Free-Volume Distributions of an Epoxy Polymer Probed by Positron Annihilation: Temperature Dependence

Q. Deng, F. Zandiehnadem, and Y. C. Jean*

Department of Chemistry, University of Missouri—Kansas City,
Kansas City, Missouri 64110

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ABSTRACT: We have performed a series of positron annihilation lifetime (PAL) experiments to measure the free-volume hole distributions in an epoxy (DGEBA/DDH/DAB) polymer (T_g = 62 °C) at temperatures between 25 and 150 °C. A Laplace inversion technique has been employed to analyze the PAL spectra to continuous lifetime distributions, and the hole volume distributions are determined from the results of ortho-positronium lifetime distributions. At each temperature, we have obtained three distinct PAL distributions with the peaks positioned at 0.07–0.12, 0.39–0.41, and 1.6–2.2 ns, respectively. The free-volume hole radii are distributed between 1.7 and 3.1 Å with a peak at 2.45 Å at room temperature, and the distributions are shifted to a larger radius as the temperature increases.

I. Introduction

The concept of free volume in a liquid proposed 4 decades[1] ago has been applied to explain the free-volume hole properties of polymers in recent years.[2] It becomes more clear that one is able to associate the macroscopic physical properties of polymers, such as pressure (P), temperature (T), and time (t) with the free-volume properties of molecular scales. For example, in 1959, Cohen and Turnbull[3] used a free-volume hole size to explain the diffusion in liquids as a function of temperature and pressure. In this model, these authors substituted liquid molecules by hard spheres and defined the free volume to be the volume difference between the space of the molecular cage made by the surrounding molecules and the van der Waals volume of the molecule in the cage.

Despite a great deal of effort expended in the theoretical development of free volume, only limited experimental data about free volumes in polymers have been reported. In recent years, free-volume hole distributions have been theoretically predicted by using molecular dynamics and kinetic theory.[4,5] In 1986, we[6] reported the mean free-volume size in an epoxy by measuring its positron annihilation lifetime (PAL) based on a spherical model for the free-volume bubbles in liquids.[7] The size of the holes surrounding the positronium atom (Ps) can be specified by minimizing the total energy as a function of the radius of the holes. In more recent experiments, we[8-13] have determined the mean free-volume hole size in polymers using the PAL method as a function of P, T, and t. In 1988, Yu et al.[14] reported an experimental distribution by analyzing the UV–vis absorption spectra of p-aminoazobenzene as a free probe in studying the photoisomerization behavior of photochromic labels in polystyrene in several processes such as aging, plastication, and volume dilation. These authors assumed a binomial function for the free-volume size distribution at the ground state of glassy polymers, with a total free volume obtained by minimizing the Helmholtz free energy.

The unique sensitivity of PAL in probing free-volume properties is due to the fact that Ps is found to be preferentially localized in the free-volume region of polymeric materials.[15] Evidence of Ps localization in free volumes has been found from temperature-, pressure-, and crystallinity-dependent experiments:[6,11,13,8] (1) the o-Ps (triplet Ps) lifetime undergoes a dramatic change as $T > T_g$ (glass transition temperature) and $T < T_g$, (2) the lifetime temperature coefficient ($\approx 10^{-3}$ K^{-1}) is 1 order of magnitude larger than the volume expansion coefficients ($\approx 10^{-4}$ K^{-1}), (3) a large variation of the positron lifetime has been observed when a polymer is under a static pressure, and the lifetime pressure coefficient ($\approx 10^{-4}$ atm^{-1}) was found to be 1–2 orders of magnitude greater than the volume compressibility, and (4) o-Ps formation is found only in amorphous regions where free volumes exist. In contrary to other techniques, PAS probes the free-volume properties directly without being significantly interfered by the bulk properties.

In PAL, the experimental measured positron annihilation rate λ is defined by the integration of the overlap between the positron density $\rho_+(\mathbf{r})$ and the electron density $\rho_-(\mathbf{r})$

$$\lambda = \text{const} \times \int \rho_-(\mathbf{r})\, \rho_+(\mathbf{r})\, \mathrm{d}r \qquad (1)$$

where the "const" is a normalization constant related to the number of electrons involved in the annihilation process. The annihilation lifetime τ is the reciprocal of the annihilation rate λ. In the free-volume model proposed for positron annihilation,[16] Ps is considered to be confined in an interstitial space between molecules. By developing eq 1, based on a simple the-particle-in-a-spherical-box[17,18] theory, a correlation between the o-Ps annihilation lifetime (τ_3) and the hole radius (R) has been obtained

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \qquad (2)$$

where $R = R_0 - \Delta R$ is the radius of the free volume, and $\Delta R = 1.656$ Å is an empirical parameter which was obtained by fitting the measured annihilation lifetimes of cavities with known sizes.[19] τ_3 and R are expressed in nanoseconds and angstroms, respectively.

In the past, a positron lifetime spectrum is resolved into a finite number of lifetime components, usually three. In a polymer containing no Ps quenching function group in its structure, the mean radius of free volume (R) can be obtained by converting the measured o-Ps lifetime (τ_3) according to eq 2. In the present work, we have developed a renascent Laplace transformation technique to obtain a continuous distribution of o-Ps lifetimes from PAL spectra and to report the free-volume distributions in an epoxy polymer at different temperatures.

II. Experiments

1. Samples of Polymers. The epoxy sample under study was prepared from the diglycidyl ether of Bisphenol "A" (DGEBA)

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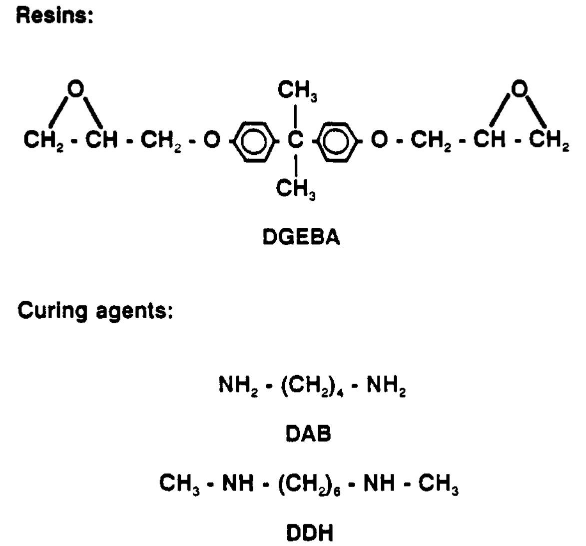

Figure 1. Chemical compositions and structures of DGEBA, DAB, and DDH for the epoxy polymer studied.

epoxy resin (Dow Chemical). Aliphatic amines of *N,N'*-dimethyl-1,6-diaminohexane (DDH) and 1,4-diaminobutane (DAB) with 97% purity (Aldrich Chemical) were used as the curing agents. The epoxy polymer employed in this study has an equivalent DGEBA/DDH/DAB ratio of (5.0):(2.8):(2.2). The samples have an intermediate cross-link density compared to the samples studied previously as a function of temperature.[6] The T_g = 62 °C was determined by DSC (differential scanning calorimetry). Detailed descriptions of sample preparations can be found in our previous paper,[6] and the chemical structures are shown in Figure 1.

2. Positron Annihilation Lifetime (PAL) Spectroscopy. The positron source, 25-μCi ^{22}NaCl (from Du Pont), was directly deposited on one of the samples and then sandwiched in between two identical pieces of the samples. The ^{22}Na source emits a prompt γ-ray of 1.28 MeV which serves as a starting signal for the timing. The annihilation γ-rays, each of energy 0.511 MeV, serve as a stopping signal for our timing purposes. The positron birth (1.28 MeV) and the annihilation γ-rays (0.511 MeV) were filtered one from the other according to the energy windows set for each of the two CFDD (constant fraction differential discriminators; Ortec 583 Model). Pulses of different heights proportional to the time interval of the two signals were produced in a time-to-pulse-height converter (TPHC). The converted signals were fed to a multichannel analyzer data buffer (Ortec Adcam model). The data from the analyzer were operated by a personal computer (IBM-PC) for the data collection and the spectrum display. The acquired spectra were transmitted to a VAX computer (8650 Model) for a complete data analysis. Figure 2 shows the spectra obtained for an epoxy at temperatures below T_g (at 40 °C) and above T_g (at 150 °C), respectively. The time resolution of the current spectrometer as measured by a ^{60}Co has a full width at half-maximum (fwhm) of 250 ps.

3. Conventional Data Analysis of a PAL Spectrum. In conventional data analysis, an experimental datum is expressed as a convoluted expression (symbol *) of the instrument resolution function and of a finite number (*n*) of negative exponentials

$$y(t) = R(t)*(N_t\sum_{i=1}^{n}\alpha_i\lambda_i e^{-\lambda_i t} + B) \qquad (3)$$

where $y(t)$ is the experimental raw data, $R(t)$ is the instrument resolution function, N_t is the normalized total count, and B is the background. λ_i is the inverse of the *i*th lifetime component (τ_i), and α_i is its intensity. To analyze the data correctly, the number of decay terms (*n*) for the positron annihilation needs to be known. The exact resolution function $R(t)$ is unknown but is often approximated by a linear combination of Gaussian type functions (GTF). The experimental data $y(t)$ are then least-squares fitted to eq 3 to obtain the fitting parameters[20] λ_i and α_i. However, there are a number of drawbacks in using this model: (i) There is a strong correlation between the parameters in the resolution function and in the lifetime function in data analysis. Often $R(t)$ can be estimated from a separate spectrum from a ^{60}Co which emits two γ-rays with energies 1.17 and 1.33 MeV within a few picoseconds. However, since the time resolution depends on the energy of the γ-rays, the resolution function measured by using the ^{60}Co radioisotope is different from the actual instrument resolution when a lifetime spectrum is collected by using a ^{22}Na positron source which emits 1.28- and 0.51-MeV γ-rays. Another better estimate of the instrument resolution is by the fitting of a reference spectrum from a sample which has a well-known lifetime, such as Al (τ = 162 ps). The obtained parameters of the GTF's for the instrument resolution function by this way are often consistent with that obtained separately in a least-squares fitting process to the sample under study. The procedure of finding the most suitable number of the GTF's and the parameters for the resolution often becomes tedious and time consuming. Moreover, GTF's may not always be the best functions for expressing the instrument resolution. (ii) There is no prior knowledge of the number of annihilation decay terms. Usually, three terms are considered adequate for a molecular sample, each representing the p-Ps, positron, and the o-Ps annihilation. While this may be true for a number of simple materials, a more careful consideration must be made in the case of polymers, amorphous solids, and organic materials. By using an arbitrary number of decay terms, one may still obtain a good fit to the data, but practically the important physical significance attached to the deduced parameters may be lost. Particularly, in polymeric materials, one knows that the Ps lifetime is a sum of the distribution from Ps annihilation in a hole distribution.

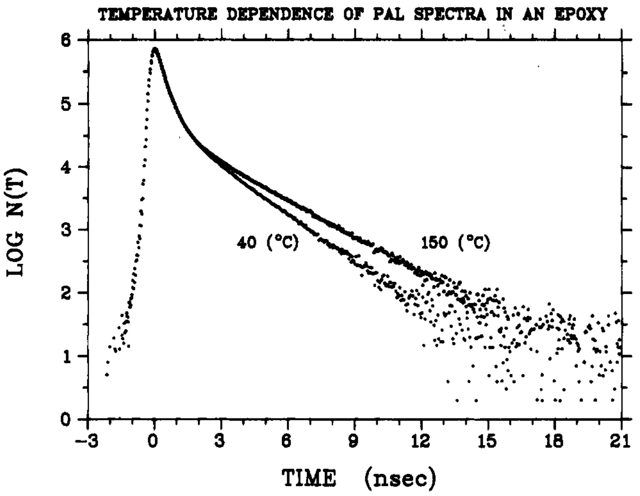

Figure 2. Raw positron lifetime spectra of an epoxy above and below T_g (=62 °C). The total count of each spectrum is 40 × 10^6. Constant backgrounds have been subtracted from the spectra.

4. Renascent Method for Continuous Lifetime Analysis. In 1982, a continuous decay form of eq 3 was suggested by Schrader[21]

$$y(t) = R(t)*(N_t\int_0^\infty \lambda\alpha(\lambda)\, e^{-\lambda t}\, d\lambda + B) \qquad (4)$$

in which the annihilation decay integral function is simply a Laplace transformation of the decay probability density function (pdf) $\lambda\alpha(\lambda)$. The exact solution of $\alpha(\lambda)$ and λ in the above equation is a very difficult mathematical problem since the resolution function $R(t)$ is not known exactly. However the solution can be obtained if one measures a reference spectrum $y_r(t)$ in which the sample has a single positron decay rate (λ_r)

$$y_r(t) = R(t)*N_r\lambda_r e^{-\lambda_r t} \qquad (5)$$

where N_r is the normalized total number of counts for the reference spectrum and λ_r is the reciprocal of lifetime (τ_r) from the reference sample. For this purpose, extra-high-purity, defect-free materials, such as Al (τ_r = 162 ps), Ni (τ_r = 108 ps), and Cu (τ_r = 122 ps), are good candidates for reference samples. The data for the reference must be obtained under the same experimental configuration and conditions as employed for the sample in order to preserve the same instrument resolution. The deconvolution procedure performed by a Laplace inversion technique in this way was first introduced by Gauduchon and Wahl[22] in 1978. The deconvolution of $y(t)$ is expressed by

$$y(t) = \frac{N_t}{\lambda_r N_r}\int_0^\infty \lambda\alpha(\lambda)\,[(\lambda_r - \lambda)G(\lambda,t) + y_r(t)]\,\mathrm{d}\lambda + B \qquad (6)$$

where eq 6 is a Fredholm integral equation which is of the general form

$$G(\lambda,t) = y_r(t)*e^{-\lambda t} \qquad (7)$$

$$y(t) = \int_0^\infty s(\lambda)\,K(\lambda,t)\,\mathrm{d}\lambda + \sum_{i=1}^{N_L}\beta_i L_i(t) \qquad (8)$$

in which, from the known kernel $K(\lambda,t)$, and the given functions $y(t)$ and $L_i(t)$, the unknown function $s(\lambda)$ and the coefficients β_i are calculated. In 1982, Provencher[23-26] developed a computer code named CONTIN for the numerical solution of this type of integral equation which frequently appears in several physical and chemical problems. Those authors used this technique to deconvolute the fluorescent lifetime spectroscopy. The code was later modified by Gregory et al.[27,28] for use in deconvoluting the continuous PAL distribution in organic materials.

There are several advantages of this renascent method over the discrete conventional method: (i) The instrument resolution is not necessary to be known. (ii) There is no need for prior knowledge of the number of annihilation lifetimes or distributions. (iii) Since CONTIN uses the principle of parsimony,[26] the given solution is a smooth solution which is most convenient for the experimental data to remove noises.

5. Experiences of Using CONTIN Program for PAL. Although the CONTIN program has been successfully used in resolving fluorescent spectra into a continuous lifetime distribution, we have experienced several limitations in applying this program to PAL spectra. First, the lifetime resolution for PAL (on the order of 200–300 ps) is a few times worse than that of fluorescent spectroscopy. This is due to the difference between these two spectroscopies: PAL monitors γ-rays while fluorescent spectroscopy monitors UV–vis light. Our resolution is limited by the rising and decay times of scintillators and photomultiplier responses. Second, strictly speaking in PAL, we do not have identical experimental conditions between a sample and a reference as exists in fluorescent spectroscopy. In order to overcome these two limitations, one needs to be very cautious in two aspects, the reference spectrum and statistics. From our experiences, the most crucial factor is the closeness of experimental conditions between the sample of interest and the reference.

We have tested the unique solutions obtained by using CONTIN methods for references: ^{207}Bi, Cu, Ni, and Al which contain a δ function or nearly single positron lifetimes. For example, a ^{207}Bi natural decay spectrum (τ = 183 ps) is deconvoluted by using a reference of the positron lifetime spectrum obtained in a ultrahigh-purity single-crystal Cu sample (τ_r = 122 ps). The results of the lifetime distribution of ^{207}Bi are shown in Figure 3. In Figure 3, we also plotted the Cu lifetime distribution (right peak at τ = 122 ps) as resolved by using its own lifetime spectrum. The Cu peak has a very sharp lifetime distribution at 122 ps with a dispersion of fwhm of less than 1 ps because the reference spectrum is its spectrum. The distribution of the deconvoluted ^{207}Bi lifetime distribution is very narrow with a dispersion of fwhm of less than 5 ps, and the lifetime is exactly at 183 ps. Similar unique and narrow solutions of lifetime distributions are also observed in Al and Ni samples. A width of 5 ps of the lifetime distribution observed in ^{207}Bi is the limiting resolvable dispersion for a single lifetime spectrum by using the current CONTIN method for PAL applications.

For the reference spectra concerned, we found that the ^{207}Bi radioisotope, which has a mean lifetime of 183 ps by emitting two γ-rays at 0.57 and 1.1 MeV, respectively, can be used only when one employs plastic scintillators as γ-ray detectors in the PAL spectrometer. When the energy windows of CFDD were set at 20% of Compton photons, we found that the deconvoluted lifetime results by using a ^{207}Bi reference agree very well with those obtained by single crystals Cu, Ni, and Al as references. But this is not the case when one uses BaF$_2$ as a γ-ray scintillator. When standard samples, such as Cu, Ni, and Al were used, it is essential that these samples are defect-free and of extra-high purity. Our experiences show that the CONTIN results will be very unstable if a source correction or a second lifetime component exceeds 10% in a reference spectrum. This can be easily tested by using the PATFIT program[19] described in the previous section to fit the PAL spectrum from the reference sample. The indication of unstable CONTIN results usually is that the number of resolvable peaks decreases to a smaller number.

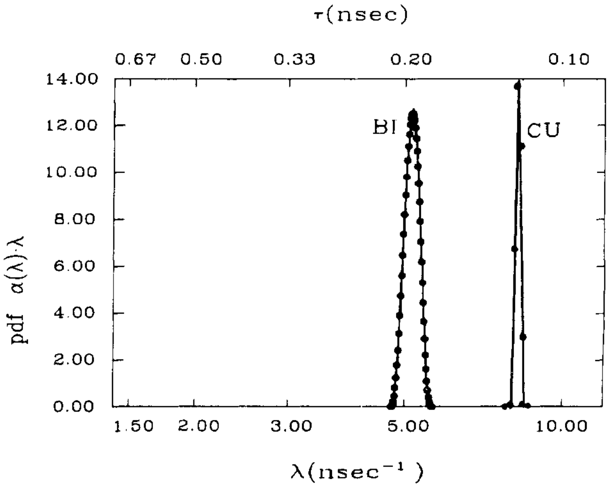

Figure 3. Density distribution function of the ^{207}Bi decay spectrum and the Cu positron lifetime spectrum. In the CONTIN method, the reference spectrum was taken as the Cu positron lifetime spectrum.

Another important factor affecting CONTIN results is the statistics of a spectrum. In order to resolve the lifetime distribution properly, we found that a minimum of the total 10 $\times$ 10^6 counts is required. When a spectrum with lower statistics was fitted, we found that the peak was broadening due to a random error of noises. We started to observe a convergent result of the peak width when the total statistics exceeded 5 $\times$ 10^6 counts. The convergence of CONTIN results occurred rapidly when the total counts were >10 $\times$ 10^6. In the current counting rate (~200 counts/s), a good CONTIN spectrum takes 2–5 days of acquiring time. Therefore, it is essential to maintain a good electronic stability over a period of 1 month for a complete series of PAL experiments. It is also desirable that the statistics are the same for a sample and a reference. Once we have taken all of these precautions into consideration, we found that the CONTIN program can be successfully used to unfold the lifetime spectra into a continuous lifetime distribution. Some other descriptions of using this program can be found in ref 28.

III. Results and Discussion

We have measured the positron lifetime spectra for an epoxy polymer at 25, 40, 66, 100, 130, and 150 °C at different statistics, 1, 5, 10, 20, and 40 $\times$ 10^6 counts. When the temperature is above T_g, the free volume increases in its content and size. As shown in Figure 2, a longer lifetime at 150 °C than at 40 °C indicates that o-Ps is annihilating with a larger hole at $T > T_g$. We first analyzed these PAL data by the conventional least-squares fitting method. A PATFIT program[20] was employed for the analysis in a discrete number of lifetimes according to eq 3 where we found n = 3 gives an excellent χ^2 (<1.1) and standard deviations. The results of τ_i and corresponding intensities I_i are listed in Table I. Following the general assertion regarding three lifetimes, three positron states exist in polymer materials. The shortest lifetime, $\tau_1 \approx$ 0.120 ns, is attributed to p-Ps (singlet Ps) annihilation, the second lifetime, τ_2 = 0.35–0.4 ns, is due to positron (not Ps) annihilation, and the third lifetime, τ_3 = 1.6–2.2 ns, is due to the o-Ps (triplet

Table I
Positron Lifetime Results in an Epoxy Analyzed by Using the PATFIT Program[20,a]

temp, °C	τ_1, ns	τ_2, ns	τ_3, ns	I_1, %	I_2, %	I_3, %	$\bar{R}$, Å
25	0.130 ± 0.002	0.396 ± 0.003	1.666 ± 0.006	28.30 ± 0.54	52.19 ± 0.47	19.52 ± 0.11	2.52
40	0.133 ± 0.003	0.393 ± 0.003	1.711 ± 0.007	22.90 ± 0.61	57.28 ± 0.54	19.81 ± 0.12	2.57
66	0.132 ± 0.003	0.396 ± 0.002	1.753 ± 0.006	22.95 ± 0.53	57.24 ± 0.47	19.81 ± 0.10	2.61
100	0.136 ± 0.002	0.405 ± 0.002	1.869 ± 0.004	26.37 ± 0.36	54.04 ± 0.32	19.58 ± 0.07	2.73
130	0.139 ± 0.004	0.413 ± 0.004	2.110 ± 0.010	24.41 ± 0.80	56.17 ± 0.73	19.42 ± 0.12	2.95
150	0.142 ± 0.005	0.409 ± 0.005	2.183 ± 0.011	23.27 ± 0.97	56.05 ± 0.89	20.67 ± 0.14	3.01

[a] All fits have $\chi^2 < 1.1$ and total counts = 40×10^6 for each spectrum. The resolutions as fitted from lifetime spectra were expressed in two gaussians: 250 ± 10 ps (90%) and 400 ± 20 ps (10%) from the resolution program of PATFIT package.[20] $\bar{R}$ is the mean radius of the free-volume hole from τ_3 according to eq 2.

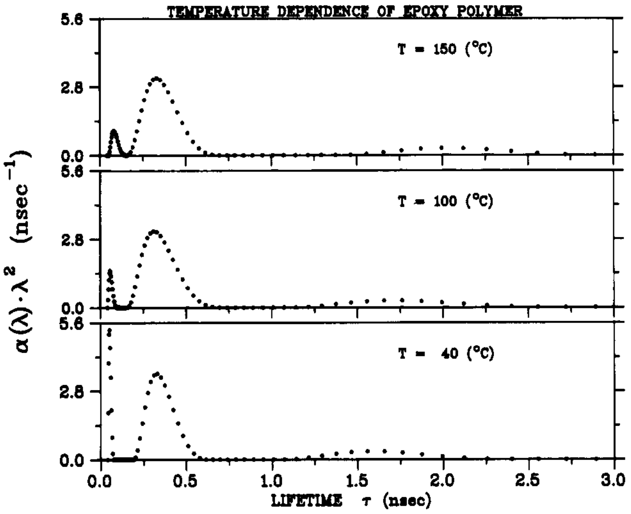

Figure 4. Positron lifetime distribution function of an epoxy polymer. The total count of each spectra is 40×10^6. The distributions of the positron lifetime were obtained by using the CONTIN program[23-28] from a reference spectrum of the positron lifetime in Cu (τ = 122 ps, 99%).

Ps) annihilation. The conventional PAL technique employs τ_3 and eq 2 to determine the mean free-volume hole radius when a positron spectrum is resolved according to eq 3 with $n = 3$. The results of the mean hole radius, $\bar{R}$, by this method are also listed in Table I.

Next, we fit the PAL spectra into a continuous lifetime according to the expressions of eqs 4–8 by using the CONTIN program.[22-27] Four reference spectra, positron lifetime spectra of annealed single crystal Al (τ_r = 162 ps, 98%), Cu (τ_r = 122 ps, 99%), and Ni (τ_r = 108 ps, 98%) and a natural lifetime spectrum of ^{207}Bi (τ_r = 183 ps, 100%), have been used to deconvolute the obtained PAL spectra. All CONTIN results show an excellent agreement: Three distinct peaks in the results of positron lifetime distributions are observed. In Figure 4 we show the results of the lifetime probability density function, $\alpha(\lambda)\ \lambda^2$, from CONTIN outputs for an epoxy polymer at 40, 100, and 150 °C, respectively. Each spectrum contains a total statistics of 40×10^6 counts, and the lifetime distributions have been normalized over the entire lifetime.

As shown in Figure 4, the left peaks (integrated area = 6.4–6.9%) represent the p-Ps lifetime distributions which have maxima at 0.07, 0.09, and 0.11 ns for T = 40, 100, and 150 °C, respectively. The middle peaks represent the positron (not Ps) lifetime distributions which have maxima at 0.340, 0.345, and 0.355 ns for T = 40, 100, and 150 °C, respectively. The right peaks represent o-Ps distributions which have maxima at 1.66, 1.74, and 2.13 ns with integrated intensities of 19.2%, 20.2%, and 21.0% for T = 40, 100, and 150 °C, respectively.

Comparing the lifetime results obtained by using the CONTIN method and by the PATFIT method, we found that in general the results agree with each other qualitatively but there are some detailed differences, particularly the results of the short-lifetime part. When we compare the mean positron lifetimes ($\bar{\tau}_i$, i = 1–3) as integrated between the lifetime integrals τ_a and τ_b for each peak

$$\bar{\tau}_i = \int_{\tau_a}^{\tau_b} \alpha\lambda\ d\tau \Big/ \int_{\tau_a}^{\tau_b} \alpha\lambda^2\ d\tau \qquad (9)$$

The results of $\bar{\tau}_1$ and $\bar{\tau}_2$ are found to be 0.065, 0.100, and 0.130 ns and 0.350, 0.360, and 0.368 ns at 40, 100, and 150 °C, respectively. The mean values of short lifetimes from CONTIN results are found to be consistently less than those from PATFIT. In PATFIT analysis, as shown in Table I, τ_1 are seen to be longer than the theoretical lifetime of p-Ps (0.125 ns) and their intensities are far greater than the theoretical $^1/_3$ value of I_3, i.e., the multiplicities between the singlet Ps (p-Ps) and the triplet Ps (o-Ps). All these observations have been known[29] due to the limited lifetime resolutions (≈250 ps) which constrain us in resolving the shortest lifetime correctly. In this case, the shortest lifetime results from PATFIT are contaminated by the longer positron lifetime component, thus leading to a lifetime longer than 0.125 ns and a greater intensity I_1. In the current CONTIN method, the difficulties in resolving the short-lifetime distribution could not be removed due to the intrinsic problem of limited resolutions as indicated from the lower values of resolved τ_1. On the other hand, we found that the integrated intensities from the peaks of the shortest lifetime distributions (Figure 4) are very close to the exact $^1/_3$ values of o-Ps intensities. They are 6.4%, 6.6%, and 6.9% for 40, 100, and 150 °C, respectively. In spite of the small discrepancies obtained in the results of p-Ps, and positron lifetimes between these two methods, we found two important and consistent results: (1) The results of long lifetimes, i.e., the τ_3 and I_3, from PATFIT and the mean lifetime and integrated intensities of the o-Ps peaks from CONTIN have excellent agreement. (2) The mean lifetimes combined from p-Ps and positron components, i.e., $\bar{\tau} = \tau_1 I_1 + \tau_2 I_2$, are essentially the same between the lifetimes from PATFIT and the integrated values from CONTIN results. The later observation indicates some limitations in utilizing the short-lifetime distributions to interpret the physical properties of polymeric materials. On the other hand, the results of long-lifetime (o-Ps) distributions are not interfered by the limited resolutions. Therefore, their resolved lifetime distributions are unique and very reliable and can be correctly used to interpret the free-volume distributions in polymers. For the purpose of clarity, we replotted the o-Ps distributions from Figure 4 in Figure 5. Then we proceed to determine the free-volume hole properties from the o-Ps distributions shown in Figure 5.

The free-volume hole radius probability density function, $f(R)$, is defined as[30] $-\alpha(\lambda_3)\ d\lambda_3/dR$ of eq 2 and is expressed as

$$f(R) = -2\Delta R\{\cos\,[2\pi(R/R_0)] - 1\}\alpha(\lambda_3)/(R_0^{\,2}) \qquad (10)$$

The fraction of o-Ps annihilating in the holes with a radius

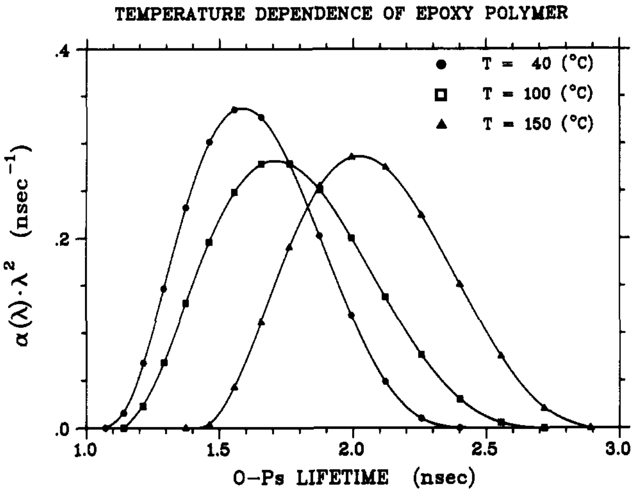

Figure 5. o-Ps lifetime distribution function of an epoxy polymer. The data were taken from the peaks on the right shown in Figure 4.

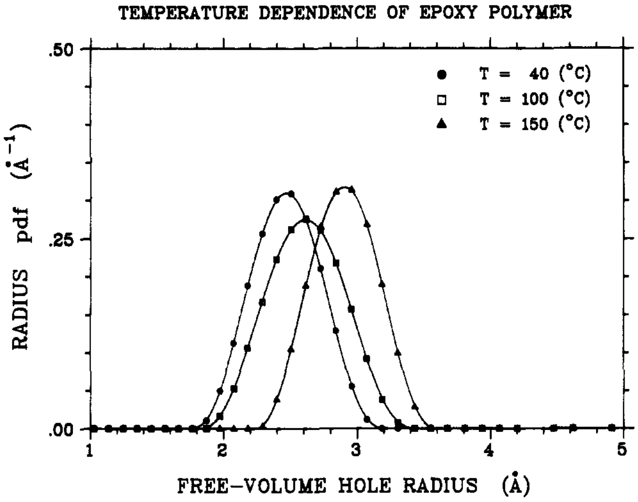

Figure 6. Hole radius distribution functions, $f(R)$, of an epoxy at different temperatures. Smooth lines were drawn through the data points for eye-guide purposes only.

between R and dR is $f(R)\ dR$. The results of the radius probability distribution function, $f(R)$, calculated according to the eq 10 for data from Figure 5 at 40, 100, and 150 °C are plotted in Figure 6. As expected, an increase in the temperature results in an enlargement of the free-volume holes; the distributions shift from the mean radius 2.45 Å to 2.61 and 2.95 Å for $T = 100$ and 150 °C, respectively. As shown in Figure 6, the hole radius distribution functions $f(R)$ are found quite symmetric and narrow and can be approximately expressed by Gaussian-type functions with fwhm of 0.7 Å.

Our results of radius distributions of free-volume holes are about on the order of interatomic distances of hydrocarbons and are consistent with the results obtained from molecular dynamic simulation[4] (2–3-Å radius). The results obtained by Yu et al.[14] for an epoxy sample with a different structure show free-volume holes as large as 12.4 Å in radius, with an average of 6.5 Å. These fairly large voids within the sample are not detected by the current PAL method. This discrepancy may be a result of different regions of sensitivity in using different probes. The Ps probe has a Bohr diameter of about 1 Å while the fluorescent probe has a size of 3–10 Å. The smaller hole distribution (radius 2–4 Å) may escape the detection limit of the fluorescent probe employed by those authors. For a larger size hole, in principle, Ps should be able to probe a size as big as 20 Å. One explanation is that the content of bigger holes may be very small compared to that of smaller holes. In the current PAL technique, the hole fraction of less than 0.1% may not be detectable.

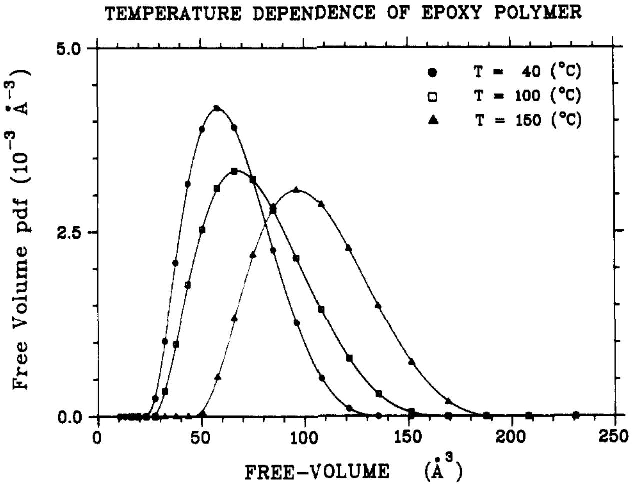

Figure 7. Hole volume distribution functions, $g(V)$ of an epoxy at different temperatures. Smooth lines were drawn through the data points for eye-guide purposes only.

It is also interesting to report the hole volume probability density function for theoretical comparison in the future. The probability density function of hole volumes, $g(V)$, can be obtained by assuming a spherical hole and is expressed as

$$g(V) = f(R)/4\pi R^2 \qquad (11)$$

The fraction of hole volume distribution as determined by o-Ps annihilation in holes with a volume between V and $V + dV$ is given by $g(V)\ dV$. The results of hole volume distribution, $g(V)$, from the $f(R)$ results of Figure 6 and according to eq 11 above are plotted in Figure 7 for epoxy at 40, 100, and 150 °C, respectively. The observed hole volumes are found to be distributed skew to larger holes. The distributions are also found to be temperature dependent: at $T > T_g$, the distributions are spreading wider at larger hole volumes than those at $T < T_g$. The long-tail distributions for larger volumes (Figure 7) are found to be similar to an exponential function as theoretically simulated by molecular dynamic methods for simple hydrocarbons[4] while the symmetric hole radius distribution functions (Figure 6) are found to be similar to γ functions as theoretically calculated by kinetic theory.[5]

Conclusion

In conclusion, positron annihilation lifetime spectroscopy along with the renascent Laplace inversion technique for data analysis has been successfully applied to measure the free-volume hole size distribution at various temperatures in an epoxy polymer. The hole radius and volume distributions are found to be between 1.6 and 4 Å and between 25 and 200 Å³, respectively.

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References and Notes

(1) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.
(2) For example, see: Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(3) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(4) Rigby, D.; Roe, R. J. *Macromolecules* **1990**, *23*, 5312.

(5) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1985**, *18*, 2239.

(6) Jean, Y. C.; Sandreczki, T. C.; Ames, D. P. *J. Polym. Sci., Part B* **1986**, *24*, 1247.

(7) Ferrell, R. A. *Phys. Rev.* **1957**, *108*, 167.

(8) Nakanishi, H.; Jean, Y. C.; Smith, E. G.; Sandreczki, T. C. *J. Polym. Sci., Part B* **1989**, *27*, 1419.

(9) Jean, Y. C.; Nakanishi, H.; Hao, L. Y.; Sandreczki, T. C. *Phys. Rev. B.* **1990**, *42*, 9705.

(10) Jean, Y. C. *Microchem. J.* **1990**, *42*, 72.

(11) Wang, Y. Y.; Nakanishi, H.; Jean, Y. C.; Sandreczki, T. C. *J. Polym. Sci., Part B* **1990**, *28*, 1431.

(12) Jean, Y. C.; Zandiehnadem, F.; Deng, Q. In *Proceedings of the MRS Symposium on the Structure, Relaxation, and Physical Aging of Glassy Polymers*; Roe, R. J., O'Rilly, J. M., Eds.; MRS Publish Pittsburgh, PA, 1991; Vol. 215, pp 163–174.

(13) Deng, Q.; Sundar, C. S.; Jean, Y. C. *J. Phys. Chem.*, in press.

(14) Yu, W. C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.

(15) For examples, see: Stevens, J. R. In *Probe and Label Techniques in: Methods of Experimental Physics*; Fava, R. A., Ed.; Academic: London, 1980; p 371 and ref 10.

(16) Brandt, W.; Berko, S.; Walker, W. W. *Phys. Rev.* **1960**, *12*, 1289.

(17) Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499.

(18) Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51.

(19) Nakanishi, H.; Jean, Y. C. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C.; Eds.; Elsevier: Amsterdam, The Netherlands, 1988; Chapter 5.

(20) Kirkegaard, P.; Eldrup, M.; Mogensen, O. E.; Pedersen, N. J. *Comput. Phys. Commun.* **1981**, *23*, 307; PATFIT (1989 version), Riso National Laboratories, Denmark.

(21) Schrader, D. M. In *Positron Annihilation*; Coleman, P. G., Sharma, S. C., Diana, L. M., Eds.; North-Holland; Amsterdam, The Netherlands, 1982; pp 912–914.

(22) Gauduchon, P.; Wahl, P. *Biophys. Chem.* **1978**, *8*, 87.

(23) van Resandt, W. R. W.; Vogel, R. H.; Provencher, S. W. *Rev. Sci. Instrum.* **1982**, *53*, 1392.

(24) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

(25) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.

(26) Provencher, S. W. CONTIN *Users Manual*; EMBL Technical Report DA05; European Molecular Biology Laboratory, 1982.

(27) Gregory, R. B.; Procyk, A. In *Positron Annihilation Studies of Fluids*; Sharma, S., Ed.; World Scientific: Singapore, 1988; p 524.

(28) Gregory, R. B.; Zhu, Y. *Nucl. Instrum. Meth. Phys.* **1990**, *A290*, 172.

(29) Jean, Y. C.; Schrader, D. M. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier: Amsterdam, The Netherlands, 1988.

(30) Gregory, R. B. *J. Appl. Phys.*, in press.