A SLOW POSITRON BEAM GENERATOR FOR LIFETIME STUDIES

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SUMMARY

We have developed a slow positron beam generator using well-annealed polycrystalline tungsten moderators and a Na$^{22}$ positron source. A 250 μc source, deposited on a 2.54 μm thick aluminized mylar, is sandwiched between two 2.54 cm x 2.54 cm x 0.0127 cm tungsten pieces. Two 2.54 cm x 2.54 cm x t cm test polymer films insulate the two tungsten moderator pieces from the aluminized mylar source holder (t may range from 0.00127 to 0.0127 cm). A potential difference of 10 to 100 volts--depending on the test polymer film thickness (t)--is applied between the tungsten pieces and the source foil. Thermalized positrons diffusing out of the moderator pieces are attracted to the source foil held at an appropriate potential below the moderator pieces. These positrons have to pass through the test polymer films before they can reach the source foil. The potential difference between the moderator pieces and the aluminized mylar is so adjusted as to force the positrons to stop in the test polymer films. Thus the new generator becomes an effective source of positrons for assaying thin polymer films for their molecular morphology.

I. INTRODUCTION

Polymers are finding increasing applications in aerospace industry. They are strong, lightweight, and can be developed to have desirable mechanical, electrical and optical properties. Some of the more challenging applications often call for polymers in the form of thin films. The properties of these films are strongly dependent on their molecular morphology. Films with the same chemical composition and density can have different physical properties depending on their processing history. It is therefore necessary to develop a technique that can give information about the internal structure of the "finished" thin polymer films.

We had previously used Positron Annihilation Spectroscopy (PAS) for measuring free volume in polymer discs$^{(1,2)}$. It was therefore decided to adapt conventional PAS to the study of thin films. The first attempt involved sandwiching the test films between suitable aluminum degraders such that positrons of progressively higher energies were forced to stop in the test films. Figure 1 shows the source-target assembly. In order to eliminate the effects of positrons annihilating in the aluminium energy degraders, lifetime spectra were taken with and without the test films in the target assembly. The difference between these two spectra represented the test film lifetime data. However, only a small fraction of the incident positron beam stopped in the test films due to the original Fermi energy$^{(3)}$ distribution of the Na$^{22}$ positrons. Consequently, it required 24 hours or more to accumulate data with adequate statistics, even with a 25 μc Na$^{22}$ source.
In order to expedite the data accumulation with better statistics, the following slow positron beam generation scheme was devised and implemented: Isotropic positron beams were allowed to penetrate a 0.0127 cm thick annealed, high purity (99.95%) tungsten foil. After quick thermalization, the incident positron beams suffered multiple elastic scattering from tungsten atoms, forcing some of the positrons to diffuse out of the same side whence they entered the foil. Since tungsten has a negative work function for positrons\(^4\), those positrons that survive annihilation and trapping would eventually diffuse out of it. These positrons can be accelerated to preselected energies by simply applying an appropriate electrical potential difference between the tungsten moderator and a metal electrode positioned in front of it. The experimental details and some applications of this concept are described in the following sections.

II. EXPERIMENTAL DESIGN

High purity (99.95%) polycrystalline tungsten foils in the form of 2.54 cm x 5.08 cm x 0.0127 cm strips were annealed in 6 x 10^{-5} pascal vacuum by repeatedly heating them to red heat and allowing them to cool down while still in vacuum. The annealed strip was cut into two 2.54 cm x 2.54 cm x 0.0127 cm pieces which served as positron beam moderators. A 250 μCi Na\(^{22}\) source deposited on a 2.54 μm thick aluminumized mylar was inserted between two moderator pieces. The test polymer films, introduced between the source foil and the moderator steps, helped electrically insulate the source holder from either tungsten strip. The source-moderator assembly is shown in figure 2.

After injection into tungsten moderator the positrons are quickly thermalized. Subsequently, they suffer multiple elastic scattering over distances of the order of 1000 Å before annihilating with the electrons\(^5\). Some of these positrons diffuse back to the entrance surface whence they are emitted with an energy spread of the order of 0.2 ev. These positrons can be accelerated to a desired energy\(^6\) by applying appropriate potential difference between the moderator and the source foil. It should be noted that the positrons strike the moderator surface isotropically, thereby enhancing their probability of eventual escape from the entrance surface. Also, the back diffusing positrons come mainly from the near surface regions because of limited acceptance time selected for the positron lifetime measurement system.

III. EXPERIMENTAL PROCEDURE

As shown in figure 2, the test polymer films are inserted between the source foil and the moderators. Consequently, all re-emitted positrons attracted towards the source foil must pass through the test films. By adjusting the voltage between the source foil and the moderator strips, all positrons emitted from the moderator surfaces can be made to stop in the test polymer films\(^6\). Thus, thin polymer films which could not be conveniently studied for their free volume characteristics using the
The multi-degrader assembly of figure 1 can be studied readily by applying appropriate voltage on the source foil.

In order to separate the moderator annihilation spectrum from the test film spectrum, it is necessary to make two separate lifetime measurements. The first measurement is made with the source foil held at -V volts. The second measurement is made with the source held at a much lower potential—such as -10 volts. The difference between these two spectra then gives the effects of annihilation in the interior of the test polymer film. By measuring the total number of counts in the lifetime spectra with +V volts at the source foil, the efficiency (ε) of the slow beam generator can be calculated as follows:

\[ \varepsilon = 2 \frac{I(-V) - I(+V)}{I(-V) + I(+V)} \]

The value of ε for the present generator is of the order of 6%.

IV. TEST OF THE SLOW POSITRON BEAM SYSTEM

In order to test the validity of the assumption that the thermalized positron beams diffusing back from the moderator surfaces do not suffer inordinate delays with respect to the 1.28 MeV gamma ray time marker, we compared the lifetimes measured in a 0.0089 cm thick teflon film using the present system with the corresponding values in a 0.254 cm thick disc obtained by using the conventional thick disc procedure. The results are summarized in Table I.

It is apparent that the agreement is reasonably good, particularly in the case of \((\tau_3/I_3)\) values which are the basis for free volume measurements in polymers.

V. APPLICATIONS

We have applied the procedure described earlier for the measurement of free volume fraction in two polyimide films. The physical properties of these films are summarized in Table II. The polyimide, PMDA/ODA, is a NASA-Langley prepared polymer which has the same chemical structure as that of Kapton® (Dupont's commercially available polyimide). The polyimide, ODPA/p-PDA, is an isomer (same chemical formula with different arrangement of chemical units) of Kapton®. Figure 3 shows the chemical structure of the two isomers. The PMDA/ODA is essentially a totally amorphous polymer while the ODPA/p-PDA has a significant level of crystallinity. This crystallinity results in a high modulus in the latter polymer, 975,000 psi, as compared to 380,000 psi for PMDA/ODA. Even though the two systems are isomers of each other, they obviously have considerable differences in their morphologies. The free volume fractions in these films were measured using the relationship
between the ortho-positronium lifetime ($\tau'$) and the average microvoid size ($R$):

$$\frac{1}{\tau'} = 2 \left( 1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin \left( 2\pi \frac{R}{R_o} \right) \right)$$

where $R_o$ = Radius of the spherical potential well
(The potential is infinite for $r > R_o$ and constant for $r < R_o$)

$$R = R_o - \Delta R$$
($\Delta R$ is the thickness of the electron layer (8) inside the potential well and has been assumed to be 0.1656 nm)

Equation 1 is based on the assumption that the orthopositronium (0-Ps) lifetime in the electron layer is $\approx 500$ picoseconds.

Positron lifetimes in the polyimide films were measured using standard fast-fast coincidence lifetime measurement technique based on the slow positron beam generator. Figure 4 shows typical lifetime spectra in ODPA-p-PDA films. The 0-Ps lifetimes and the corresponding values of the average free volume cell volumes, $\langle V_f \rangle$, in the two films are summarized in Table III. Clearly, ODPA-p-PDA films have large-sized microvoids, but comparatively fewer of them.

VI. CONCLUDING REMARKS

A slow positron beam generator suitable for Positron Annihilation Spectroscopic measurements in thin ($\leq 0.0254$ cm) polymer films has been developed. Its efficiency, determined by the ratio of the total counts in the "Difference" spectrum and the total counts in the moderator lifetime spectrum, is of the order of 6%. Furthermore, the present scheme also successfully resolves the difficult timing problem that can be encountered with the positron moderator foils.
REFERENCES


TABLE I. Comparison Between Positron Lifetimes Observed With the Present System and the Values Obtained Using a Conventional Procedure

<table>
<thead>
<tr>
<th></th>
<th>Present System 250 µc/0.0089 cm</th>
<th>Conventional System 25 µc/0.254 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tilde{\tau}_1 / I_1 )</td>
<td>( \tilde{\tau}_2 / I_2 )</td>
<td>( \tilde{\tau}_3 / I_3 )</td>
</tr>
<tr>
<td>241 ps 62%</td>
<td>725 ps 17%</td>
<td>3281 ps 21%</td>
</tr>
<tr>
<td></td>
<td>291 ps 64%</td>
<td>999 ps 16%</td>
</tr>
</tbody>
</table>

TABLE II. Physical Properties of Test Polyimide Films (*)

<table>
<thead>
<tr>
<th>No.</th>
<th>Film Composition</th>
<th>Film Thickness</th>
<th>Coefficient of Thermal Expansion (µm/m °C)</th>
<th>Density (gm/cc)</th>
<th>Tensile Modulus at 25 °C (psi)</th>
<th>Saturation Moisture (v/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMDA-ODA</td>
<td>0.0043 cm</td>
<td>23.3</td>
<td>1.414±0.003</td>
<td>380,000</td>
<td>4.46</td>
</tr>
<tr>
<td>2</td>
<td>ODPA-p-PDA</td>
<td>0.0051 cm</td>
<td>23.8</td>
<td>≥ 1.45</td>
<td>975,000</td>
<td>2.61</td>
</tr>
</tbody>
</table>

### TABLE III. Summary of Free Volume Results in the Test Polyimide Films

<table>
<thead>
<tr>
<th>No.</th>
<th>Film Composition</th>
<th>Positron Lifetime Values</th>
<th>( &lt;V_f&gt; )</th>
<th>( N(\text{(*)}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \tau_1/I_1 ) \hspace{1cm} ( \tau_2/I_2 )</td>
<td>(A)(^3)</td>
<td>(Number of Free Volume Cells per Cubic Centimeter)</td>
</tr>
<tr>
<td>1</td>
<td>PMDA-ODA</td>
<td>108/68% \hspace{1cm} 535 ps/32%</td>
<td>0.44</td>
<td>1.0 ( \times ) 10(^23)</td>
</tr>
<tr>
<td>2</td>
<td>ODPA-p-PDA</td>
<td>244 ps/81% \hspace{1cm} 849 ps/19%</td>
<td>11.10</td>
<td>2.4 ( \times ) 10(^21)</td>
</tr>
</tbody>
</table>

\(*\) \( N = \frac{\text{Sat. Moisture Volume/cc}}{<V_f>} = \frac{\text{Total Fractional Free Volume/cc}}{\text{Average Volume of a Free Volume Cell (cc)}} \)
Figure 1. Schematic diagram of the source target assembly
Figure 2. Schematic diagram of the moderator-source assembly
Figure 3. Chemical structure of the PMDA/ODA and ODPA/p-PDA polymers
Figure 4(a). A typical lifetime spectrum in polyimide ODPA-p-PDA film
Figure 4(b). A typical lifetime spectrum in polyimide ODPA-p-PDA film

Moderator bias: +10 volts

Positron annihilation events

Channel number
Figure 4(c). A typical "difference" lifetime spectrum in polyimide ODPA-p-PDA film.
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