Free-Volume Hole Properties in Thermosetting Plastics Probed by Positron Annihilation Spectroscopy: Chain Extension Chemistry

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ABSTRACT: Free-volume hole sizes and fractions in a series of thermosetting plastics (tetraglycidyldiaminodiphenylmethane (TGDDM), diglycidyl ether of Bisphenol A (DGEBA) cross-cured with diaminodiphenyl sulfones (DDS)) are measured by using positron annihilation lifetime (PAL) spectroscopy. Relevant mechanical properties are measured in these polymers which have different configurational isomers and chain extensions of curing oligomers. Correlations between the obtained free-volume hole properties and fracture toughness and stiffness are observed. Applications of positron annihilation spectroscopy to determine materials parameters and engineering problems are discussed.

I. Introduction

In recent years, thermosetting plastics have been developed for engineering and structural applications because of their superior mechanical properties, chemical stability, and light weight.[1] A key problem in utilizing this type of polymer is the alteration of materials and mechanical properties with time, *i.e.*, physical and chemical aging.[2] One increasingly promising approach to understanding the origin of this key problem is through the study of free-volume properties.[3] The free-volume concept has been popularly used to explain this problem because of its conceptual simplicity and its atomic and molecular scale. However, because of their brief duration (as short as 10^{-13} s) and small dimension (as small as 10^{-10} m), the determination of free-volume properties has been a challenge to polymer scientists.

There are many physical techniques available to characterize the open spaces and defects in polymeric materials. Figure 1 summarizes the existing methods in terms of two physical parameters: time and dimension. As shown in Figure 1, mechanical measurements take place over a long duration and at a macroscopic scale, while free-volume measurements take place over an extremely short time and at a microscopic atomic scale. Most common physical methods, such as scanning tunneling microscopy (STM), small-angle neutron scattering (SANS), fluorescence spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction, and optical microscopy, are for dimensions between these extremes. Their applicable dimension varies from 10^{-9} to 10^{-3} m. However, except for fluorescence, these conventional methods are only apt to probe static voids and defects.

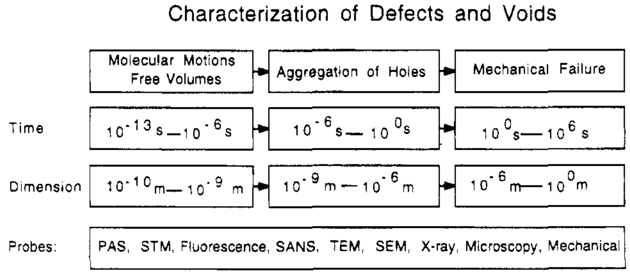

Figure 1. Different time and dimension scales pertaining to existing techniques for the characterization of defects and voids.

Positron annihilation spectroscopy (PAS) is an innovative nuclear technique which has been recently developed for polymer characterization.[4] It uses the positron, the antiparticle of electrons, as the probe, and monitors positron−electron annihilation signals in materials under study. Because of its positive charge, the positron is repelled by ion cores when it is injected into a polymeric sample. Therefore annihilation signals are mainly contributed from the open spaces, *i.e.*, the free volume, holes, voids, and interfaces. In polymeric materials, before annihilation occurs, the positron can also extract an electron from molecules, thus forming a neutral atom, positronium (Ps). As a result of different spins, Ps can exist either in a singlet state, as parapositronium (p-Ps), or in a triplet state, as orthopositronium (o-Ps). o-Ps is particularly useful in the application of PAS to polymers because of its long lifetime compared to other positronic states: on the order of 10^{-9} s. Existing positron annihilation lifetime (PAL) studies as a function of temperature, pressure, and time show that o-Ps is localized in the free-volume holes of polymers.[5−7] Since PAL measures the average electron density in a free-volume hole, a direct relationship between the dimension and o-Ps lifetime is expected: a larger hole results in a longer Ps lifetime. In recent years, we have established an analytical equation between the o-Ps lifetime and the hole radius.[8] The relationship has been further developed for a hole with an ellipsoidal shape.[9] Furthermore, the formation probability of o-Ps as resolvable from a PAL spectrum provides a measure for the fractional free volume (f_v).

The current PAL technique is useful in resolving the free-volume hole dimension and distribution ranging from 1 to 20 Å and a time of motion as short as a few 10^{-10} s. Figure 2 presents as a schematic diagram the

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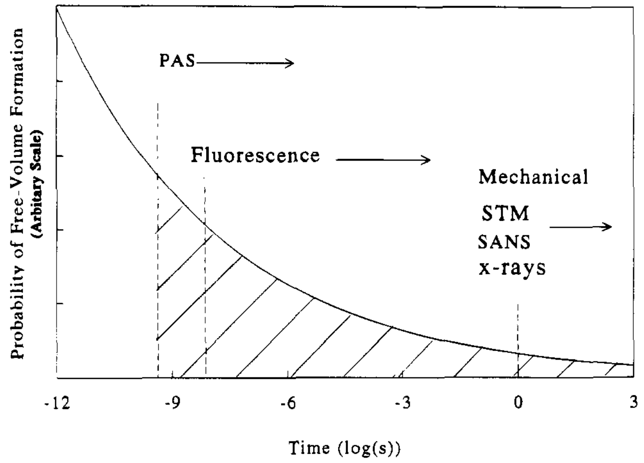

Figure 2. Schematic plot of the probability of free-volume hole formation vs the time of formation. PAS (positron annihilation spectroscopy) probes those holes formed as briefly as a few 10^{-10} s, while conventional methods are mainly used for static holes.

range that o-Ps is capable of probing. Contrary to conventional probes (except fluorescence), PAS covers all free volumes created at times from a few 10^{-10} s and longer. Although some portion still escapes the detection of PAS—*i.e.*, those free-volume holes formed at times shorter than 10^{-10} s—a major portion of free volume is detectable by PAS. Fluorescence is another probe which can trace the origin to as short as a few 10^{-9} s. However, the large size of the molecule labeled as a fluorescence probe (on the order of a few hundreds of Å^3) significantly perturbs the origin of free volume in polymers. This perturbation mainly affects the smaller volumes, which are particularly relevant to material behaviors of polymers. Other atomic probes, such as STM, SANS, etc., are not applicable to probe these free-moving holes. On the other hand, the volume determined by o-Ps also includes static holes. The probability of free-volume formation is presumed to be dramatically decreased as a function of time, as schematically shown in Figure 2. It is also known that o-Ps lifetime becomes less sensitive to those holes with a size greater than 10 Å. Since most static holes and voids have a relatively large size, *i.e.*, larger than 10 Å, their contributions in PAL results can be considered as a constant background or less important. Therefore PAS has been considered as a unique method to determine free-volume hole properties in polymeric materials.

Macroscopic data from mechanical measurements are most relevant to industrial applications of polymeric materials. The purpose of this study is to search for the relationship between microscopic free-volume hole properties by PAS measurements and macroscopic properties by mechanical measurements in the same materials. Although there are some existing attempts, those results are all inconclusive.[10-12] Our strategy is to investigate properties by varying molecular structures, *i.e.*, configurational isomers and chain extensions in similar polymers. In this paper, we present a systematic study of parallel PAS and mechanical measurements in selected thermosetting polymers of varied chemical structures with various functional groups.

II. Experiments

A. Sample Preparation and Characterization. Two common epoxy-based materials are selected in this study: tetraglycidyldiaminodiphenylmethane (TGDDM) and diglycidyl ether of Bisphenol A (DGEBA). The curing agents are amine-based materials: diamino diphenyl sulfone (DDS) with various configurational isomers and diamino polysulfone oligomers (DPO) with different chain lengths. The chemical structures of base materials are shown in Figure 3. The raw epoxy materials were supplied by Dow Chemical and Ciba-Geigy. The curing agents with different chain lengths of oligomer and different configurational isomers were synthesized by methods described elsewhere.[13] The synthesized curing agents were characterized by using appropriate analytical techniques: gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis (at Hercules Inc.).

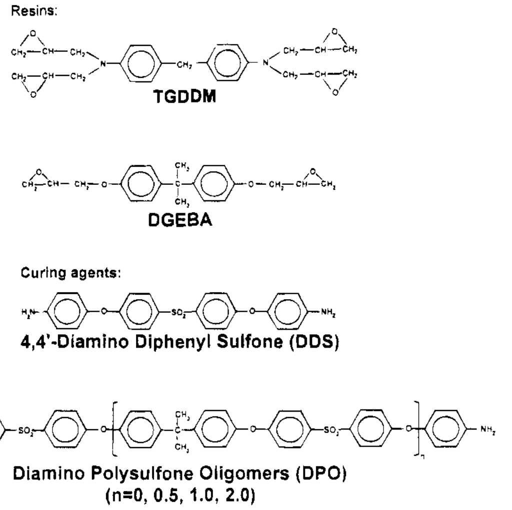

Figure 3. Base chemical structures of epoxies and curing agents for thermosetting polymers in this study.

Thermosets were polymerized with a stoichiometric ratio (1:1) between epoxies and curing agents at selected temperatures and atmospheric pressure. The synthesized polymers were further postcured at various temperatures for different periods of time to vary their material and mechanical properties. The T_gs of these materials were determined by differential scanning calorimetry (DSC). Relevant mechanical properties—shear modulus or stiffness (G'), critical stress intensity factor (K_{1C}), fracture toughness (G_{1C}), and compression strength after impact (CAI)—were measured by using appropriate Instron and MTS instruments at Hercules Inc. Standard ASTM sample preparations and testing procedures were followed. Thermomechanical properties of these thermosetting plastics for this study are listed in Table 1.

B. Positron Annihilation Lifetime (PAL) Spectroscopy. The positron annihilation lifetimes of polymers were determined by detecting the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ-rays (0.511 MeV). A fast–fast coincidence circuit of the PAL spectrometer with a lifetime resolution of 260 ps as monitored by using a ^{60}Co source was used to record all PAL spectra. Each PAL spectrum contains 1×10^6 counts. The counting rate was about 200 cps. Detailed descriptions of PAL can be found elsewhere.[4-7]

C. Mean Free-Volume Hole Size and Fraction. All of the PAL spectra obtained were analyzed by using the PATFIT program.[14] PAL spectra were decomposed into two to five terms of negative exponentials. In these polymers, we found that three-lifetime results give the best χ^2 (<1.1) and most reasonable standard deviations. The shortest lifetime ($\tau_1 \approx$ 0.12 ns) is the lifetime of p-Ps and the intermediate lifetime ($\tau_2 \approx$ 0.40 ns) is the lifetime of the positron. The longest lifetime ($\tau_3 \approx$ 1–3 ns) is due to o-Ps annihilation. In the current PAL method, we employ the results of o-Ps lifetime to obtain the mean free-volume hole radius by the following semiempirical equation:[8]

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \qquad (1)$$

Table 1. Thermomechanical Properties of Thermosetting Plastics

samples[a]	T_g[b] (°C)	G'[c] (10^{10} dyn/cm^2)	K_{1C}[d] (MPa m$^{1/2}$)	CAI[e] (kG/in.^{2})	G_{1C}[f] (J/m^2)
TGDDM/33′DDS (1:1)	231	2.1 ± 0.1	0.66 ± 0.04		75 ± 25
TGDDM/44′DDS (1:1)	260	1.8 ± 0.1	0.74 ± 0.04		111 ± 25
DGEBA/43′DDS (1:1)	170	1.4 ± 0.1			170 ± 25
DGEBA/42′DDS (1:1)	140	1.5 ± 0.1		52.6 ± 5	140 ± 30
DGEBA/33′DDS (1:1)	213	1.5 ± 0.1	0.60 ± 0.04		88 ± 25
DGEBA/44′DPO (1:1) (n = 0)	230	2.1 ± 0.1	0.73 ± 0.04	44.6 ± 5	94 ± 25
DGEBA/44′DPO (1:1) (n = 0.5)	200	1.3 ± 0.1			314 ± 30
DGEBA/44′DPO (1:1) (n = 1)	190	1.2 ± 0.1			538 ± 30
DGEBA/44′DPO (1:1) (n = 2)	135	1.1 ± 0.1			660 ± 40

[a] In samples, the first pair of parentheses refers to the stoichiometric ratio between epoxies and curing agents and ***n*** in the second pair of parentheses is the number of chain extensions of oligomers (see Figures 3 and 4). [b] T_g is determined by DSC measurements. [c] G': shear modulus (stiffness) at room temperature. [d] K_{1C}: critical stress intensity factor. [e] CAI: compression strength after impact. [f] G_{1C}: fracture toughness.

Table 2. Positron Lifetime Results of Thermosetting Plastics[a]

sample	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	hole radius R (Å)	hole volume V_f (Å^3)	hole fraction f_v (%)
TGDDM/33′DDS (1:1)	372 ± 3	52.4 ± 0.2	1448 ± 9	19.7 ± 0.2	2.27 ± 0.05	49.0 ± 3.7	1.74 ± 0.07
TGDDM/44′DDS (1:1)	383 ± 2	49.5 ± 0.2	1499 ± 9	21.9 ± 0.2	2.34 ± 0.05	53.7 ± 3.7	2.11 ± 0.07
DEGBA/43′DDS (1:1)	383 ± 3	46.1 ± 0.2	1607 ± 9	24.1 ± 0.2	2.45 ± 0.05	61.6 ± 3.8	2.67 ± 0.08
DGEBA/42′DDS (1:1)	405 ± 2	50.2 ± 0.2	1728 ± 9	14.0 ± 0.2	2.58 ± 0.05	71.9 ± 4.0	1.82 ± 0.09
DGEBA/33′DDS (1:1)	408 ± 5	51.3 ± 0.3	1542 ± 13	14.7 ± 0.3	2.39 ± 0.05	57.2 ± 3.6	1.51 ± 0.06
DGEBA/44′DPO (1:1) (n = 0)	403 ± 6	51.3 ± 0.2	1532 ± 15	18.9 ± 0.3	2.38 ± 0.05	56.5 ± 3.7	1.91 ± 0.06
DGEBA/DPO (1:1) (n = 0.5)	402 ± 3	43.4 ± 0.3	1724 ± 9	23.8 ± 0.2	2.58 ± 0.04	71.9 ± 2.0	3.08 ± 0.07
DGEBA/DPO (1:1) (n = 1)	390 ± 3	43.0 ± 0.2	1699 ± 9	24.6 ± 0.2	2.55 ± 0.04	69.5 ± 2.0	3.10 ± 0.07
DGEBA/DPO (1:1) (n = 2)	393 ± 3	43.6 ± 0.2	1816 ± 9	25.0 ± 0.2	2.67 ± 0.05	79.7 ± 2.0	3.58 ± 0.07

[a] τ_1 was fixed at 125 ps during data analysis; all fits have $\chi^2 < 1.1$. Free-volume radii were calculated from the correlation equation between τ_3 and R (eq 1). In samples, the numbers in the first pair of parentheses refer to the weight ratio of epoxy and amine of polymers; the numbers in the second pair of parentheses refer to the number of sulfone units in the oligomers (see Figure 3 for chemical structures).

where τ_3 (o-Ps lifetime) and R (hole radius) are expressed in nanoseconds and angstroms, respectively. $R_0 = R + \Delta R$, where ΔR is the fitted empirical electron layer thickness (=1.66 Å).

The fractional free volume (%) is expressed as an empirically fitted equation:[15]

$$F_v = CV_fI_3 \qquad (2)$$

where V_f (in Å^3) is the volume of free-volume holes calculated by using the spherical radius (R) of eq 1 from τ_3 (in ns), I_3 (in %) is its intensity, and C is empirically determined to be 0.0018 from the specific volume data.[15] Results of positron lifetime analysis are shown in Table 2.

III. Results and Discussion

The PAL results in nine thermosets are listed in Table 2. The free-volume hole radii, hole volumes, and fractions are calculated from the o-Ps lifetime (τ_3) and its intensity (I_3) as described above. The current results of hole sizes and fractions are consistent with those reported in epoxy polymers.[5,16]

A. Configurational Isomers. Local molecular packings of polymers are highly affected by the configuration of monomers. Comparing two pairs of thermosets—TGDDM and DGEBA with 33′- and 44′DDS—the 33′ isomers cross-link with epoxies at certain angles different from the 44′ isomers, which are at a perpendicular angle. One expects that the 44′ isomers with a straight cross-linking structure have a more flexible packing than the 33′ isomers. As shown in the free-volume results (Table 2), the f_v values are found to be larger from the 44′ isomers than from the 33′ isomers. For the same reason, the thermoset from the 43′ DDS isomer and DGEBA shows a larger free volume than that from the 42′, 44′, and 33′ isomers. It is interesting that, among the four isomers of DDS cured with DGEBA, we find the free-volume fraction decreases in the following order: DGEBA/43′DDS > /44′DDS > /42′DDS > /33′DDS. The size of the free volume follows the same trend as that of fractional free volume with respect to the chemical configuration of the isomers.

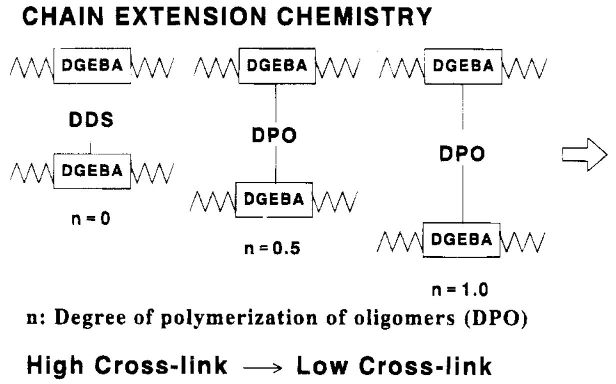

Figure 4. Schematic presentation of chain extension chemistry for DGEBA/DPO thermosets. Note that DDS is the same as DPO with n = 0.

B. Chain Length of Curing Agents. In a series of DGEBA/DPO thermosets with a controlled chain length of DPO curing agents, the free-volume results are rather interesting. As schematically shown in Figure 4, the length of DPO oligomers increases as the number of sulfone units (n) increases (see Figure 3). As the chain length increases, the cross-link density of the thermoset decreases due to the increasing flexibility of the chain motion. Therefore, both open space and motions between DPO chains in polymers are expected to increase accordingly. As expected, the results of the free-volume properties (Table 2) in these four thermosets vary as the chain length of the oligomers increases. Figure 5 shows the variation of o-Ps lifetime (τ_3) and its intensity (I_3) as a function of number of chain extensions of oligomers, n.

The variations of free volume and its fraction vs the chain extension length are plotted in Figure 6. The increase in f_v and V_f with respect to the cross-linking

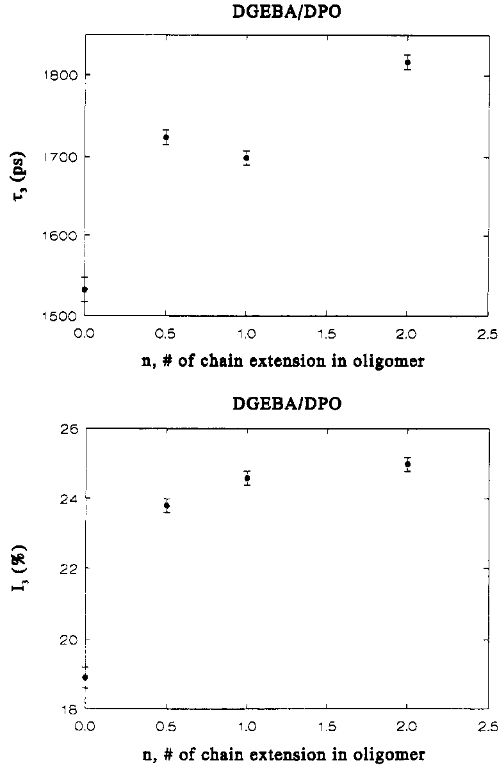

Figure 5. Variations of o-Ps (τ_3) and its intensity vs number of chain extensions in DGEBA/DPO thermosets. See Figures 3 and 4 for the structures of oligomers (DPO).

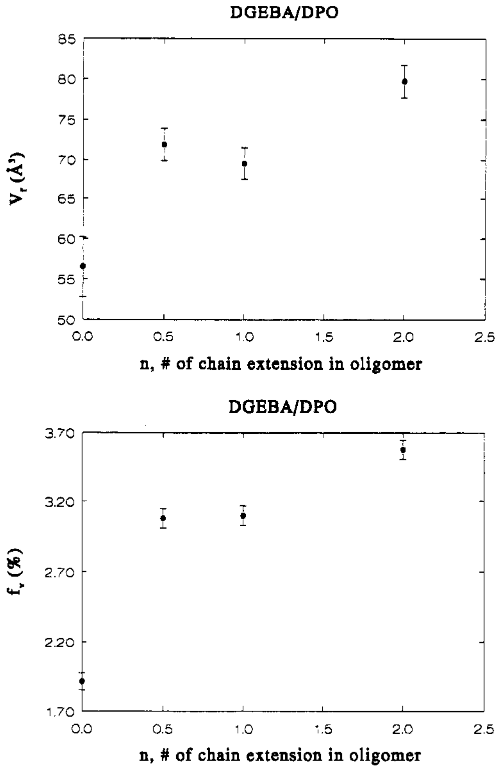

Figure 6. Variations of fractional free volume (f_v) vs the number of chain extensions in DGEBA/DPO thermosets. The number of chain extensions (n) is defined in Figure 3 and schematically shown in Figure 4.

chain length results from the large changes in local packing as materials are polymerized. The lengthier the extension, the more chain–chain motion is allowed. This leads to an increase of free-volume fraction with an increase in degree of chain extension of curing agents. It is worth mentioning that despite this strong correlation, we found that there is no significant difference in density among these polymers. This is further evidence that o-Ps is a unique probe for local free volumes in polymers.

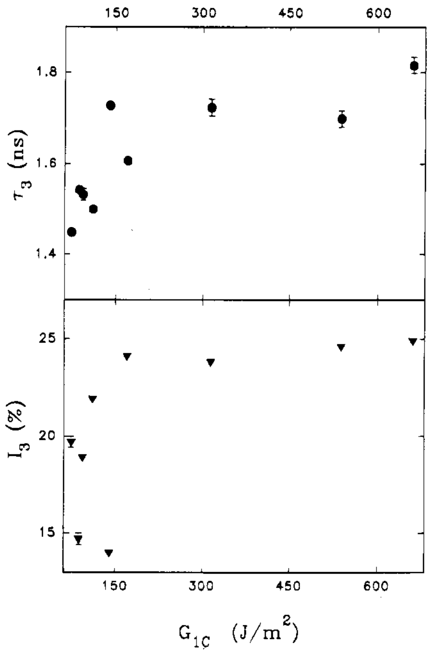

Figure 7. Results of o-Ps lifetime (τ_3) and its intensity vs fracture toughness of thermosets.

C. Mechanical Properties. As shown in Figure 1, mechanical properties are relevant at a time and dimension 13–10 orders of magnitude greater than those relevant to free-volume properties. One of the most intriguing questions in our field is: To what degree do mechanical properties depend upon the molecular-scale free-volume properties?

Next we compare the free-volume results (Table 2) with the mechanical properties (Table 1). In spite of the fact that some thermomechanical results are not available due to difficulties in measurement, we found two clear correlations: (1) the fracture toughness (G_{1C}) increases as the fractional free volume (f_v) increases and (2) the stiffness (G') decreases as f_v increases. Although there is an increasing trend of free-volume fraction (f_v) and critical stress intensity factor (K_{1C}), their correlation is not as clear as these two properties.

The fracture toughness of a material depends on its ability to absorb or dissipate energy, which in turn requires chain mobility. Therefore, impact resistance is expected to increase when flexibility is increased. Networks based on flexibilized diamines exhibit very high values of toughness. According to Delvigs,[17] the incorporation of flexibilized diamines into epoxy networks is expected to improve the fracture toughness and impact strength. Unfortunately, we were unable to obtain a complete set of data on the compression strength after impact (CAI) due to experimental difficulties; thus, its relationship with free volume is not conclusive. On the other hand, the above discussion has given a number of indications that there exists a correlation between fracture toughness of epoxy polymers and their free volumes.

Plots of the o-Ps lifetime, τ_3, and its intensity, I_3, as a function of fracture toughness (G_{1C}) in various epoxies are presented in Figure 7. There is a trend that the average free-volume hole size (reflected from the τ_3 value) and number of holes (reflected from I_3) increase as the toughness increases. However, the correlation between fractional free volume and fracture toughness is clear. In Figure 8, the free-volume fraction, f_v, of

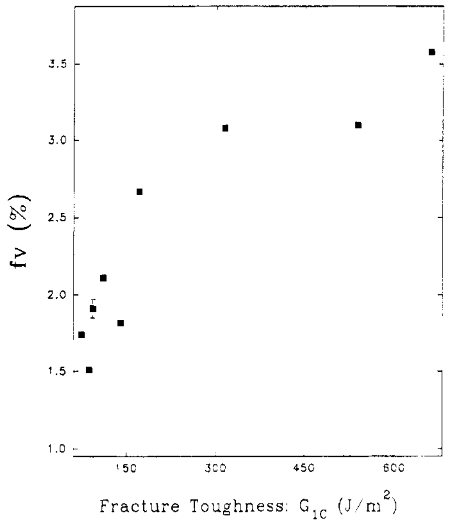

Figure 8. Correlation between fractional free volume and fracture toughness of thermosets.

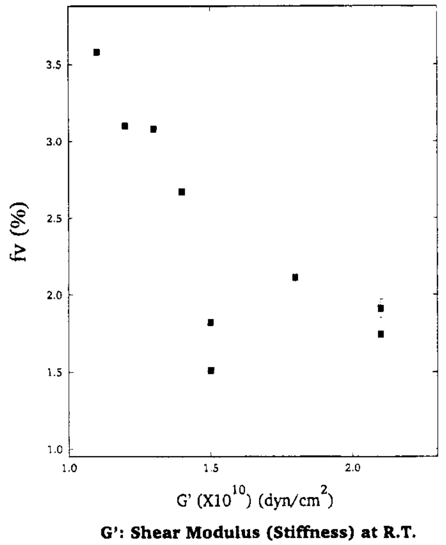

Figure 9. Anticorrelation between fractional free volume and stiffness of thermosets.

various epoxy polymers is plotted against the fracture toughness of these materials. Since the stiffness is a reciprocal property of the fracture toughness, we expect the correlations with f_v to be opposite, as plotted in Figure 9.

In Figures 8 and 9, we observe a clear correlation between fracture toughness and free-volume fraction, f_v, obtained experimentally by PAL, and an anticorrelation between stiffness and f_v in epoxy thermosets. A polymer with a higher fracture toughness has a higher value of free-volume fraction. This is understandable since the mechanical response of a polymer glass depends on the amount of flow occurring during the failure process. The major structural parameter controlling the flow processes in glassy polymers is thus directly related to the free volume.

G_{1C} is a measure of the energy required to extend a crack over a unit area; this is termed the fracture energy or fracture toughness. A basic aim of fracture mechanics is to identify fracture criteria, such as G_{1C}, which are independent of the geometry of the cracked body and, ideally, even of the test conditions, *e.g.*, test temperature. Thus new knowledge of fracture mechanics parameters linking with molecular-scale free volume should greatly assist in developing a more fundamental understanding of the fracture process and should be of considerable use in practical areas of material selection and development, engineering design, and life prediction.

IV. Conclusion

In this study, we present a systematic analysis of free-volume hole properties using PAL in varying chain extension chemistry of thermosetting plastics. We have observed correlations between macroscopic mechanical properties and the atomic-scale free volumes in epoxy thermosets, not only qualitatively but also quantitatively. More systematic and parallel studies with PAL and mechanical measurements will be very fruitful for future applications of PAS to the polymer industry. We conclude that the PAL technique may be used to provide information and clues for the improvement of material properties in polymers and for future industrial applications.

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