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AN INVESTIGATION OF PHYSICAL PROPERTIES OF THERMOPLASTIC POLYIMIDES

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ABSTRACT

Thermoplastic polyimides are a class of promising high temperature polymers for aerospace applications. NASA-developed LARC-TPI is a prominent member of this family of polymers. We have measured its physical characteristics as a function of its curing schedule. The results and their possible interpretations are discussed in this report.

INTRODUCTION

Langley Research Center Thermoplastic Polyimide (LARC-TPI) is one of the most promising thermoplastic polyimides developed at Langley. It has high mechanical strength and retains it at elevated temperatures (over 250°C). It also absorbs a very low amount of moisture. Although LARC-TPI possesses flow properties that are significantly superior to those of conventional polyimides, further improvements in its ease of processability are desirable to expand its use as a high performance matrix resin for aerospace applications. We have undertaken a study to determine the effect of the imidization cure schedule on the processability and resulting polymer properties of LARC-TPI. It is hoped that by varying the cure temperatures and processing techniques, the rheological characteristics of the resins can be optimized. As a first step in this direction, we have investigated the effects of different curing temperatures/cycles on their properties.

The test samples were prepared according to two different cure schedules. (No measurements of the molecular weights of the final products could, however, be made because of the insolubility of the polyimides.) These samples were studied in detail for their physical characteristics. The results are summarized in the following sections.

EXPERIMENTAL PROCEDURE AND RESULTS

The test sample discs were prepared according to the following curing/molding prescriptions.

(a) Preparation of Thermoplastic Polyimide (TPI) Molding Powders

LARC-TPI polyamic acid resin, 29.1% solids in 2-methoxyethyl ether (diglyme), was obtained from Mitsui Toatsu Company of Japan. This resin was diluted to 15 weight percent solids by addition of dimethylacetamide (DMAC). The

polymer was precipitated by slowly dripping the resin into a blender of distilled water. The precipitate was filtered and washed three times with additional distilled water. The resulting powder was dried in a vacuum oven at room temperature overnight.

The powder was imidized according to two different cure schedules: (1) The TPI polyamic acid powder was heated in a forced air oven for 1 1/2 hours at 100°C, 1 hour at 180°C and 1 hour at 220°C; (2) The powder was heated as above, with an additional curing for 1 hour at 300°C.

(b) Preparation of TPI Molded Discs

Three molded discs each were prepared from the TPI powders which had been imidized to 220°C and 300°C. For each disc, 2.00 grams of the imide powder were placed in a 2.86 cm diameter steel mold. The molding conditions used for the 220°C-cured powder were as follows:

(a) Maximum Temperature = 349°C
(b) Time at Maximum Temperature = 15 minutes
(c) Maximum Pressure = 2500 psi

Molding pressure was increased to 5000 psi for the 300°C-cured powder, the maximum temperature and time at maximum temperature remaining the same.

These conditions yielded 2.86 cm diameter, 0.24 cm thick discs. The increased pressure required to obtain satisfactorily molded discs of the 300°C-cured powder is indicative of less melt flow in the higher temperature-cured polyimide. X-ray diffraction studies with Cu-K_α x-rays showed that both types of discs were completely amorphous, i.e., had no measurable crystallinity in them. Figure 1 shows the nominal chemical structure of LARC-TPI polymer.

(c) Saturation Moisture Contents

The "as received" sample discs were first desiccated in a vacuum oven at 100°C. They were then immersed in distilled water at 90°C for several weeks until their weights stabilized. The saturation moisture uptakes of the various discs are summarized in the table below. Within the accuracy of the measurements, the average saturation moisture contents of the discs are approximately equal.

Table I
Summary of Saturation Moisture Contents
of the Various LARC-TPI Discs

No.	Sample Classification	Saturation Moisture Content (Weight %)
1	(220°C-Cured Samples)	2.94
2		2.87
3		2.89
		Av = (2.90±0.03)
1	(300°C-Cured Samples)	3.14
2		2.94
3		2.85
		Av = (2.98±0.11)

(d) Density Measurements

The sample densities were calculated on the basis of their measured dimensions and weights. The results are summarized in Table II below. Clearly, the density of the samples cured at 220°C is lower than density of the samples cured at 300°C.

Table II
Summary of Densities of Various
LARC-TPI Discs

No.	Sample Classification	Density (gm/cc)
1	(220°C-Cured Samples)	1.112
2		1.170
3		1.081
		Av = (1.121±0.045)
1	(300°C-Cured Samples)	1.328
2		1.347
3		1.357
		Av = (1.344±0.014)

(e) Shear Stress Measurements

Short bar shear stress measurements were made for two samples of each type. Three small bars were cut from each sample and subjected to known loads. The results are summarized in Table III below. The shear stress value for the 300°C-cured samples is considerably higher than that for the 220°C-cured samples.

Table III
Summary Shear-Stress Values
of LARC-TPI Samples

No.	Sample Classification	Shear Stress (psi)
1	(220°C-Cured Samples)	577±12
2		453±49
		Av = (515±66)
1	(300°C-Cured Samples)	3246+1325
2		3295±522
		Av = (3271±712)

(f) Infrared Spectroscopy Measurements

Fourier transform spectra of the two types of TPI powders were measured and are shown in figure 2. Although both spectra contain an anhydride peak at ~1856 cm^{-1}, the greater absorption in the amic acid-OH region (3000-3500 cm^{-1}) and the presence of amide-II band (1540 cm^{-1} in the 220°C-cured powder indicate that the lower-temperature-cured TPI powder is not fully imidized. The presence of un-imidized polyamic acid in the 220°C-cured powder may have contributed to its increaseed moldability. However, the water of further imidization generated during the molding process may have resulted in void formation. The remaining polyamic acid component would also have contributed to lowering the mechanical strength of the 220°C-cured discs.

Photographs of the fracture surfaces of the two types of discs showed small voids in the specimens molded from the 220°C-cured powder that were not present in the 300°C-cured discs (see figure 3). These voids, of course, would also lead to lower densities observed in the discs prepared from the 220°C-imidized powder.

(g) Positron Lifetime Measurements

Positron lifetime measurements were made in each type of samples, using standard fast-fast coincidence lifetime measurement techniques. The lifetime system resolution, as measured with a Co^{60} source, was approximately 300 picoseconds. Figure 4 shows a typical lifetime spectrum in LARC-TPI samples. The lifetime spectra were analyzed using the RESOLUTION program[1] which automatically calculates the lifetimes and the relative intensities of the two components after subtracting a flat background from the raw spectrum. The results are summarized in Table IV below. It appears that the lifetimes (both short and long) are slightly smaller in the higher-temperature-cured samples, though the errors on the longlife values are too large to permit a definitive statement about them.

Table IV
Summary of Positron Lifetime Measurements in LaRC-TPI Samples

Sample Classification	Positron Lifetime Measurements			
	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
	(Short Lifetime Parameters)		(Long Lifetime Parameters)	
220°C-Cured Samples	381±2	98.9±0.5	1660±200	1.1±0.5
300°C-Cured Samples	374±2	98.8±0.6	1628±219	1.2±0.6

DISCUSSION

On the basis of the data summarized in Tables 1, 2 and 4, it appears that the samples cured at 300°C have slightly higher saturation moisture content, higher density, but approximately comparable positron annihilation characteristics. Table 3 shows that the bar shear stress value in the samples cured at 300°C is over six times larger than in the 220°C-cured samples! The saturation moisture content data, though inconclusive, are somewhat surprising in view of the results shown in figures 2 and 3. If the lower-temperature-cured discs have higher free volume, they are also expected to have higher saturation moisture content as well as higher positron lifetime. Even though the mean τ_2-values in the 220°C-cured samples are slightly higher than the corresponding values in the higher-temperature cured samples, the errors on the individual values are so large that no definite conclusion can be drawn about their true values.

If we associate higher density and higher strength with higher molecular weight, we would again have expected lower positron lifetime as well as low saturation moisture content in the 300°C-cured samples. Merrigan et al[2] and Chuang et al[3] have reported that the orthopositronium annihilation mean life in polymers goes down as the polymer molecular weight goes up. However, West et al[4] report that the mean life value remains essentially unchanged when the molecular weight of the polymer (polystyrene) changes from 10^3 to 2 x 10^6 amu! Our own measurements in polystyrene also show no changes in orthopositronium annihilation rates when the molecular weight changes from 19,800 to 860,000 amu. Even though we cannot extrapolate the polystyrene data to the thermoplastic polyimides, it does appear that the observed positron lifetime data are not inconsistent with the assumption of higher molecular weights for the 300°C-cured samples. But the problem of slightly higher saturation moisture content of 300°C-cured discs remains somewhat surprising. It is possible that the water diffusion process in these discs is aided by an optimal molecular architecture of the 300°C-cured samples.

CONCLUDING REMARKS

The experimental results reported in this paper show that the polyimide samples cured at higher temperature have higher density and higher shear strength. Photographs of the fracture surfaces suggest that the higher temperature-cured discs have fewer microvoids and may therefore be expected to have lower free volume and correspondingly lower saturation moisture content. This is not consistent with the observed satu-

ration moisture contents in the two types of samples. The experimentally observed saturation moisture content in the 220°C-cured samples is (2.90+0.03) w/0 as opposed to (2.98+0.11) w/o for this 300°C-cured samples. Normally, positron lifetime data can shed some light on the issue of free volume in polymers. Unfortunately, the probability of positronium formation in polyimides is rather low, thereby necessitating inordinately long times for adequate data statistics. Such statistics are necessary to definitively resolve the issue of relative free volume in polyimides as a function of their curing temperatures. It is possible that the slightly higher saturation moisture content in the 300°C-cured samples is due to its altered chemical architecture which allows additional water molecule bond sites on the polymer chains. In view of the foregoing discussion it would appear that the polyimide discs cured at higher temperatures may well have higher molecular weights.

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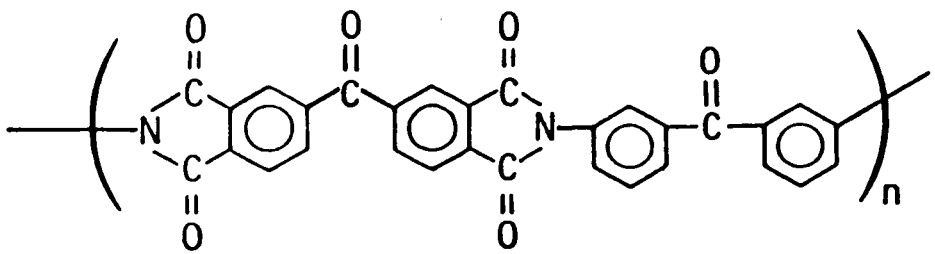


LaRC-TPI

Figure 1. Chemical structure of LaRC-TPI.

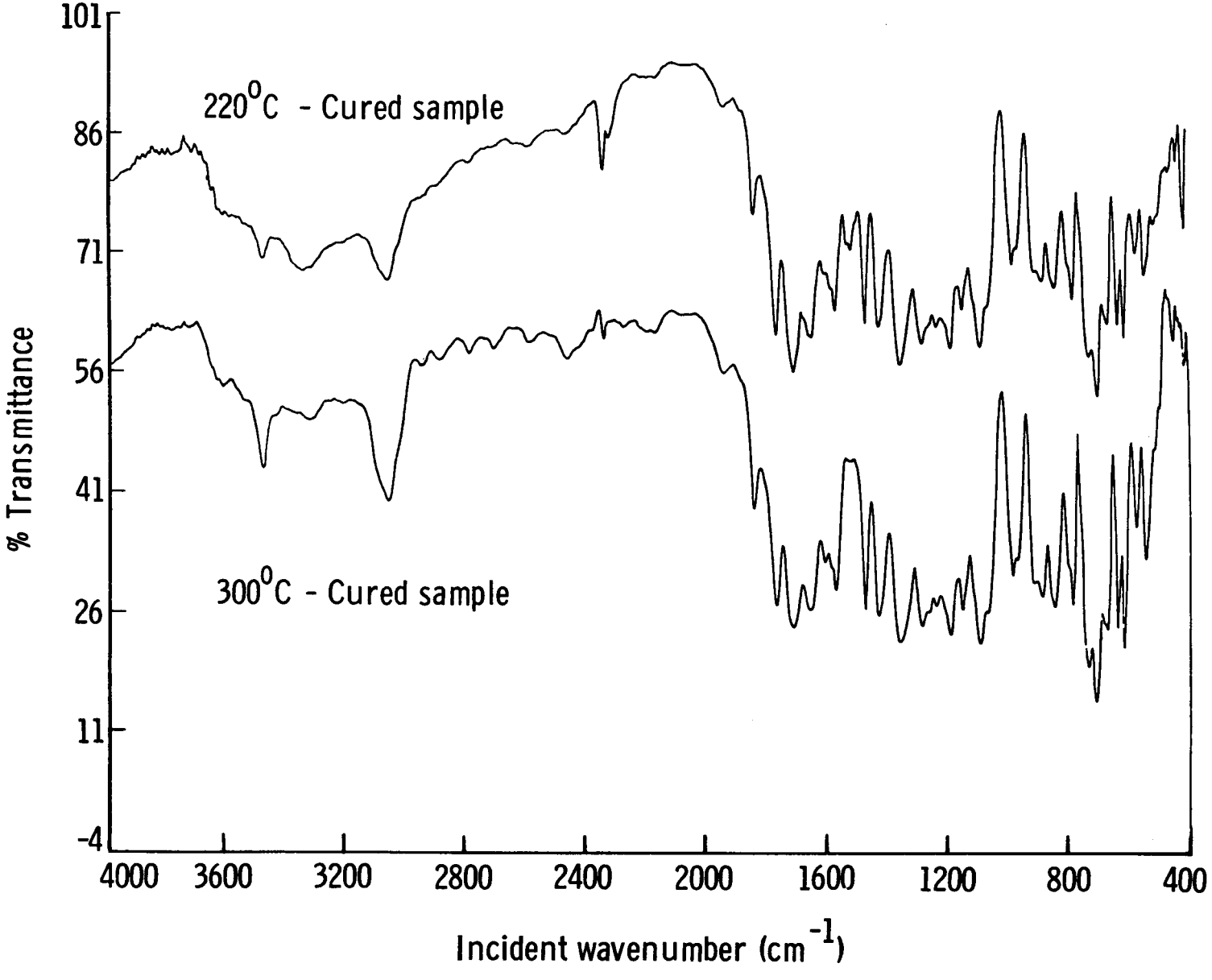
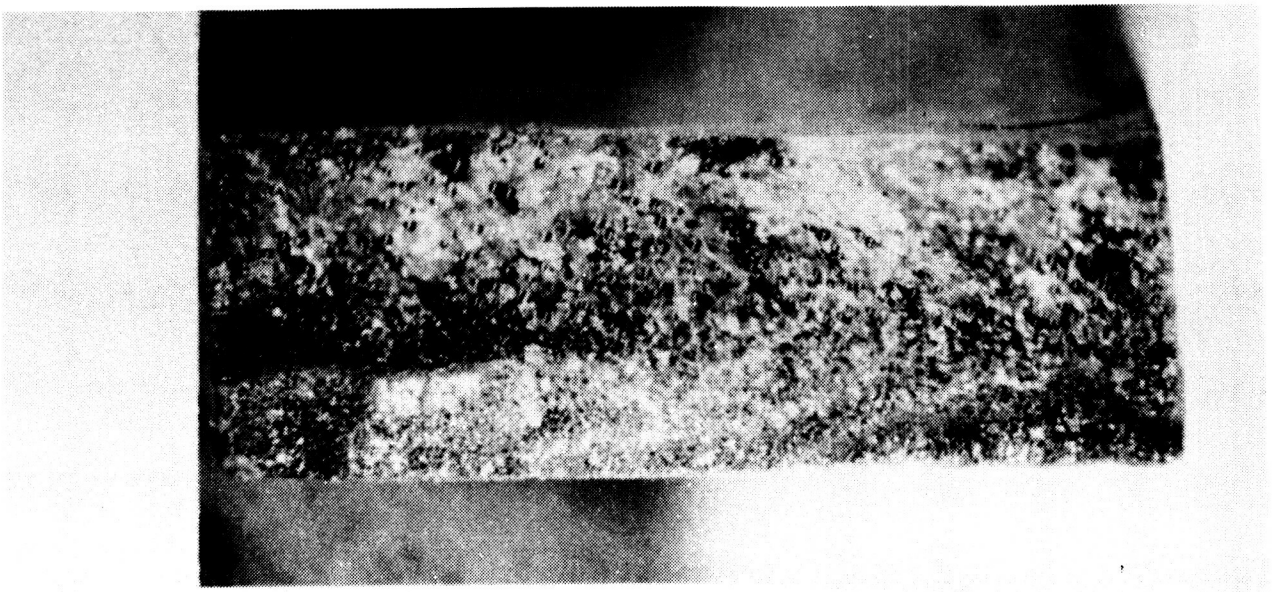
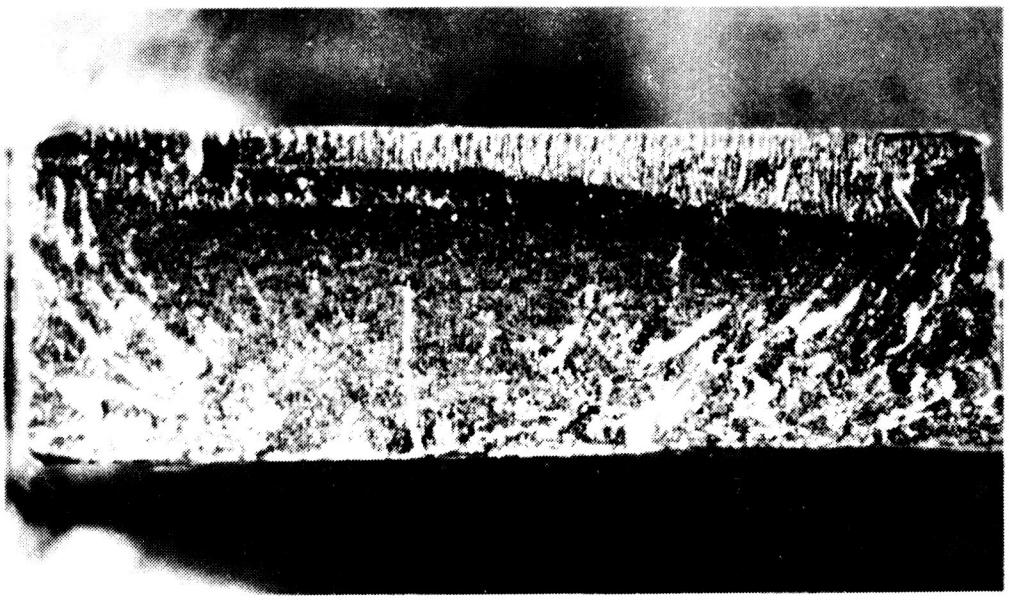


Figure 2. Infrared transmission spectra of the two types of TPI powders.



(a) Curing temperature = 220°C



(b) Curing temperature = 300°C

Figure 3. Photographs of the fracture surfaces in the thermoplastic polyimide samples cured at two different temperatures.

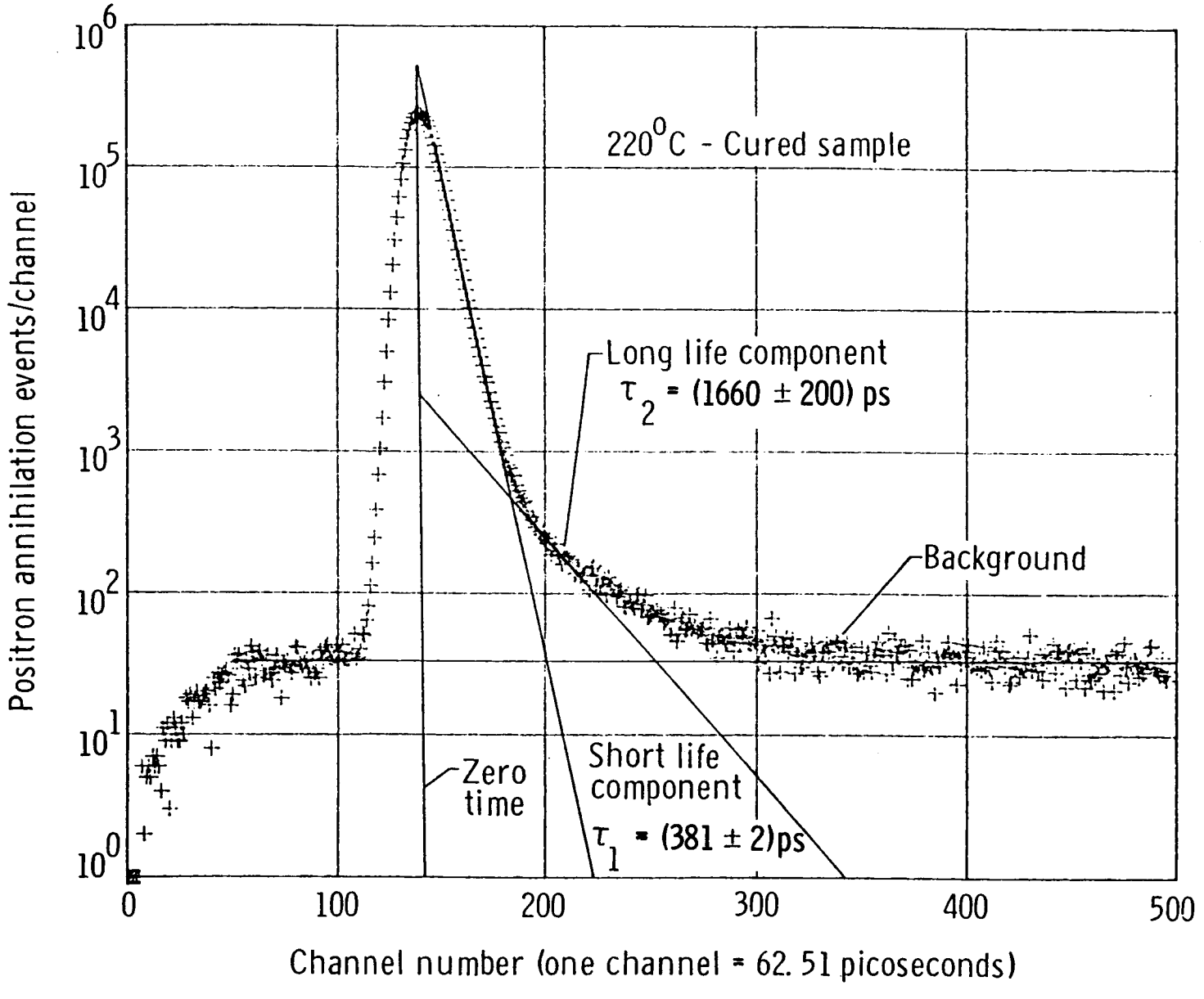


Figure 4. A typical positron lifetime spectrum in a LaRC-TPI sample.

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16. Abstract

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