-volume and the lowest gas permeability ^[13].

PU membranes obtained by varying the ratio of the structural constituents, polypropylene oxide and polybutadiene (PBDO) were studied.

The values of the radius and the normalized fractional free-volume decrease with the increasing PBDO content until about 50% due to the coexistence of two phases corresponding to separate domains of the two segments and the values remain about constant due to the formation of a homogeneous phase. The PU membrane (0% PBDO) presents low gas permeability in contrast to the high values of its radius and fractional free-volume that there are other factors involved in the permeation as chain flexibility, chemistry at the free-volume walls, diffusion barriers, etc. Indeed, the interconnectivity and transmissibility between holes may play a dominant role in that process ^[14].

The measurements also point out the temperature dependence of the free-volume in the Ag^+ -doped polyperfluorosulfonate membrane (PSM) and exhibit relatively high permeability for 1-butene compared with n-butane and 1, 3-butadiene ^[15]. The free-volume of the amorphous phase varies irregularly with the pendant size group change. Transport properties depend on the free-volume and the mobility of the segments creating the supermolecular structure of the membrane $^{[16]}$.

3 Conclusions

Based on the positron annihilation measurements several polymeric membranes were prepared to study different characteristics which have been applied to the control of the gas flow, to the application of fieldassisted positron moderation, to the alteration of the structural conformation of a polymeric chain, to the observation of hydrophilic / hydrophobic characteristics, to the study of vacancy profiles associated with salt selectivity, and to the measurement of the relationship between the gas permeability and the free-volume. Through modification of the membranes, their physical and chemical properties were changed. In this work a comparison between modified and unmodified membranes was made on the concept of free-volume holes and in correlation to gas permeation properties.

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