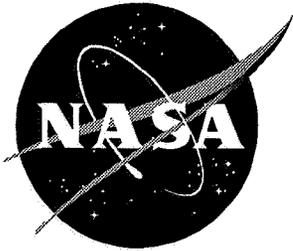


# A Method for Characterizing Thermoset Polyimides

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## Abstract

*Thermoset polyimides have great potential for successfully meeting tough stress and temperature challenges in the advanced aircraft development program. However, studies of structure-property relationships in these materials have not been very successful so far. Positron lifetime spectroscopy (PLS) has been used to investigate free volumes and associated parameters in a series of variable, segmental molecular weight samples. The free volume correlates well with the molecular weight  $M_c$ , the cross-link density  $\nu$ , and the coefficient of thermal expansion (CTE) of these materials. Currently, no other techniques are available for direct measurement of these parameters, particularly for polymers in solid phase. Experimental results and their interpretations are presented.*

## Introduction

The next generation of transport aircraft may fly at supersonic speeds and must have long-term durability. At supersonic speeds future transports will experience high stress and high temperatures. Graphite fiber-polymer matrix composites have a high potential for successfully meeting these high-stress, high-temperature challenges. These composites can be used successfully up to 350°C, and they have superior corrosion resistance, excellent chemical resistance, good dimensional stability, and excellent dielectric properties. However, definitive studies of structure-property relationships in these materials are either scarce or have not yet been made. Our preliminary studies of selected composite materials indicated that thermoset polyimides may prove to be better matrix material than the thermoplastic polyimides. Therefore, a decision was made to conduct a detailed study of the microstructural characteristics of recently developed thermoset polyimide resins (Pater, Soucek, Chang, and Partos 1991). The long-term, thermal-aging effects in these polymers are expected to be strongly related to their cross-link densities (Pater, Whitley, Morgan, and Chang 1991). According to the kinetic theory of rubber elasticity (Ferry 1970), the cross-link density  $\nu$  in thermoset polymers is inversely related to the average molecular weight  $M_c$  between the cross-links. Direct correlations between molecular weights and free-volume cell sizes in linear polymers (Singh and Eftekhari 1992) and between dielectric constant and free-volume fractions in polyimide films (Eftekhari, St. Clair, Stoakley, Sprinkle, and Singh 1994) had been established previously. These studies clearly established that the physical-electrical properties of polymeric materials are strongly dependent on their molecular architecture. Therefore, it was desirable to measure free-volume cell sizes  $V_f$  and free-volume fractions  $f$  in a series of variable, segmental, molecular weight cross-linked polymer samples. These parameters would then be correlated with the cross-link densities and the coefficient of thermal expansion (CTE) of the test samples.

Positron lifetime spectroscopy (PLS) has been used to measure free-volume cell sizes and free-volume fractions in the test samples. This technique is nondestructive, relatively simple, and highly accurate; it provides a cost-effective procedure for characterizing thermoset polyimides. The experimental procedures and the results of various measurements are described in the following sections.

## Experimental Procedures

### Sample Preparation

The high-temperature LaRC™ RP-46 series polyimide resins were prepared from three monomer reactants: 1) the monomethyl ester of 5-norbornen-2,3-dicarboxylic acid (NE), 2) the dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and 3) the 3,4'-oxydianiline (3,4'-ODA). Five resin systems, in which the formulated molecular weight (FMWT) varied from 1500 to 21000 g/mol, were synthesized. The monomer reactants were dissolved in methanol to give a 50-percent monomeric solution by weight. The monomeric solution was concentrated in a vacuum oven at 250°C for 1 hr to yield an imidized prepolymer. The preimidized oligomer was finally cured at 325°C for 1 hr under pressure. The FMWT of the resin samples was calculated as follows:  $FMWT = (n) \text{ molecular weight (MWT) of BTDE} + (n + 1) \text{ MWT of (3,4'-ODA)} + 2\text{MWT of NE} - 2(n + 1) \text{ (MWT of H}_2\text{O} + \text{MWT of CH}_3\text{OH)}$ , where  $n$  is the molar ratio of the monomer reactants and the by-products that are formed during the imidization. (In this paper  $M_c$  will be used as the symbol for FMWT.)

The samples used in positron lifetime measurements were processed as discs varying from 1 mm to 4 mm thick; X-ray diffraction measurements in the test samples showed that all samples were almost totally amorphous.

### Free-Volume Measurements

Positron lifetime measurements were made using a conventional fast-fast coincidence system with a time

resolution  $\approx 280$  psec. A 25  $\mu\text{Ci}$   $^{22}\text{Na}$  source, deposited on an 8.5- $\mu\text{m}$  thick Kapton<sup>1</sup> foil and sandwiched between two discs of the sample, was located between two plastic scintillation detectors. Positron lifetimes were measured at room temperature and ambient pressure. Several measurements were made with each sample in order to check the reproducibility of the spectrometer. Normally, each spectrum contained more than  $10^6$  counts in the spectrum that was accumulated in approximately 8 hr.

The measured lifetime spectra were analyzed using the computer program PATFIT88 (Kirkegaard, Pedersen, and Eldrup 1989). Two-lifetime component analyses invariably gave higher values of the goodness-of-fit parameter  $\chi^2$ . Three-lifetime component fits that resulted in lower  $\chi^2$  values were tried, but the intensity of the third lifetime component was very small ( $<0.5$  percent). This result indicates that the microvoids or free-volume cells are too small for the formation and localization of positronium atoms. Therefore, the second lifetime component  $\tau_2$  from the three-lifetime component analysis, which is caused by the positron annihilation at the defect sites (microvoids) in the resin matrix, has been used to calculate the microvoid "size" in the present series of samples. A typical positron lifetime spectrum in a resin sample is shown in figure 1. It is important to note experimentally that the standard deviation of the second lifetime components is very small, which is the result of the exceptionally high intensity of the second lifetime component. Since the free-volume cell size is a very sensitive function of the lifetime values, the magnitude of error on the measured lifetime value is very important.

#### Coefficient of Thermal Expansion Measurement

The density of each resin sample was measured using a Troemner specific gravity chain-balance system and a graduated cylinder filled with distilled water. Densities of the samples are needed for calculating their cross-link densities (Ferry 1970). The coefficient of thermal expansion of the resin samples was obtained by measuring the sample volumes at two temperatures. These measurements were made with the same Troemner balance that was used for the sample density measurements. Measurements were repeated at least four times, and samples were desiccated before each repeat measurement. The physical properties of the resin samples are summarized in table I. Positron lifetime results are presented in table II.

<sup>1</sup>Kapton<sup>®</sup> is a trademark of E. I. du Pont de Nemours & Co., Inc.

## Results

The second lifetime component in each sample corresponds to the positrons that are trapped at the potential defects (free-volume cells) in the resin matrix. These free-volume cells result from fluctuations in the packing density and morphology of the polymer chains. As discussed earlier, these free-volume cells are too small for the formation of positronium, the bound state of a positron-electron pair. The positrons are potentially trapped at these smaller free-volume cells and they subsequently annihilate there. The radii  $R$  (in nm) of the free-volume cells and the trapped positron lifetime  $\tau_2$  (in nsec) are related as follows (Singh and Eftekhari 1992):

$$\frac{1}{4\tau_2} = 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R} \quad (1)$$

where  $\Delta R = 0.1659$  nm.

Equation (1) differs from the conventional model (Nakanishi, Wang, and Jean 1987) for positronium-forming media in having  $1/4 \tau_2$  in place of  $1/2 \tau_3$  on the left-hand side. A detailed discussion of this modification of the conventional relation can be found elsewhere (Singh, et al. 1992). The free-volume cell size volume  $V_{f2}$  is calculated by assuming that the cell is spherical in shape and is given by  $4/3\pi R^3$ .

The cross-link density  $\nu$  and the molecular weight  $M_c$  of the polymer are inversely related according to the kinetic theory of rubber elasticity (Ferry 1970):

$$\nu = \frac{\rho}{M_c} \quad (2)$$

where  $\rho$  is the resin density.

Using the measured density and the formulated molecular weight, the cross-link density was calculated. These values, along with the calculated free-volume cell size  $V_{f2}$  and the coefficient of thermal expansion data, are summarized in table III. Figures 2–4 show the correlation between free-volume cell size  $V_{f2}$  and the molecular weight  $M_c$ , between free-volume cell size and cross-link density  $\nu$ , and between the free-volume cell size and the coefficient of thermal expansion (CTE), respectively.

## Discussion

It is clear from the data presented in table III and illustrated in figures 2 and 3 that the free-volume cell size correlates well with the segmental molecular weight and the cross-link density of the resins. By extending the free-volume model of Singh and Eftekhari to the cross-linked thermoset polyimide resins of the present studies,

we find that free-volume size and molecular weight are related by a similar expression; that is,

$$V_{f2} = AM_c^B \quad (3)$$

where  $A$  and  $B$  are constants ( $A = 5.37 \pm 0.11$ ;  $B = 0.037 \pm 0.002$ ).

The value of  $B$  found in the present study is considerably smaller than the value of  $B$  found in a previous study of linear polymers and epoxies that was conducted in this laboratory. However, equation (3) still estimates the molecular weight of the solid polymers (resins) reasonably well in the mass range of 1500 to 21 000 g/mol. It is interesting that the correlation between free-volume and cross-link density fits a similar relationship, which is to be expected, since sample density variations are rather small (table I), and the cross-link density is inversely proportional to molecular weight; that is,

$$V_{f2} = A_1 v^{-B_1} \quad (4)$$

where  $A_1$  and  $B_1$  are constants ( $A_1 = 47.13 \pm 0.1$ ;  $B_1 = 0.040 \pm 0.002$ ).

The cross-link density is known to affect significantly many of the physical and mechanical properties of the cross-linked systems. Hence, accurate experimental measurement of this quantity is important in many applications. Most of the currently available methods for calculating cross-link density require the polymer system to be in equilibrium in a liquid solution. A simple relation of the type in equation (4) shows that by measuring the free-volume size by a well-established technique such as positron lifetime spectroscopy, cross-link density of the sample can be readily obtained without dissolving the sample in an appropriate solvent. A new dimension to the present set of measurements is added if we examine the relation between  $V_{f2}$  and the CTE. Although the experimental results are rather scattered, they still follow the trend which fits into a relation of the following type:

$$V_{f2} = A_2(\text{CTE})^{B_2} \quad (5)$$

where  $A_2$  and  $B_2$  are constants ( $A_2 = 14.03 \pm 0.71$ ;  $B_2 = 0.076 \pm 0.003$ ). That the results follow this trend is not surprising because the free-volume fraction  $f = kV_{f2}I_2$  is expected to affect the CTE. Equation (5) can be readily transformed to the form

$$f = A_2^*(\text{CTE})^{B_2} \quad (6)$$

where  $A_2^* = A_2/mk$ ;  $m$  is the slope of the graph (fig. 5) and  $k$  is a structural constant (Eftekhari et al. 1994) where the product  $V_{f2}I_2$  is plotted as a function of free-

volume cell size  $V_{f2}$ . Thus, it appears that the free-volume cell size is a unique parameter, the measurement of which should enable calculation of other material properties such as  $M_c$ ,  $v$ , and the CTE, at least in the sample molecular weight range of 1500 to 21 000 g/mol.

## Conclusions

The results of this study have demonstrated that free-volume cell size in thermoset polyimides is a versatile, useful parameter that relates directly to the polymer segmental molecular weight, the cross-link density, and the coefficient of thermal expansion. Thus, a determination of free-volume cell size provides a viable basis for complete microstructural characterization of thermoset polyimides and also gives direct information about the cross-link density and coefficient of thermal expansion of the test samples. Since the product (of free-volume cell size and the relative intensity of its associated lifetime component) is proportional to the porosity of the sample (on a microscopic scale), a measurement of free-volume cell size provides a direct indication of its dimensional stability under variable thermal and mechanical loads.

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Table I. Physical Properties of Test Polyimide Resins

Sample	Density, g/cm <sup>3</sup>	Molecular wt, g/mol
RP-46-5	1.36	1500
RP-51	1.40	9000
RP-67T-1	1.47	10000
RP-47	1.37	15000
RP-49-2	1.35	21000

Table II. Summary of Positron Lifetimes in Polyimide Resin Samples

Sample	$\tau_1$ , psec	$\tau_2$ , psec	$\tau_3$ , psec	$I_1$ , percent	$I_2$ , percent	$I_3$ , percent
RP-46-5	138 ± 8	379 ± 1	2011 ± 230	17 ± 1	82 ± 1	<0.5
RP-51	114 ± 5	383 ± 2	2400 ± 200	19 ± 1	80 ± 1	<0.5
RP-67T-1	138 ± 8	384 ± 2	2347 ± 213	17 ± 1	82 ± 1	<0.5
RP-47	129 ± 10	385 ± 1	2619 ± 394	16 ± 1	83 ± 1	<0.5
RP-49-2	145 ± 10	387 ± 1	2449 ± 269	16 ± 1	83 ± 1	<0.5

Table III. Summary of Free-Volume, Cross-Link Density, and CTE Results

Sample	$V_{f2}$ (Å <sup>3</sup> )	$\nu$ (cls/cm <sup>3</sup> ), × 10 <sup>19</sup>	CTE/°C, × 10 <sup>-4</sup>	Porosity parameter ( $V_{f2}I_2$ ), arbitrary units
RP-46-5	7.04 ± 0.1	54.50 ± 5.0	1.26	577
RP-51	7.54 ± 0.1	9.37 ± 0.9	2.25	603
RP-67T-1	7.56 ± 0.1	8.86 ± 0.9	4.39	620
RP-47	7.58 ± 0.1	5.37 ± 0.5	2.14	629
RP-49-2	7.78 ± 0.1	3.87 ± 0.4	4.85	646

Note: The CTE values have a 5-percent error.

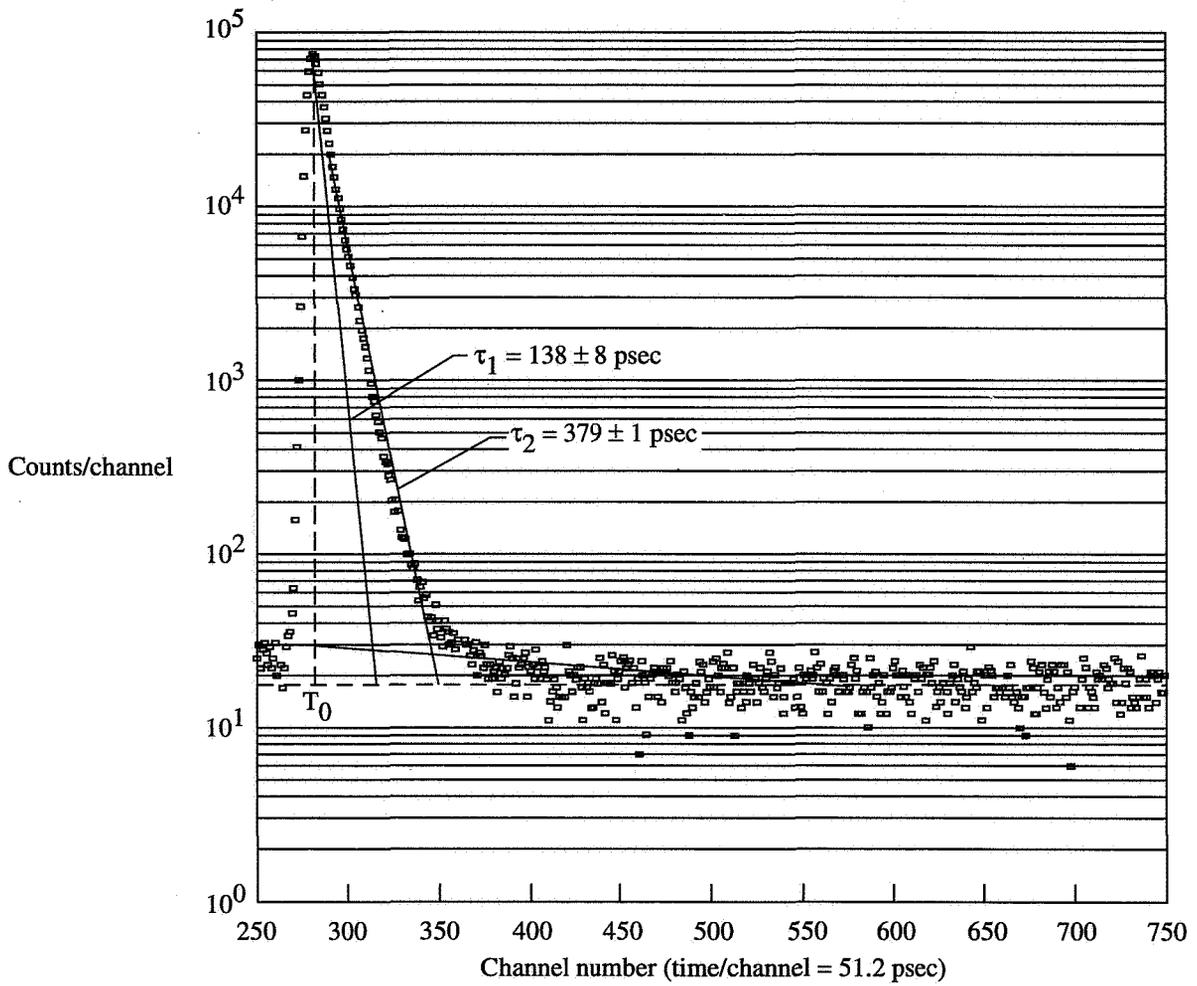


Figure 1. Typical positron lifetime spectrum in RP-46 resin test sample.  $T_0$  is the time-zero channel. The third lifetime component value is not shown.

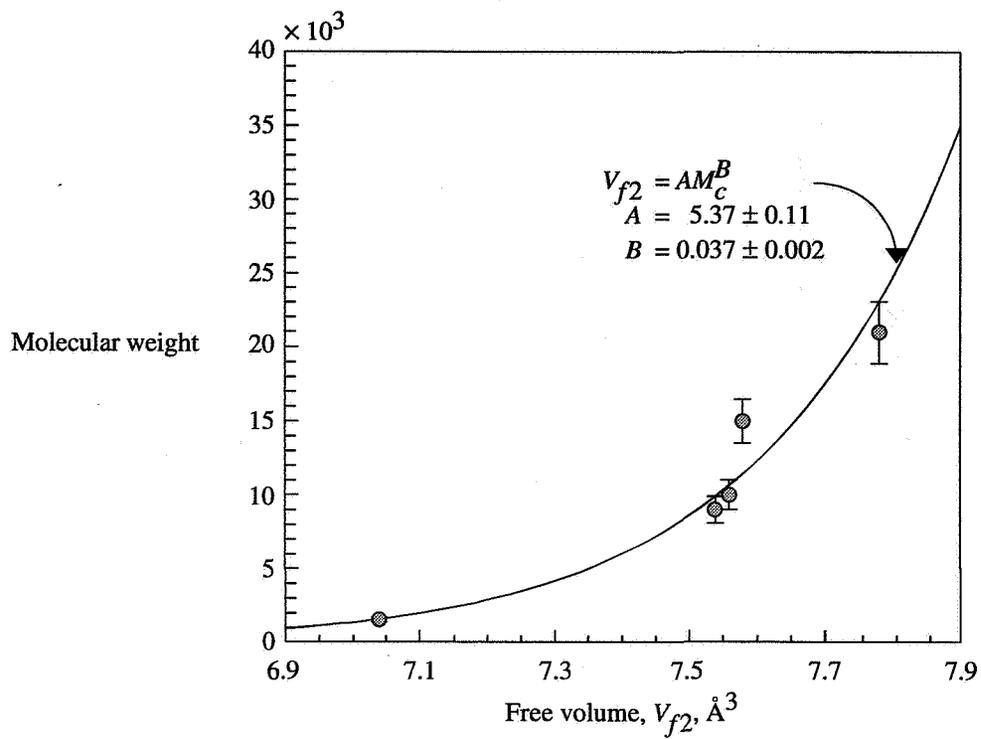


Figure 2. Plot of free-volume cell size and segmental molecular weight of test samples. The solid curve is a fit of data to equation (3).

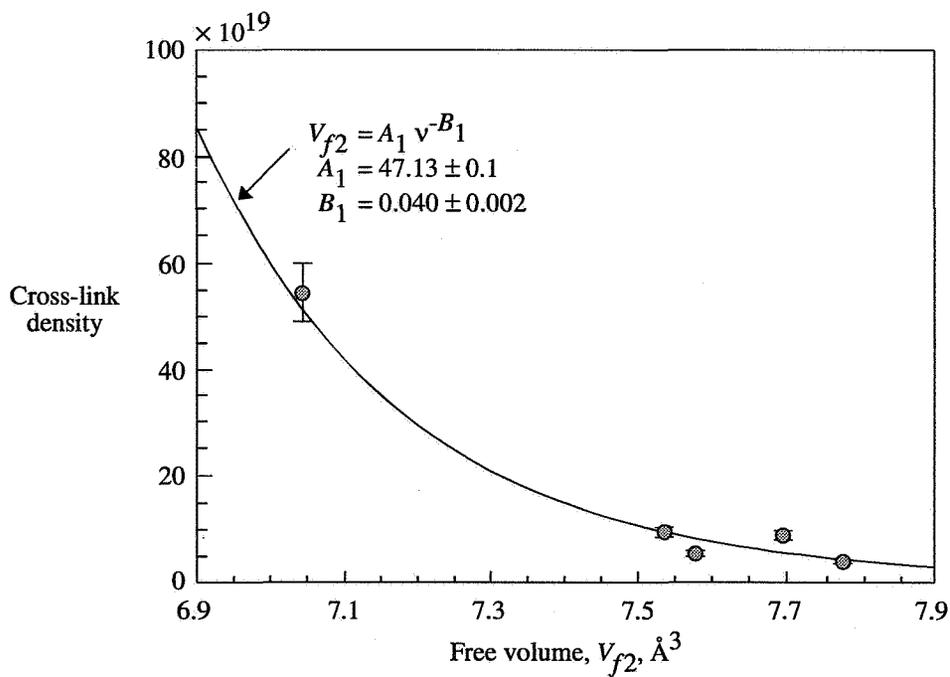


Figure 3. Plot of free-volume cell size and cross-link density of test samples. The solid curve is a fit of data to equation (4).

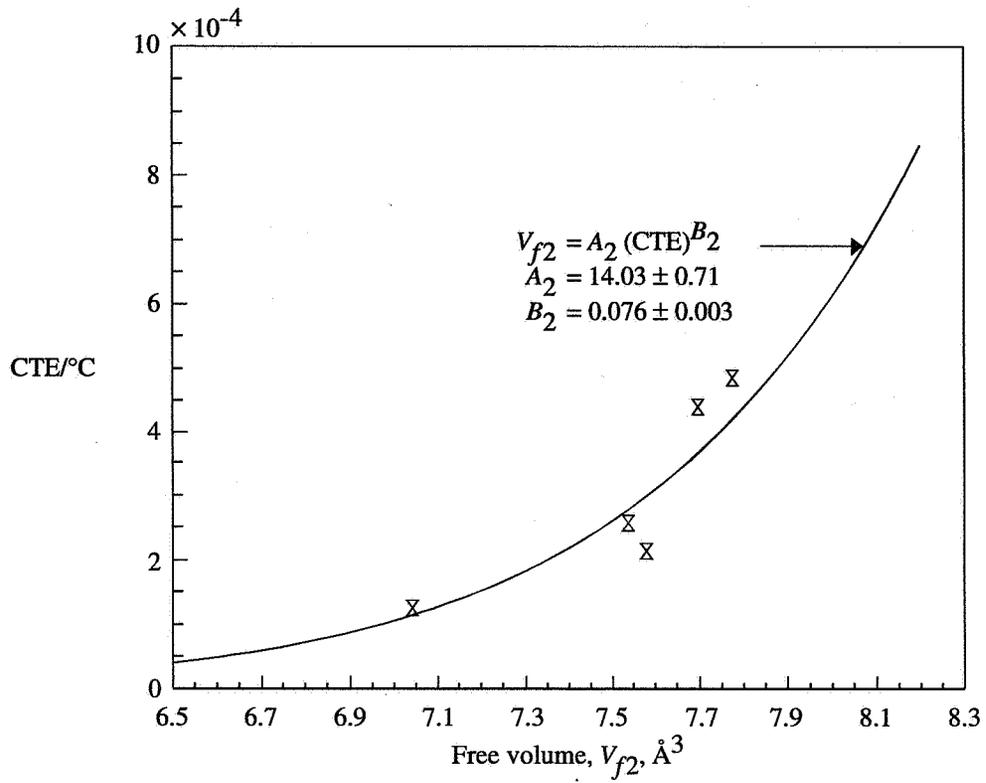


Figure 4. Plot of free-volume cell size and coefficient of thermal expansion of test samples. The solid curve is a fit of data to equation (5).

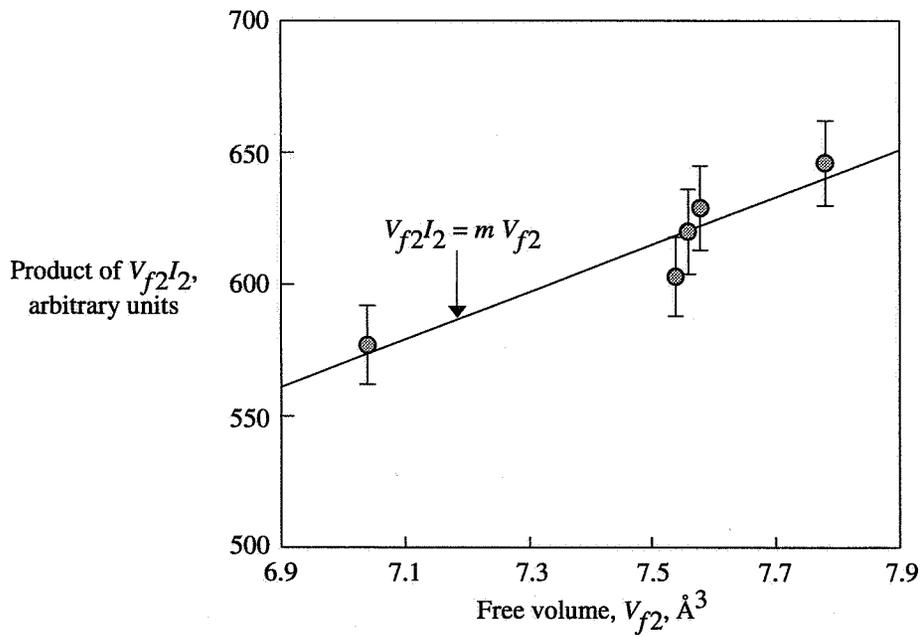


Figure 5. Plot of free-volume cell size and product of  $V_{f2}$  and  $I_2$  in the test samples. The solid line is a linear fit of experimental points.

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