MICROSTRUCTURAL CHARACTERIZATION OF POLYMERS WITH POSITRONS

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Positrons provide a versatile probe for monitoring microstructural features of molecular solids. In this paper, we report on positron lifetime measurements in two different types of polymers. The first group comprises polyacrylates processed on earth and in space. The second group includes fully-compatible and totally-incompatible Semi-Interpenetrating polymer networks of thermosetting and thermoplastic polyimides. On the basis of lifetime measurements, it is concluded that free volumes are a direct reflection of physical/electromagnetic properties of the host polymers.
Key words: Polymers, Positron Lifetime Spectroscopy, Free Volume, Dielectric Constant, Electrostatic Interactions.

INTRODUCTION

We have been using positron annihilation spectroscopies to infer host polymer properties for a number of years. Our earlier studies of epoxies (1), polyamides (2) and polyimides (3) have indicated that positronium (Ps) atoms form readily in epoxies and polyamides, but do not seem to form in polyimides studied. These conclusions were drawn as a result of the observations that lifetime spectra did not have a significant longlife component in the case of polyimides. Of course, one could argue that Ps atoms could have formed and been quenched so fast that they could not be distinguished from localized positron annihilations. This, however, can not be the case since the availability of quenching electrons is directly related to the formation of positronium atoms. If the quenching electrons were that readily available, they would rather annihilate with free positrons than let them enter the microvoids to form Ps atoms for subsequent fast quenching. Also, the experimentally observed relative intensities of the short and intermediate lifetime components in polyimides argue against the formation of Ps atoms in them (4). We will review here the positron behavior in two different categories of polymers: (i). Contact Lens Polymers (Epoxies), and: (ii). Semi-Interpenetrating Polymer Networks (S-IPN) of polyimides. The contact lens samples studied included earth- and space- processed rods. The S-IPN samples included fully- compatible and totally-incompatible thermoset and thermoplastic constituents.

EXPERIMENTAL PROCEDURES

Material Preparation

Contact lens samples were synthesized from methyl methacrylate and varying amounts of cross-linking ethylene glycol di-methacrylate. The polymerization process was initiated at 40 ^{0}C by using thermal catalysts. The S-IPN samples were synthesized from three different types of polyimides. LaRC^{TM} - RP46 / LaRC^{TM} - IA polymers where the thermosetting and the thermoplastic components were fully compatible and LaRC^{TM} - RP46 / LaRC^{TM} - SI polymers where the two components were totally-incompatible. The relative concentration of the two components varied from 100 : 0 to 0 : 100 percent by weight.

Positron Lifetime Measurements

Positron lifetime measurements were made using a standard fast - fast coincidence measurement system. A 25 μC Na^{22} positron source, deposited on a 2.54 μm thick kepton foil folded on itself, was sandwiched between 2.54 cm x 2.54 cm x 0.25 cm test coupons and the spectra were accumulated for 24 hours. This counting period produced a total of more than 10^5 counts in the peak and over 10^6 in each spectrum. The time resolution of the lifetime system was 265 picoseconds. All measurements were made at room temperature and in dry samples. The lifetime spectra were analyzed with PATFIT program (5).

EXPERIMENTAL RESULTS

Contact Lens Samples

The positron lifetime spectra in these materials exhibited 3-clear components. The longest lifetime components (τ_3) are associated with the quenching of orthopositronium (O-Ps) atoms. These lifetimes are quantitatively related (6) to the dimensions of the microvoids where O-Ps atoms form and annihilate. The free volume fractions (f) have been calculated using the relation: $f = CI_3Vf_3$, where C has been determined by equating f in N4a samples with its saturation moisture content. This is acceptable since H_2O molecules can not enter these materials chemically. The results are summarized in Tables I and II. Also listed in the table are the densities of various samples. The densities of various samples are consistent with their free volume fractions. The designations Top/Bottom refer to the top and bottom of the glass tube in which the sample rods were polymerized.

TABLE I. Summary of Orthopositronium Lifetimes and Associated Parameters of the Earth - Processed Contact Lens samples.

Sample Designation		Top/Bottom	τ_3(ps)/I_3(%)	f (%)	ρ (gm/cc) (± 0.0020)
N4a	{Two percent cross-	Top	2487 ± 13/ 20.8 ± 0.1	1.40 ± 0.02	1.1686
N4a	linking agent}	Bottom	2498 ± 11/ 21.3 ± 0.1	1.45 ± 0.03	1.1689
N4b	{Five percent cross-	Top	2122 ± 20/ 23.2 ± 0.3	1.17 ± 0.04	1.1836
N4b	linking agent}	Bottom	2283 ± 14/ 22.4 ± 0.2	1.30 ± 0.03	1.1796

TABLE II. Summary of Orthopositronium Lifetimes and Associated Parameters of Space-Processed Contact Lens Samples.

Sample Designation		Top/Bottom	τ_3(ps)/I_3(%)	f (%)	ρ (gm/cc) (± 0.0020)
N4a	{Two percent cross-	Top	2498 ± 14/ 21.9 ± 0.2	1.49 ± 0.03	1.1685
N4a	linking agent}	Bottom	2498 ± 14/ 22.2 ± 0.2	1.51 ± 0.03	1.1686
N4b	{Five percent cross-	Top	2046 ± 14/ 23.1 ± 0.3	1.09 ± 0.03	1.1836
N4b	linking agent}	Bottom	2183 ± 13/ 22.7 ± 0.3	1.21 ± 0.03	1.1820

S-IPN Samples

The lifetime spectra in these samples were also analyzed into 3-components. However, the intensities of the third components (τ_3) in all S-IPN samples were very low (< 1 %) and these were, therefore, attributed to the background. The intermediate lifetime components (τ_2) were the strongest in all S-IPN samples. We attribute these components to the trapped positron annihilations rather than fast-quenched O-Ps atoms. Just like the O-Ps annihilation lifetimes, the trapped positron annihilation lifetimes can be quantitatively related (7) to the trap dimensions. The lifetime results, free volume fractions, densities and dielectric constants of S-IPN samples are summarized in Tables III and IV. The free volume fractions (f) have been calculated by equating f in LaRC™ - IA with its saturation moisture content. This is justifiable since hydration of this thermoplastic polyimide is miniscule. It is instructive to note distinct differences between the properties of the compatible and incompatible S-IPN samples.

DISCUSSION

Polymeric rods produced in microgravity environment should be homogeneous in composition and density, compared with 1-g processed materials, where the bottom samples may be more compacted than the

samples from the top section of the rods. However, the data summarized in Tables I and II show no differences in the free volume and densities of the two types of contact lens samples. A closer investigation of the exact geometrical orientations of the processing chambers revealed that the polymerization cylinders in the ground laboratory and the space shuttle bay were in horizontal planes as opposed to the vertical orientations that the experimental plans called for. Under these circumstances, we should have expected what we actually observed! We do, however, find some interesting differences in the case of S-IPN materials.

TABLE III. Summary of Positron Lifetime and Associated Parameters in Fully-Compatible S-IPN Samples (8).

Sample Composition LaRC™- RP46 : LaRC™ - IA	τ_2 (ps) / I_2 (%)	f (%)	ρ (gm/cc)	ε (10 GHz) (± 2%)
0 : 100	488 ± 3/80.0 ± 2.0	2.81 ± 0.08	1.3402 ± 0.0029	2.82
25 : 75	422 ± 5/79.3 ± 3.0	2.58 ± 0.12	1.3815 ± 0.0028	3.01
35 : 65	399 ± 4/78.9 ± 2.9	2.48 ± 0.10	1.3668 ± 0.0020	3.11
50 : 50	394 ± 1/79.4 ± 0.1	2.48 ± 0.09	1.3713 ± 0.0041	3.14
65 : 35	400 ± 2/76.3 ± 1.4	2.42 ± 0.07	1.3629 ± 0.0032	3.14
75 : 25	399 ± 2/79.6 ± 1.8	2.50 ± 0.07	1.3546 ± 0.0036	3.13
100 : 0	400 ± 4/81.4 ± 2.2	2.56 ± 0.08	1.3572 ± 0.0020	3.13

TABLE IV. Summary of Positron Lifetimes and Associated Parameters in Totally-Incompatible S-IPN Samples.

Sample Composition LaRC™- RP46 : LaRC™ - SI	τ_2 (Ps) / I_2 (%)	f (%)	ρ(gm/cc) (± 0.0020)	ε (10 GHz) (± 2%)
0 : 100	400 ± 2/93.2 ± 0.4	2.48 ± 0.12	1.3727	3.13
25 : 75	394 ± 1/93.4 ± 0.5	2.47 ± 0.12	1.3696	3.13
35 : 65	397 ± 2/95.0 ± 1.0	2.52 ± 0.14	1.3630	3.12
50 : 50	395 ± 1/92.3 ± 0.4	2.44 ± 0.11	1.3667	3.13
65 : 35	396 ± 2/93.1± 0.8	2.47 ± 0.13	1.3620	3.13
75 : 25	398 ± 2/93.2 ± 0.3	2.48 ± 0.11	1.3693	3.13
100 : 0	396 ± 1/94.7 ± 0.6	2.51 ± 0.08	1.3789	3.12

For the compatible LaRC™ - RP46/LaRC™ - IA samples, it is found that the free volume appears to go through a minimum at 50:50 composition. The densities and dielectric constants also follow a consistent trend as seen in data summarized in Table V and illustrated in Figures 1 and 2. For the incompatible LaRC™ - RP46/ LaRC™ - SI samples, on the other hand, no such trends were observed. The stiffness of the LaRC™ - SI

TABLE V. Comparison Between the Experimental and Computed Values of the Densities and Dielectric Constants of Fully-Compatible S - IPN Samples (8).

Sample Composition	Density (ρ), gm/cc		Dielectric Constant (ε) at 10 GHz	
LaRC™- RP46 : LaRC™- IA	Experimental	Computed	Experimental	Computed
0 : 100	1.3402 ± 0.0029	1.3402 ± 0.0029	2.82 ± 0.06	3.10 ± 0.03
25 : 75	1.3815 ± 0.0028	1.3558 ± 0.0031	3.01 ± 0.06	3.11 ± 0.03
35 : 65	1.3668 ± 0.0020	1.3620 ± 0.0036	3.11 ± 0.06	3.12 ± 0.03
50 : 50	1.3713 ± 0.0041	1.3714 ± 0.0045	3.14 ± 0.06	3.12 ± 0.03
65 : 35	1.3629 ± 0.0032	1.3672 ± 0.0034	3.14 ± 0.06	3.13 ± 0.03
75 : 25	1.3546 ± 0.0036	1.3643 ± 0.0026	3.13 ± 0.06	3.12 ± 0.03
100 : 0	1.3572 ± 0.0020	1.3572 ± 0.0020	3.13 ± 0.06	3.11 ± 0.03

ρ (computed) = $w_1\rho_1 + w_2\rho_2 + (1/2)\alpha\beta(\rho_1\rho_2)$, where $\alpha = 0.0168 \pm 0.0031$ and β = Molecular chain overlap parameter.
ε (computed) = $\{(1-f)/(\varepsilon_R) + (f)/(\varepsilon_{Air})\}^{-1}$, where $\varepsilon_R = 3.30 \pm 0.03$.

chain precluded any electrostatic effects observed for the more compliant LaRC™ - IA member (8).

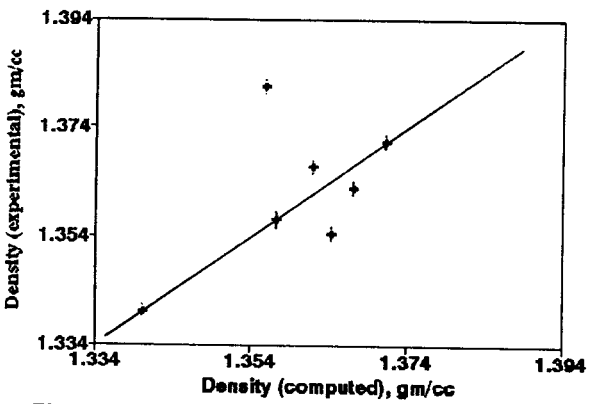

Figure 1. Comparision Between the Experimental and the Computed Values of Densities of Fully-Compatible S-IPN Samples.

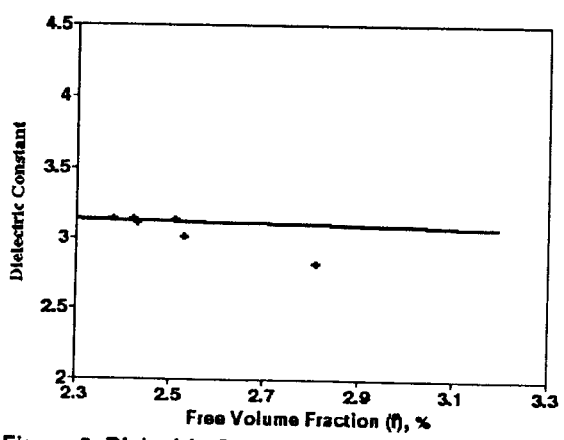

Figure 2. Dielectric Constant vs Free Volume Fraction in Fully-Compatible S-IPN Samples.

CONCLUDING REMARKS

Positrons are ideal probes for monitoring microstructural properties of polymers. We have observed direct correlations between the atomic scale free volume holes and macroscopic mechanical and electromagnetic properties of the polymeric materials - not only qualitatively but also quantitatively.

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