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13. ABSTRACT (Maximum 200 words) Positron annihilation spectroscopy has been used to measure free-volume characteristics of selected epoxies. Fluorene resins, a new family of high-temperature thermosetting resins, were selected as the test medium. Experimental results indicate that the free-volume cell size V_f varies with the molecular weight between the cross-links M_c according to an equation of the form $V_f = AM_c^B$, where A and B are structural constants. In two of the samples, the concentration of bulky fluorene groups was increased in the network backbone by replacement of some of the conventional bisphenol A epoxy resin with fluorene-derived epoxy resin. This resulted in an increase in their glass transition temperature for a given level of cross-linking. It has been found that in these samples, the Doppler broadening of the annihilation peak decreases with the increasing fluorene content, presumably due to enhanced damping of the chain motions.				
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Abstract

Positron annihilation spectroscopy has been used to measure free-volume characteristics of selected epoxies. Fluorene resins, a new family of high-temperature thermosetting resins, were selected as the test medium. Experimental results indicate that the free-volume cell size V_f varies with the molecular weight between the cross-links M_c according to an equation of the form $V_f = AM_c^B$, where A and B are structural constants. In two of the samples, the concentration of bulky fluorene groups was increased in the network backbone by replacement of some of the conventional bisphenol A epoxy resin with fluorene-derived epoxy resin. This resulted in an increase in their glass transition temperature for a given level of cross-linking. It has been found that, in these samples, the Doppler broadening of the annihilation peak decreases with the increasing fluorene content, presumably due to enhanced damping of the chain motions.

Introduction

We recently developed (refs. 1 and 2) a free-volume model for molecular weights of linear polymers. According to the model, the free-volume cell size V_f in the polymers increases with increasing molecular weight M according to an equation of the form

$$V_f = AM^B \quad (1)$$

where A and B are structural constants. For a given type of polymer, A and B are constant for the entire class. The model has been tested on a variety of linear, amorphous polymers. We decided to extend the model to cross-linked amorphous epoxies because they constitute a major part of polymers currently used in industry. Fluorene epoxy resin, a high-performance thermosetting epoxy developed by the 3M Company, was selected as the test medium. The test results are described in the following sections.

Experimental Procedures

Sample Preparation

In a set of seven epoxy compositions, the molecular weights between cross-links were systematically varied by a combination of fluorene chain-extending and cross-linking curatives (refs. 3 and 4). The molecular weight of the network linear segment M_c in the test samples varied from 350 to 6900 amu. As expected, the glass transition temperature T_g decreased steadily as we increased the segmental molecular weight. In a second set of samples, M_c was held fixed and T_g was increased by increasing the concentration of bulky fluorene segments in the network

backbone by replacing a portion of bisphenol A epoxy resin in the initial set with a fluorene containing diglycidyl ether epoxy resin. The fluorene segment was incorporated at 35 and 65 percent by weight; those levels caused an increase of 10 and 25°C, respectively, in T_g values. The physical properties of the samples are summarized in table I.

All samples were cured at or above T_g for 16 hr to ensure complete cure and were cooled by simply turning off the oven. The samples were characterized for T_g by differential scanning calorimetry and by dynamic mechanical analysis for the shear modulus and the T_g values.

Positron Lifetime Measurements

Test samples were molded in the form of 1- by 1- by 1/8-in. disks for positron lifetime measurements. A 50- μ C Na²² source was sandwiched between the test samples and the target assembly was interposed between two scintillation counters in a conventional lifetime geometry. Positron lifetimes were measured at room temperature and atmospheric pressure with a standard fast-fast coincidence counting technique. The coincidence system time resolution was about 225 psec. The spectra were analyzed with the POSITRONFIT-EXTENDED (ref. 5) and PAPLS (ref. 6) computer programs. In all cases, it was found that the three-component analysis gave the best fit to the spectra. Figure 1 shows a typical lifetime spectrum in a selected epoxy sample.

Experimental Results

Measurement of Saturation Moisture Content

Fluorene resins are reported to have very low equilibrium moisture absorption due to the presence of hydrophobic fluorene groups and the reduction of hydroxyl group density from lower cross-linking (refs. 3, 4, and 7). Free volume and moisture uptake in a sample are strongly related. It was decided to measure saturation moisture values in the test samples before lifetime measurements were made in them. First, samples were desiccated by heating them to 100°C in a vacuum oven until their weights stabilized. Then, they were saturated with water at 100°C until their weights stabilized again. By comparing the weights of the desiccated and the saturated samples, their saturation moisture contents were determined. The saturation moisture levels are summarized in table II. The samples were desiccated again for lifetime measurements. It was noted that the samples did not return to their previous desiccated-state weights, which suggests that some water was retained permanently. This water would

presumably bind chemically to the hydroxyl sites created in the epoxy specimens during preparation. The number of such sites would be highest in the most heavily cross-linked samples (i.e., samples with the lowest M_c values (ref. 7)). The third and fourth columns in table II list the maximum values of physical (unbonded) and chemical (chemically bonded) water contents. The physical saturation moisture content should provide a measure of the total free volume—and hence the free-volume fraction—in the test samples.

Figure 2 shows chemical saturation moisture content as a function of sample segmental molecular weight. Clearly, the amount of chemically bonded water is highest in the most heavily cross-linked samples because a hydroxyl group is formed at each cross-linked site.

Measurement of Free Volume

Positron lifetime measurements were made in the desiccated samples. The results are summarized in table III. The free-volume cell sizes V_f associated with the second and third lifetime components of the positron lifetime spectra were then calculated from the following relation between the positron lifetime and the radius of the cell where the positron annihilated (ref. 8):

$$\frac{1}{2\tau} = \left(1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin 2\pi \frac{R}{R_0}\right) \quad (2)$$

where

τ positron lifetime in nanoseconds

R radius of the cell in nanometers

$R_0 = R + \Delta R$

$\Delta R = 0.1656$ nm

The free-volume size V_f is given by $\frac{4}{3}\pi R^3$. By associating the second and the third lifetimes with the positronium atoms trapped in the respective cells, one can calculate the effective cell sizes in the test specimens from the following equation:

$$\bar{V}_f = \frac{V_{f2}I_2 + V_{f3}I_3}{I_2 + I_3} \quad (3)$$

where I_2 and I_3 are the relative intensities of the second and the third lifetime components.

The last column in table III lists these \bar{V}_f values. Extending the free-volume model of Singh and Eftekhari (ref. 1) to the cross-linked epoxies, we obtain

$$\bar{V}_f = AM_c^B \quad (4)$$

where $A = 23.78 \pm 0.50$ and $B = 0.059 \pm 0.006$. Note that the value of B in the fluorene resins is much smaller than the value observed in the poly(arylene ether ketone) samples studied earlier (ref. 2). This may be due to the inability of the molecular chains to adjust freely in the cross-linked epoxies. Figure 3 shows a comparison between the M_c values calculated from equation (4) and the values obtained (refs. 3, 4, and 7) from known ratios of the diprimary and disecundary amines in the stoichiometric epoxy resins. A more direct test of the model is provided by the comparison between \bar{V}_f (experimental) and \bar{V}_f (calculated) values summarized in table IV. Clearly, the agreement is reasonably good.

Discussion

A close examination of the free-volume data summarized in table III and illustrated in figure 4 shows that the free-volume size distribution in all test samples is bimodal. The smaller, dominant group increases from 5.4 to 8.8 \AA^3 , whereas the larger, but weaker group decreases from 151 to 142 \AA^3 as M_c increases from 350 to 6900 amu. Because both groups are associated with positronium atom formation, it is appropriate to determine an effective free-volume cell size for each specimen from equation (3). These \bar{V}_f values are used to calculate the molecular weights and are compared with experimentally measured values. As seen from the comparison illustrated in figure 3 and the data summarized in table IV, it appears that the Singh-Eftekhari model (ref. 1) can be successfully extended to cross-linked epoxies.

The bimodal free volume has never been observed in linear polymers. It may be due to the inability of the free-volume cell sizes to grow unobstructedly because of the cross-links between the neighboring chains in the cross-linked polymers.

Another noteworthy feature of the data in table III is that samples 7 and 8 not only have equal molecular weights but also equal \bar{V}_f values, even though they have greatly different fluorene contents in their molecular chains. Clearly, these fluorene-containing members of the $M_c = 1075$ group would not fit the model with the same structural constants A and B as sample 2 with $M_c = 1075$ but without fluorene in its backbone. If B is held at 0.059 for the three members, the respective A 's are calculated to be

$$A(2) = 23.65 \pm 0.50$$

$$A(7) = 24.78 \pm 0.50$$

$$A(8) = 25.04 \pm 0.50$$

It appears that the structural constant A increases with the increasing fluorene content in the polymer backbone, as expected.

We also measured Doppler broadening (ref. 9) of the annihilation peak for samples 2, 7, and 8. The Doppler system efficiency was ≈ 26 percent and it had an energy resolution of 1.26 keV for bismuth-207 radiation (569.6 keV). These results are summarized in table V and illustrated in figure 5. It is clear that the Doppler width of the annihilation peak decreases as the fluorene content increases in the epoxy backbone. This decrease is expected because the bulky fluorene in the chains is expected to dampen their motion.

Concluding Remarks

The Singh-Eftekhari free-volume model has been extended to cross-linked epoxies with reasonable success. It has been noted that the epoxies exhibit bimodal distributions in free-volume cell size. However, because both groups of cells participate in positronium atom formation, an effective free-volume parameter can be determined to represent the test specimen architecture in molecular weight determinations.

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References

1. Singh, J. J.; and Eftekhari, A.: Free Volume Model for Molecular Weights of Polymers. *Nucl. Instrum. & Methods Phys. Res.*, vol. B63, 1992, pp. 477-483.
2. Singh, Jag J.; Eftekhari, Abe; Hinkley, Jeffrey A.; St. Clair, Terry L.; and Jensen, Brian J.: *Free Volume Variation With Molecular Weight of Polymers*. NASA TM-4326, 1992.
3. Schultz, W. J.; Portelli, G. B.; Jordan, R. C.; and Thompson, W. L.: Fluorene Resins—A New Family of High Temperature Thermosetting Resins. *Polymer Prepr.*, vol. 29, no. 1, June 1988, pp. 136-140.
4. Schultz, William J.: Epoxy Resins, Fluorene Systems. *International Encyclopedia of Composites*, Volume 2, Stuart M. Lee, ed., VCH Publ., Inc., c.1990, pp. 101-105.
5. Kirkegaard, P.: Positronfit Extended: A New Version of a Program for Analyzing Positron Lifetime Spectra. *Comput. Phys. Commun.*, vol. 7, no. 7, July 1974, pp. 401-409.
6. Singh, Jag J.; Mall, Gerald H.; and Sprinkle, Danny R.: *Analysis of Positron Lifetime Spectra in Polymers*. NASA TP-2853, 1988.
7. Jordan, Robert C.; Baker, Julie A.; Schultz, William J.; and Portelli, Gene B.: Moisture Effects in Fluorene Thermoset Resins. *Materials—Processes: The Intercept Point, Volume 20 of International SAMPE Technical Conference*, Soc. for the Advancement of Material and Process Engineering, 1988, pp. 576-589.
8. Nakanishi, H.; Wang, S. J.; and Jean, Y. C.: Microscopic Surface Tension Studied by Positron Annihilation. *International Symposium on Positron Annihilation Studies of Fluids*, Suresh C. Sharma, ed., World Scientific Publ. Co., Inc., 1988, pp. 292-298.
9. Song, Cao Bi; and Yu, Wang Yun: A Method for Estimating the Positron Annihilation Lineshape in Metals. *Positron Annihilation*, Paul G. Coleman, Suresh C. Sharma, and Leonard M. Diana, eds., North-Holland Publ. Co., 1982, pp. 906-908.

Water (22.1 keV/ 25.0 keV) 0.6205+0.0018 0.6228+0.0044 0.6263+0.0037 0.6270+0.0011 0.6226 Acetic
 Acid (22.1 keV/ 25.0 keV) 0.5153+0.0048 0.5115+0.0072 0.5125+0.0084 0.5186+0.0018 0.5106
 a2-Chloroisodurene (87.7 keV) 0.1757+0.0047 0.1786+0.0044 0.1778+0.0049 0.1770 Bromobenzene
 (87.7 keV) 0.5625+0.0018 0.5597+0.0053 0.5513+0.0057 0.5556+0.0090 0.5508 Cetyl Bromide (87.7 keV)
 0.3612+0.0036 0.3602+0.0032 0.3623+0.0048 0.3615

(*)The errors quoted are entirely due to statistical fluctuations in the number of photons registered in the counting system.

Table III

Radiation Source X = 25 cms 50 cms Fe55 (5.9 keV) 0.51 Io 0.26 Io

Table I. Summary of Physical Properties of the Test Samples

Sample	* M_c , amu	T_g , °C	Fluorene epoxy, percent by weight
0	350	223	0
1	725	194	0
2	1075	189	0
3	1700	179	0
4	2500	175	0
5	4500	174	0
6	6900	165	0
7	1075	199	35
8	1075	214	65

*The M_c values have been calculated for the known ratios of the diprimary and the disecundary amines in the stoichiometric epoxy resin based on complete chemical reaction. Swelling experiments were also performed to verify that the M_c relationships were generally correct (ref. 7). All M_c values have an error of ± 10 percent.

Table II. Summary of Saturation Moisture Contents of the Test Specimens

[All values are in percent by weight]

Sample	Initial saturation content*	Subsequent saturation content*	Permanently retained moisture content*
0	1.95	0.87	1.08
1	1.74	.85	.89
2	1.63	.84	.79
3	1.57	.83	.74
4	1.56	.84	.72
5	1.48	.73	.75
6	1.54	.86	.68
7	1.66	.79	.87
8	1.66	.79	.87

*All saturation moisture content values have an error of ± 4 percent.

Table III. Summary of Positron Lifetime Spectra in the Test Polymers

[All \bar{V}_f values have an error of ± 5 percent]

Sample	Positron lifetime values, psec/percent			Free-volume cell size, \AA^3		
	τ_1/I_1	τ_2/I_2	τ_3/I_3	V_{f_2}	V_{f_3}	\bar{V}_f
0	$137 \pm 1/54.1 \pm 0.2$	$714 \pm 6/37.6 \pm 0.2$	$2553 \pm 64/8.4 \pm 0.2$	5.4	151.3	32.0
1	$134 \pm 1/52.2 \pm .2$	$720 \pm 7/38.5 \pm .2$	$2527 \pm 67/9.4 \pm .7$	5.6	148.1	33.5
2	$137 \pm 1/52.9 \pm .2$	$770 \pm 9/35.9 \pm .3$	$2477 \pm 80/9.4 \pm .4$	7.6	142.9	35.7
3	$151 \pm 1/56.9 \pm .2$	$800 \pm 10/33.7 \pm .3$	$2545 \pm 80/9.4 \pm .4$	8.3	141.7	37.4
4	$142 \pm 1/54.9 \pm .2$	$774 \pm 9/35.3 \pm .3$	$2532 \pm 73/9.8 \pm .3$	7.7	149.1	38.4
5	$135 \pm 1/53.8 \pm .2$	$767 \pm 10/34.5 \pm .3$	$2460 \pm 71/10.7 \pm .4$	7.4	141.7	39.1
6	$129 \pm 1/51.8 \pm .2$	$801 \pm 8/36.4 \pm .3$	$2476 \pm 61/10.8 \pm .3$	8.8	142.8	39.5
7	$135 \pm 1/52.1 \pm .2$	$753 \pm 8/37.3 \pm .3$	$2427 \pm 57/11.4 \pm .3$	6.8	137.5	37.4
8	$129 \pm 1/50.7 \pm .2$	$747 \pm 7/37.9 \pm .3$	$2464 \pm 57/11.4 \pm .3$	6.6	141.7	37.8

* \bar{V}_f has been calculated as follows:

$$\bar{V}_f = \frac{V_{f_2} I_2 + V_{f_3} I_3}{I_2 + I_3}$$

where I_2 and I_3 are the intensities of the second and the third lifetime components.

Table IV. Comparison Between the Calculated and the Experimental Values of \bar{V}_f Sizes in the Test Samples

[All units are in \AA^3 ; all values have an error of ± 5 percent]

Sample	\bar{V}_f (experimental)*	\bar{V}_f (calculated)*
0	32.0	33.6 ± 0.2
1	33.5	$35.1 \pm .2$
2	35.7	$35.9 \pm .2$
3	37.4	$36.9 \pm .2$
4	38.4	$37.7 \pm .2$
5	39.1	$39.1 \pm .2$
6	39.5	$40.1 \pm .2$

*The known values of M_c in equation (4) were used to calculate \bar{V}_f .

Table V. Summary of Doppler Widths of Annihilation Peaks in the Test Samples

Sample	Fluorene content, by percent of weight	Doppler width,* keV
2	0	3.41 ± 0.02
7	35	$3.31 \pm .02$
8	65	$3.24 \pm .02$

*The Doppler widths of the annihilation peaks are determined by their full width at half maximum height.

Figure 1. A typical lifetime spectrum in epoxies.

Figure 2. Molecular weights versus chemical saturation moisture content.

Figure 3. Comparison between the experimental and computed molecular weights.

Figure 4. Bimodal distribution of free-volume cells.

Figure 5. Doppler width versus fluorene content.