NASA Technical Memorandum 84532

NASA-TM-84532 19820023570

POSITRON LIFETIME STUDIES IN THERMOPLASTIC POLYIMIDE TEST SPECIMENS

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JULY 1982

NASA
National Aeronautics and
Space Administration

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TEST SPECIMENS

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ABSTRACT

Positron lifetime measurements have been made in two thermoplastic polyimide materials recently developed at Langley. The long component lifetime values in polyimidesulfone samples are 847 ± 81 Ps (dry) and 764 ± 91 Ps (saturated). The corresponding values in LARC-thermoplastic imides are 1080 ± 139 Ps (dry) and 711 ± 96 Ps (saturated). Clearly, the presence of moisture has greater effect on positron lifetime in LARC-thermoplastic imides than in the case of polyimidesulfones. This result is consistent with the photomicrographic observations made on frozen water-saturated specimens of these materials.

INTRODUCTION

We have been investigating the dependence of positron lifetime on the moisture content of polymeric materials for several years.[1-3] Generally, the introduction of moisture in the test specimens causes a noticeable reduction in the positron lifetime. This phenomenon, presumably, results from the fact that the positrons have a tendency to be localized in regions with lower than average ionic density--such as voids or free volume cells.[4] Some of the so-localized positrons form positronium (Ps) atoms there. As the water enters the medium, it forces the positronium wave function to spill over on to the regions of normal molecular electrons, thereby facilitating their pickoff annihilation. This effect is quite pronounced in epoxies and polyamides studied.[1-3] However, it is not so apparent in the polyimide

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specimens investigated mainly due to very low intensity of the long-life component in their positron annihilation spectra. Low intensity of the long-life component suggests low free volume, i.e., more closely linked molecular chains characteristic of high strength polymers. NASA scientists have been studying polyimide and graphite-fiber reinforced polyimide composites for high temperature airframe applications for several years. Polyimides are also prime candidates for future use in the Shuttle program. Recently, two promising thermoplastic polyimide materials have been developed at Langley.[5,6] They are polyimidesulfone and LARC-thermoplastic imide (TPI). These newly-developed polymers are similar in many respects. They are almost identical in chemical structure as seen in figure 1, have similar adhesive strengths and behave similarly on aging. However, it is easier to process polyimidesulfones than LARC-TPI's. Furthermore, polyimidesulfones foam during processing whereas LARC-TPI's do not. The nature of the foam is such that it appears to be due to water or some other solvent coming out rather than the sulfone group. This is rather puzzling since water is expected to be hydrogen-bonded in the polyimidesulfone. It was therefore decided to investigate if the positron annihilation behavior in these two materials is different. Positron lifetime measurements were made in both specimens in dry and fully water-saturated states. These measurements, as well as the other phenomena observed when the water-saturated polyimide specimens were frozen, are described in the following sections.

EXPERIMENTAL PROCEDURE

a. Specimen Preparation.-The polyimide specimens were prepared in the form of thin circular discs summarized in Table I.

Table I

Geometrical Details of the Test Specimens

No.	Material	Spec. No.	Geometrical Dimensions	Specimen Volume
1	Polyimidesulfone	1	Diameter = 2.864 cm Thickness = 0.148 cm	0.954 cc
		2	Diameter = 2.865 cm Thickness = 0.135 cm	0.871 cc
2	LARC-TPI	1	Diameter = 2.869 cm Thickness = 0.156 cm	1.009 cc
		2	Diameter = 2.873 cm Thickness = 0.149	0.966 cc

The specimens were weighed in the as-received condition (i.e., ambient state) and then desiccated for 307 hours at 110°C and 102 hours at 150°C. The desiccated specimen weights were measured. The specimens were then saturated by boiling them in distilled water at 100°C for 162.83 hours and reweighed. The specimen weights in various states are summarized in Table II.

Table II

Summary of Specimen Weights in Various States

No.	Material	Spec No.	Weight of the Specimen, mg			Moisture Content (w/o)	
			Dry	Ambient	Saturated	Ambient	Saturation
1	Polyimide-sulfone	1	1327.55	1341.10	1367.13	1.02	2.98
		2	1225.87	1239.24	1262.50	1.09	2.99
2	LARC-TPI	1	1373.17	1393.00	1412.22	1.44	2.84
		2	1309.93	1332.94	1348.23	1.76	2.92

It is apparent from these results that the saturation moisture contents of the two polyimides are about the same. However, the ambient moisture contents of the specimens after they had been left in the laboratory air for about 1 month after their preparation are distinctly different, being much higher in LARC-TPI than in polyimidesulfone. It would thus appear that though the free volumes of the sample are roughly equal, the diffusion coefficient for moisture penetration in thermoplastic imides is considerably larger than in polyimidesulfone. We shall refer to this observation again, later in the discussion of the results.

b. Positron Lifetime Measurement.-A 10-microcurie Na^{22} positron source was sandwiched between the two coupons of the test material. The source-test coupon sandwich was wrapped in a thin (25.4 μm) aluminum foil and sealed with vinyl tape to prevent moisture pickup or loss during the positron lifetime measurement. The positron lifetime was then measured as usual by determining the time interval between the detection of the 1.28-MeV gamma ray emitted almost simultaneously with the emission of the positron and the detection of one of the two 0.511-MeV annihilation photons.[2,7] The positron lifetimes were recorded by a spectrometer using a fast-slow coincidence method described elsewhere.[7] The lifetime resolution of the system was approximately 450 picoseconds. Figure 2 shows a schematic diagram of the experimental system used in the lifetime measurements.

EXPERIMENTAL RESULTS

Positron lifetimes were measured in totally dry and fully water-saturated states of the test specimens. Figure 3 shows the positron lifetime spectrum in dry and saturated polyimidesulfone specimens. Figure 4 shows similar results for LARC-TPI specimens. It is noted that neither material exhibits a strong long-life component, although its presence is unmistakable. Figure 5 shows a comparison between the lifetime spectra in water-saturated states of the two materials. The results are summarized in Table III.

Table III

Summary of Positron Lifetime Results in the Test Materials

No.	Material	Status	Positron Lifetime Values	
			$\left(\frac{I_2}{I_1}\right)^{(*)}$	(Long Component Lifetime)(**)
1	Polyimidesulfone	Dry Saturated	2.5% 2.9%	847 ± 81 Ps 764 ± 91 Ps
2	LARC-TPI	Dry Saturated	1.0% 4.0%	1080 ± 139 Ps 711 ± 96 Ps

(*) I_1 and I_2 refer to the areas under the short-lifetime and long-lifetime components, respectively. It is apparent from the I_2/I_1 values listed that the long-life component is very weak in both materials, thus making the long-lifetime values subject to rather large errors (see last column).

(**) Long component refers to the component with long lifetime. It is this component which responds sensitively to the changes in the properties of the medium produced by diffusing water.[2]

While preparing for positron lifetime measurements in water-saturated states of the test materials, an interesting (and highly relevant) phenomenon was observed. After saturation with water, the specimens were stored overnight in a freezer for positron lifetime measurements the next day. Storage in the freezer was effected to avoid moisture loss during the overnight wait. Next morning, it was observed that the polyimidesulfone specimens had developed severe internal crazing (or cracks) whereas the LARC-TPI specimens did not appear to have suffered any visible effects. The same type of phenomenon was observed during a repeat test. The internal crazing/stressing in the polyimidesulfones persisted even after the specimens had been desiccated for over 100 hours at 120°C. The implications of the phenomenon in polyimidesulfones will be discussed in the following section.

DISCUSSIONS

On the basis of the data shown in Table II, it is noted that even though the polyimidesulfone and LARC-TPI have almost the same saturation moisture content, their ambient moisture levels are markedly different. For example, the ambient moisture level in LARC-TPI is almost 50% higher than in the polyimidesulfone. These data indicate that the total free volume fractions in the two materials are the same but the moisture diffusion constant in LARC-TPI is considerably higher. A logical extension of this indication could be that there are fewer, but larger, free volume cells in the polyimidesulfone and more numerous, but smaller, free volume cells in LARC-TPI. These inferences are consistent with the observed effects of moisture on the positron lifetimes in the two types of test materials (See Table III). It is noted that the moisture-induced reduction in positron lifetime is larger in LARC-TPI than in polyimidesulfone. This result would be expected if the LARC-TPI coupons had a larger number of smaller-sized free volume cells. On filling of these cells with water, the positronium atoms would be forced against the cell walls. This would enhance the positronium wavefunction overlap with the surrounding molecular electrons. Because of the larger surface area presented by the smaller voids in the LARC-TPI, the effects of the overlap would be more pronounced in LARC-TPI than in polyimidesulfone. That this inference is valid is further supported by the accidental observations that the LARC-TPI did not experience as severe internal stressing as polyimidesulfone when water-saturated samples of these materials were frozen. Because of the expansion of water on freezing, the internal stressing effects would be more marked in polyimidesulfone with larger voids than LARC-TPI with smaller voids. The presence of larger free volume cavities in polyimidesulfone could be the result of foaming observed during the processing of these materials.

CONCLUDING REMARKS

As a result of positron lifetime studies in two Langley-developed thermoplastic polyimides, it is concluded that the polyimidesulfones have fewer but larger free volume cells in them. These voids are presumably produced when the moisture/solvent leaves the matrix during the processing cycles. LARC thermoplastic polyimides, on the other hand, have more numerous but smaller-sized voids in them thereby facilitating moisture diffusion. Because of the presence of larger-sized voids in polyimidesultone, this material would be more susceptible to internal stressing on freezing of water-saturated components.

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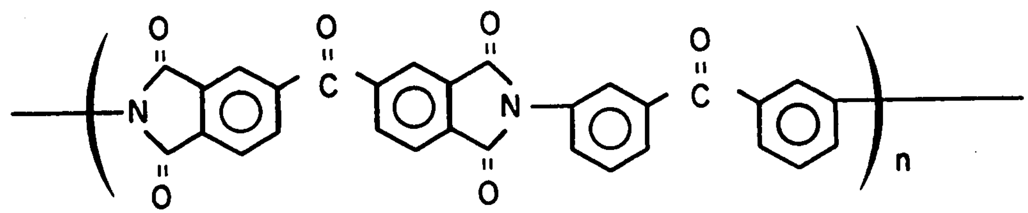
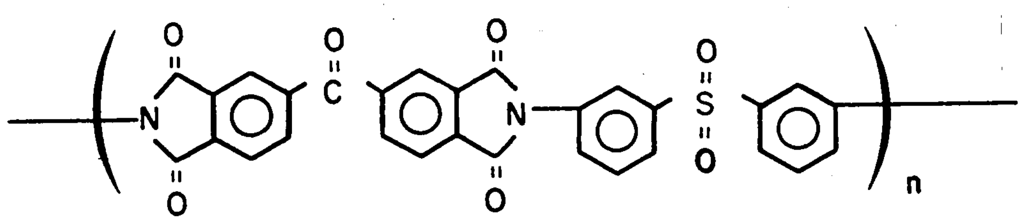


LARC - TPI



POLYIMIDESULFONE

FIGURE I - THERMOPLASTIC POLYMIDE STRUCTURE

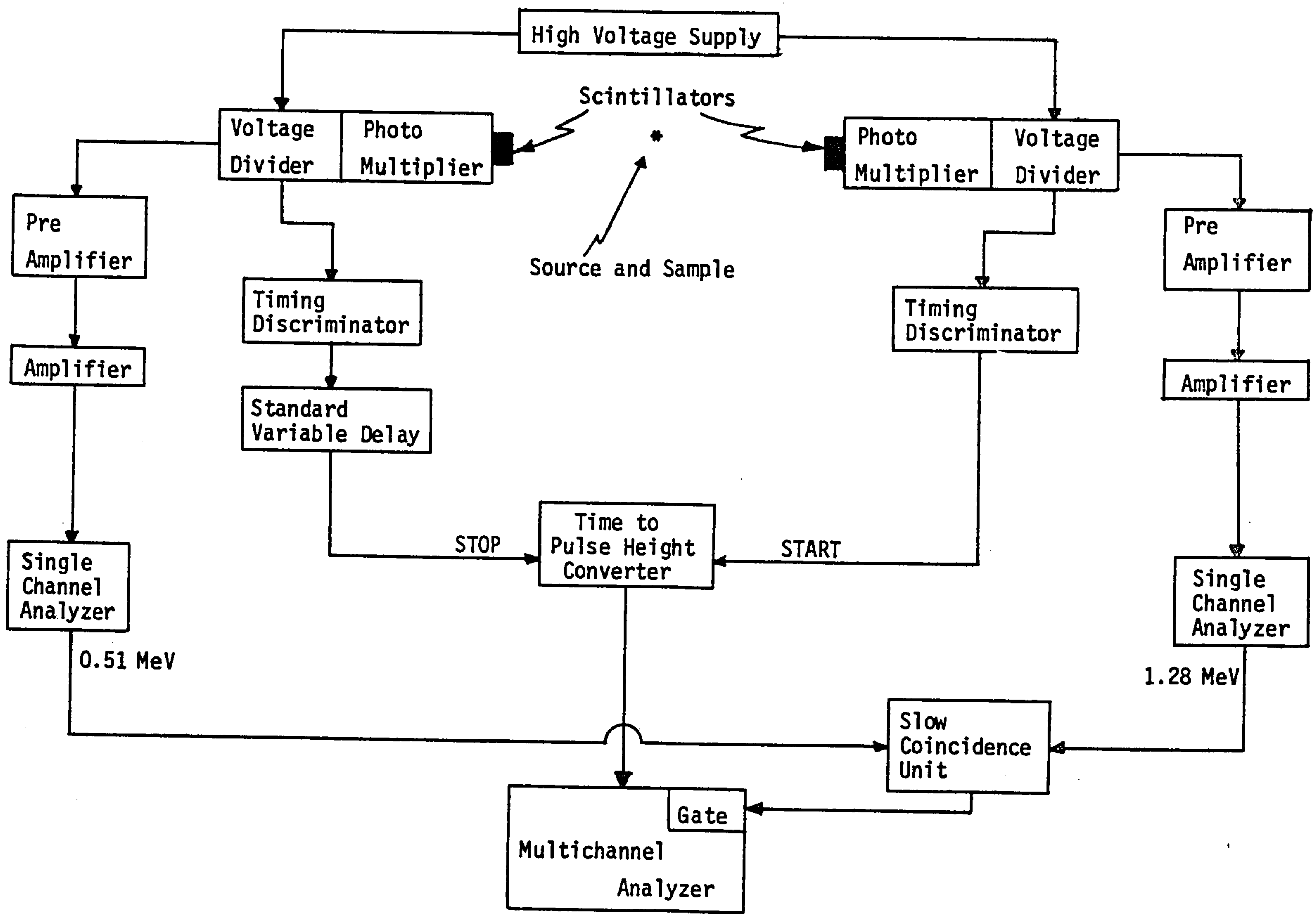


Figure-2. Fast-slow coincidence system for determining positron lifetime spectra.

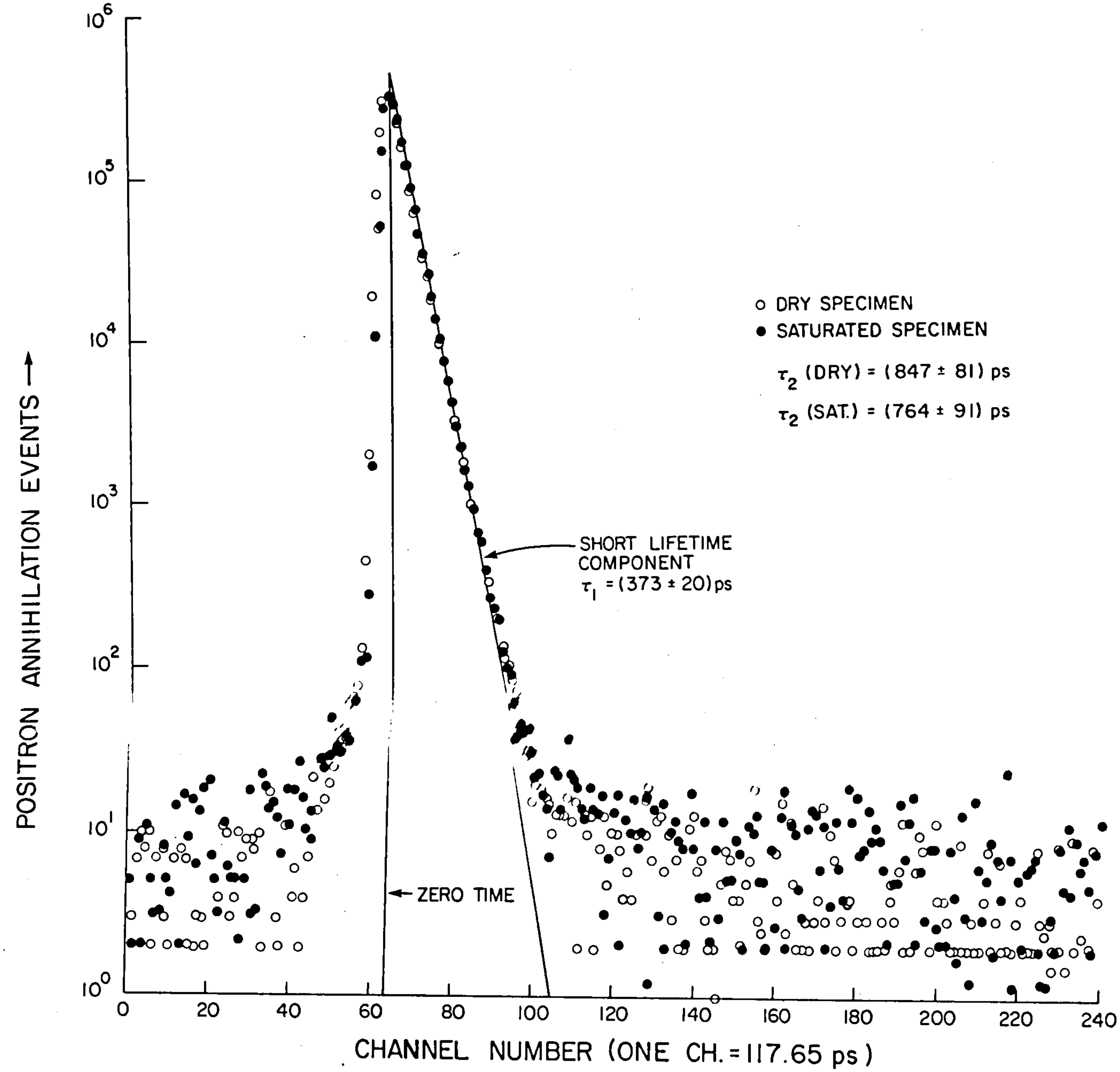


FIGURE 3 - POSITRON LIFETIME SPECTRA OBSERVED IN DRY AND WATER-SATURATED POLYIMIDESULFONE SPECIMENS.

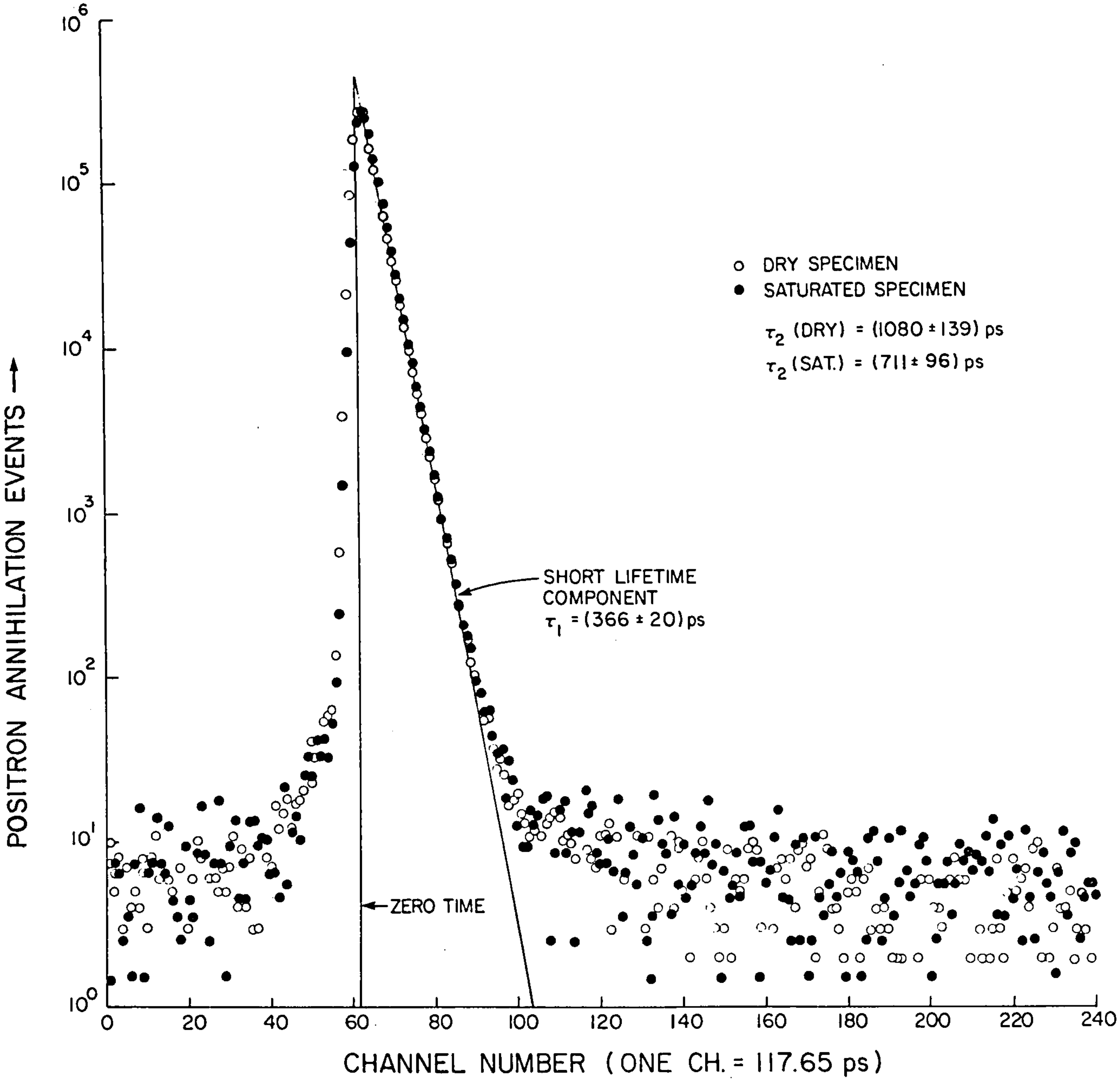


FIGURE 4 - POSITRON LIFETIME SPECTRA OBSERVED IN DRY AND WATER - SATURATED THERMOPLASTICIMIDE (TPI) SPECIMENS

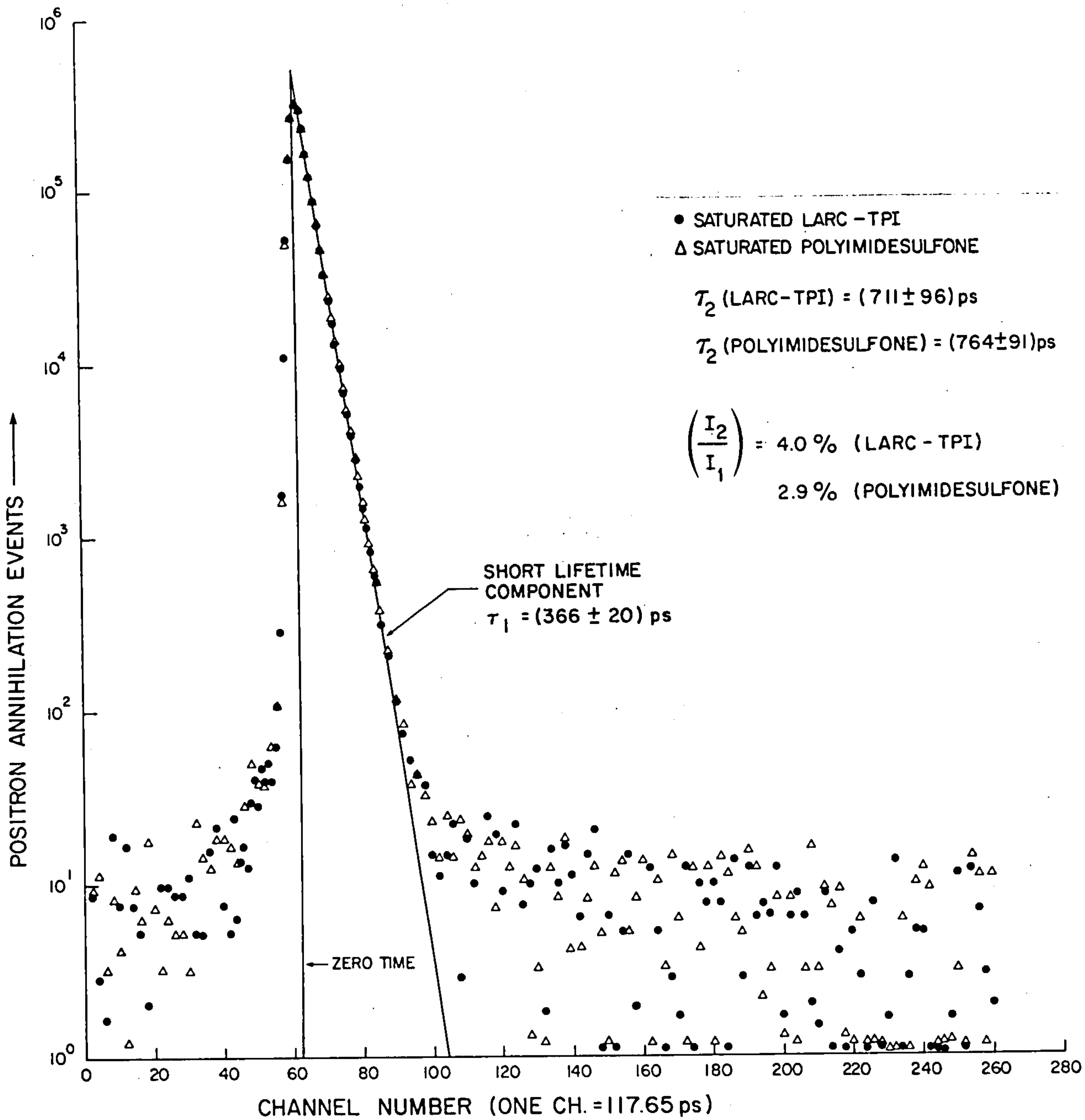
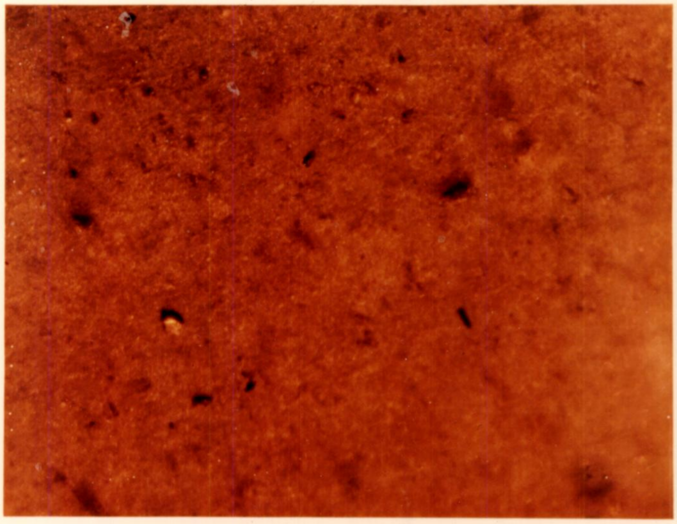
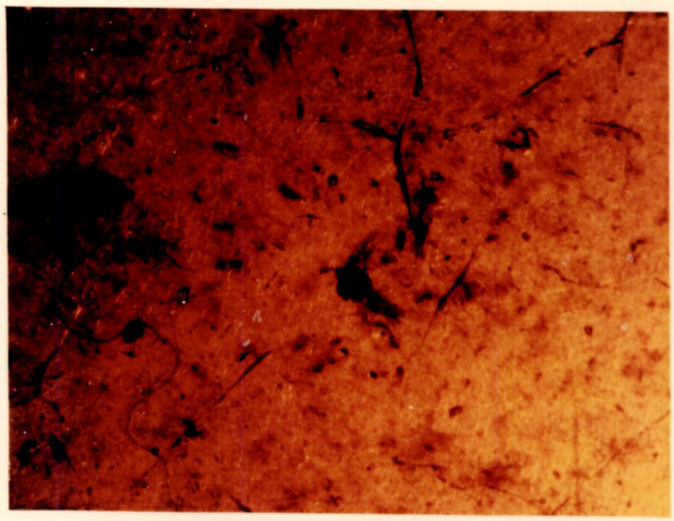


FIGURE 5 - COMPARISON BETWEEN THE POSITRON LIFETIME SPECTRA OBSERVED IN WATER - SATURATED THERMOPLASTICIMIDE AND POLYIMIDE - SULFONE SPECIMENS.



(a) BEFORE SATURATION (AMBIENT MOISTURE CONTENT)



(b) AFTER FREEZING (SATURATION MOISTURE CONTENT)

FIGURE 6- TYPICAL PHOTOMICROGRAPHS OF A POLYIMIDESULFONE SPECIMEN.

1. Report No.
NASA TM-84532

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Positron Lifetime Studies in Thermoplastic Polyimide Test Specimens

5. Report Date
July 1982

6. Performing Organization Code
505-33-23-05

7. Author(s)
Jag J. Singh, Terry L. St. Clair, William H. Holt, and Willis Mock, Jr.

8. Performing Organization Report No.

9. Performing Organization Name and Address
Langley Research Center
Hampton, VA 23665

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, DC 20546

13. Type of Report and Period Covered
Technical Memorandum

14. Army Project No.

15. Supplementary Notes

16. Abstract

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17. Key Words (Suggested by Author(s))
Positron, Positron Lifetime, Moisture in Polymers, Saturation Moisture, Free Volume, Thermoplastic Polyimides, Polyimidesulfones

18. Distribution Statement
UNCLASSIFIED - Unlimited

Subject Category 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	13	A02

*For sale by the National Technical Information Service, Springfield, Virginia 22161