

Positron annihilation and polymerization of epoxy resins

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The polymerization of bisphenol-A epoxy resin mixed with a curing agent (methyltetrahydrophthalic anhydride) was followed from the liquid to the solid state using the positron annihilation lifetime (PAL) technique at several curing temperatures. With the commencement of polymerization, the intensity, I_3 , of *ortho*-positronium started to increase, followed by a sharp decrease of its lifetime, τ_3 . When the curing temperature was raised further, I_3 increased to a large value, indicating further propagation of the polymer networks. When the polymerization was terminated, τ_3 reached the smallest value and I_3 reached a large saturation value. PAL is a powerful technique for studying microscopic structural changes and state transitions of polymers.

(Keywords: positron annihilation in epoxy resins; polymerization; epoxy resins; phase transition of polymers; cavity in polymer)

INTRODUCTION

Positrons emitted from a radio-isotope positron source have average energies of a few hundred kilo-electronvolts; however, they lose their energy quickly in substances through inelastic collisions, and finally annihilate with electrons, emitting 0.51 MeV gamma rays. In liquids and polymers, a part of the positrons forms positronium (Ps) by picking up an electron from the substance. Positronium has two spin states — *ortho*-positronium (*o*-Ps) and *para*-positronium (*p*-Ps) — which have lifetimes of 140 and 0.123 ns *in vacuo*, respectively. The details of positron annihilation (PA) are described elsewhere^{1,2}.

In liquid, Ps is known to create a cavity, called a 'Ps bubble', around itself. In molecular solids and polymers, Ps is considered to be trapped in large vacancies in a disordered area or in a large free volume hole in the amorphous region. Thus Ps exists inside a cavity, either as a bubble or as a vacancy. It is annihilated through a pick-off process, the rate of which depends on the size of the cavity², being faster in a smaller cavity, i.e. *o*-Ps lifetime becomes shorter in small holes.

While the lifetime of *o*-Ps can be related to the size of the cavity, its intensity is often considered to be related to the number of cavities. In polymers, the intensity appears to increase with increasing fraction of amorphous region in which the Ps cavity is contained³. There is also evidence that Ps formation is affected by chemical properties of the functional groups on the polymer

chains⁴. In liquids, where Ps forms a bubble by itself, Ps formation is affected by characteristics of molecules such as surface tension, viscosity, chemical reactivity, etc.⁵, and the number of cavities cannot be related to the intensity. Interpretation of the *o*-Ps intensity in liquid is thus not simple, but undoubtedly it reflects characteristics related to the microstructure of the substance.

Utilizing these characteristics, positron annihilation lifetime (PAL) measurements have been applied to study the nature of polymers and have been considered to be a useful tool for investigating microstructures of polymers⁶⁻⁸. PAL has also been applied to study the state transition of polymers, and phase changes have been observed in Ps formation intensities and its lifetime at the glass transition temperatures and melting points⁹⁻¹¹.

Polymerization of epoxy resins has been investigated by various methods, such as chemical reactions, temperature variations, electrical or mechanical properties, etc.¹²⁻¹⁴. These techniques give information on a macroscopic level. Using PAL, polymerization can be studied from the viewpoint of microstructures of the order of nanometres.

Polymerization of epoxy resins was studied by Suzuki *et al.*¹⁵: samples were cooled to room temperature for PAL measurements after they were heated or kept at a curing temperature for a few hours. Hence there was an ambiguity in the temperature control of samples and the transition from liquid to solid was not clearly observed. In the present work, the temperature of the samples was controlled precisely and PAL measurements were carried out while the temperature of the epoxy samples was slowly changing or kept at a fixed curing temperature.

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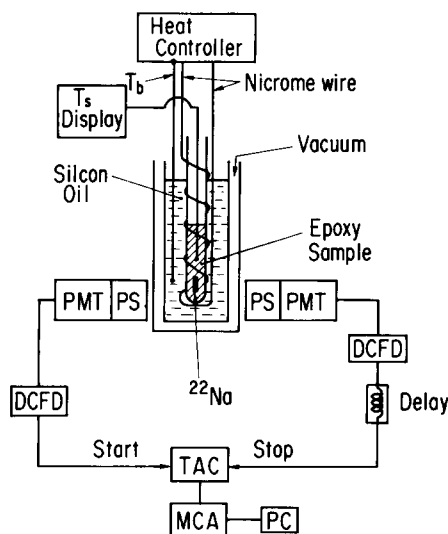


Figure 1 Experimental set-up for positron annihilation: PS, plastic scintillator; PMT, photomultiplier tube; DCFD, differential constant fraction discriminator; TAC, time to amplitude converter; MCA, multi-channel analyser; T_b , bath temperature; T_s , sample temperature

EXPERIMENTAL

The experimental set-up shown in *Figure 1* was the same as that used in ref. 15 except for the temperature control. A conventional fast-fast coincidence PAL system, having plastic scintillation detectors ($45\text{ mm}\phi \times 40\text{ mm}$, Naton 136) mounted on a Hamamatsu H1949 photomultiplier, was employed. The system time resolution was 0.27 ns full-width at half maximum (*FWHM*). A positron source was prepared by depositing and drying about $5.6 \times 10^5\text{ Bq}$ of aqueous $^{22}\text{NaCl}$ on a thin nickel foil of 2.8 mg cm^{-2} and area $5\text{ mm} \times 5\text{ mm}$, which was then covered with the same size of foil. The positron source was immersed in the liquid sample in a test tube of 8 mm i.d.

The curing reaction of epoxy resin is exothermic and the sample temperature differs depending on the curing temperature. Since it takes 1 h to obtain one PAL spectrum, it is necessary for the reaction to proceed slowly. The polymerization reaction takes more than 10 h when the curing is started¹⁵ at 70°C , hence it is desirable to perform the experiment at low temperature. PAL spectra were recorded automatically every hour, with about 0.5×10^6 events being collected in one spectrum.

The temperature was controlled as follows (see *Figure 2*). The sample temperature was raised linearly from 20°C to 70°C over 4 h. The temperature of the first curing was fixed at 70°C for 30 h in order to attain complete polymerization. The temperature was then raised from 70 to 100°C and from 100 to 150°C at a rate of 5°C h^{-1} . The samples were cured at 100 and 150°C for 6 h. After that the samples were cooled from 150 to 20°C at the rate of 5°C h^{-1} . After this hardening process, the solidified sample was measured again while it was heated from 20 to 200°C at a rate of 5°C h^{-1} , then kept for 1 h at 200°C and finally cooled to 20°C at the same rate.

The temperatures of the sample (T_s) and the heat bath (T_b) were monitored and the latter temperature was used for control. Since the speed of temperature change was extremely slow, the difference (ΔT) between T_s and T_b was quite small and $\Delta T/T$ was less than 1%. In the following the temperature referred to is T_b .

A bisphenol-A type epoxy resin ($M_w \approx 380$) was

cured with methyltetrahydrophthalic anhydride (MTPA, $M_w \approx 166$, henceforth referred to as hardener) with dimethylaminomethyl phenol (DMP-30) as a catalyst. These samples were liquid at room temperature. The mixing ratio of resin/hardener/catalyst was about 100/88/1 by weight.

The lifetime spectra were analysed by the program POSITRON FIT¹⁶ with a three-component model.

RESULTS AND DISCUSSION

Lifetimes (τ_3) of the long-lived component during curing reactions

Before the chemical reaction commences, monomers of resin and hardener in the liquid state are mobile. As the samples are kept at the curing temperature, these monomers start to undergo chemical reactions and the number of unreacted monomers decreases, resulting in a gel state consisting of a mixture of solid and liquid. After the gel time has elapsed, the sample enters the solid state from the liquid state. *Figure 2* shows τ_3 through the whole period of measurement and *Figure 3* shows τ_3 and I_3 during the first 45 h. In the liquid state τ_3 is 2.45 ns at 20°C and, after 4 h, increases to 2.58 ns at the beginning of curing at 70°C .

The relation between τ_3 and the volume of cavities in

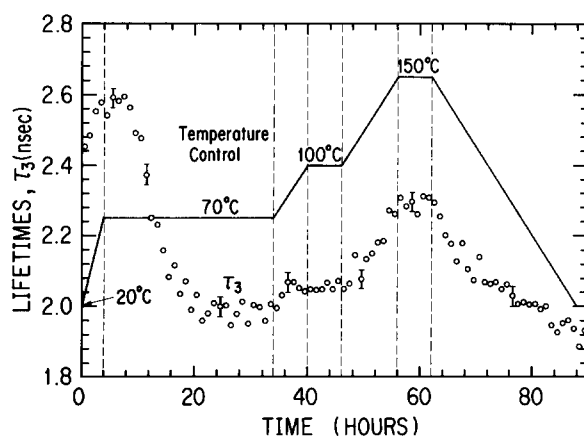


Figure 2 Lifetimes of the long-lived component, τ_3 , versus time for the whole period of measurements. Temperature control is also shown

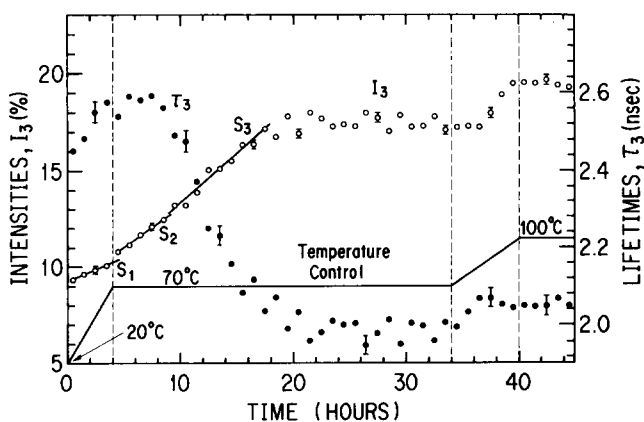


Figure 3 Lifetimes and relative intensities for the first 45 h of measurements shown in *Figures 2* and 4. S_1 , S_2 and S_3 are rates of increase of I_3

which Ps is trapped is given as⁷:

$$\tau_3 = 0.5 \left\{ 1 - R/(R + DR) + 1/(2\pi) \sin[2\pi \times R/(R + DR)] \right\}^{-1} \quad (1)$$

where the cavities are assumed to be spherical with a radius of R and an electron layer of thickness $DR = 0.166 \text{ nm}$ (1.66 \AA). From this equation, the volume is estimated to be 142 \AA^3 at 20°C and 156 \AA^3 at 70°C . The increase in volume can be explained by the increase in temperature of the liquid sample.

τ_3 remains constant for 5 h from the beginning of curing at 70°C and then starts to decrease sharply. It takes another 13 h to reach a constant τ_3 of 1.98 ns (96 \AA^3). For the duration of the decrease in τ_3 , polymer chain growth, branching and cross-linking should be proceeding and three-dimensional networks developing. Thus the sample becomes solid and the size of cavities for Ps is reduced.

Polymerization is accompanied by a change in the specific volume (V_s) of mixed samples of resin and hardener. The relation between V_s and τ_3 can be explained as follows. With increasing temperature, V_s increases because of volume expansion. This increase corresponds to the increase of τ_3 during the first 4 h in a liquid state. With the propagation of polymerization, curing shrinkage occurs, i.e. V_s decreases, and the state of the sample changes from liquid to solid. The sharp change of τ_3 reflects this change of state.

Gel time is generally defined as the time at which the greatest rate of change of the exothermic reaction is attained. However, in this experiment the gel time cannot be obtained from the variation of the temperature of the sample, because the temperature is almost constant during polymerization at 70°C . In PAL measurements the gel time may be defined as the point of the greatest rate of change of τ_3 . After that, τ_3 stays constant, which suggests that the main curing reaction has terminated.

Figure 3 shows that, when the temperature of the sample is raised from 70°C , τ_3 increases simultaneously but stops at 85°C . A small overshoot in τ_3 is observed around 90°C and it becomes constant at the second curing temperature of 100°C .

Above 116°C τ_3 increases gradually and shows a sharp increase at around 135°C . At 150°C , τ_3 is 2.29 ns (126 \AA^3). After 6 h at 150°C , the sample is cooled to 20°C and τ_3 becomes 1.94 ns , which is almost the same as that reached after the first curing at 70°C .

Intensity (I_3) of the long-lived component during curing reactions

The intensity, I_3 , of the long-lived component versus time after heating is also shown in Figures 3 and 4. For the first 21 h I_3 increases; the rate of increase, $\Delta I_3/\Delta(\text{time})$ (S_1 , S_2 and S_3 in Figure 3), changes in connection with τ_3 . From room temperature to 70°C , positron annihilation takes place in a liquid state and the rate of increase is $0.18\% \text{ h}^{-1}$ (S_1). Although the temperature of the sample is fixed at 70°C and τ_3 remains constant for the next 5 h, I_3 increases at a rate of $0.33\% \text{ h}^{-1}$ (S_2). This suggests that polymerization is in progress even while τ_3 or the size of Ps bubbles is constant, and a greater part of the sample is still in the liquid state. When τ_3 starts to decrease, i.e. polymerization is accelerated, the variation of I_3 increases further ($S_3 = 0.50\% \text{ h}^{-1}$). Thus, the rate of increase of I_3 is greatest while three-

dimensional networks are developing. I_3 becomes constant when τ_3 reaches a constant value and the polymerization reaction at 70°C is almost finished, where the sample becomes solid.

In liquid, Ps formation is affected by the chemical characteristics of the molecules in the medium. The three rates of increase given above may be explained by the reaction between resin and hardener. In a separate measurement at room temperature, the intensities I_3 in neat resin and neat hardener are found to be about $18.5 \pm 0.3\%$ ($\tau_3 = 2.33 \pm 0.05 \text{ ns}$) and $7.6 \pm 0.3\%$ ($\tau_3 = 2.53 \pm 0.05 \text{ ns}$), respectively. This implies that Ps formation is suppressed in the hardener. I_3 in the mixed liquid of resin and hardener is 9% (Figure 3), which is probably due to the effect of hardener. S_1 is the rate in the liquid state and can be explained mainly by the increase of temperature. When the sample is cured at 70°C , polymerization takes place and the hardener molecules start to be consumed by the reaction, resulting in a decrease in their number. Hence the suppression of Ps formation by hardener is decreased as polymerization proceeds. Thus, S_2 may be explained mainly by the decrease in the number of hardener molecules. S_3 is due to the combined effect of the polymerization and the decrease in the number of hardener molecules.

When the temperature of the sample is raised further from 70°C , I_3 does not change until the temperature reaches 90°C , whereas, as discussed before, τ_3 starts to increase almost simultaneously and reaches a constant value at 90°C . These findings show that at first the size of cavity increases and there is some delay in the response of I_3 . The increase in I_3 at around 90°C may correspond to an increase in the number of cavities as the result of promoted expansion of three-dimensional networks. Around this temperature, τ_3 or the size of cavities slightly decreases and this suggests the possible rearrangement of the network.

As shown in Figure 4, the variation of I_3 above 100°C is similar to those of τ_3 . Around 135°C , I_3 also shows the same sharp increase as τ_3 and, at 150°C , reaches 28% . After cooling, I_3 decreases to 25% at 20°C and the decrease from the maximum at 150°C is only 3% , which is 16% larger than I_3 of the original liquid. While τ_3 is restored to the value at the start of curing at 70°C , I_3 remains at a high value after cooling to room temperature.

Positron annihilation in solid epoxy samples

Epoxy resin cured as described above was heated again

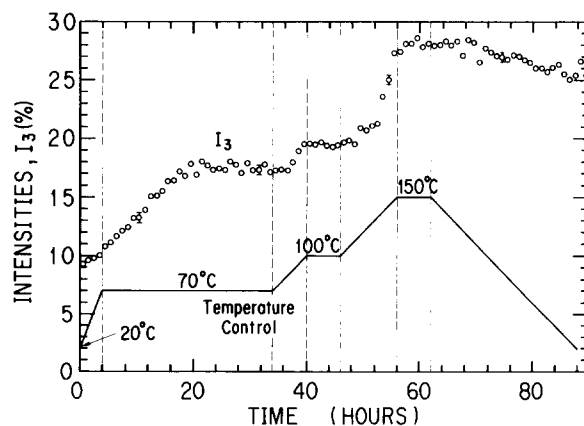


Figure 4 Relative intensities, I_3 , of long-lived component versus time for the whole period of measurements

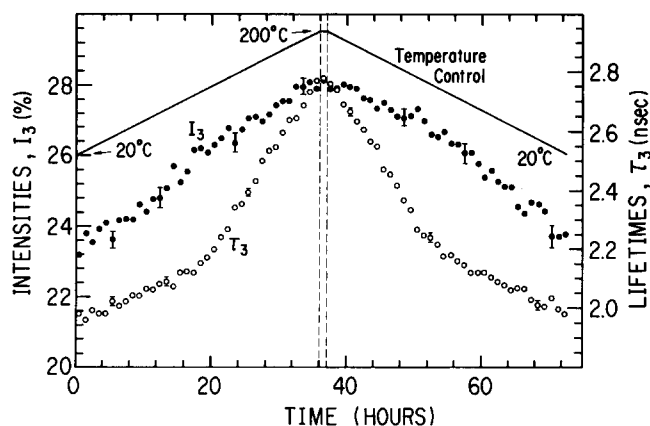


Figure 5 Lifetimes and relative intensities of the long-lived component versus time for the solid sample, which was formed by the process shown in Figures 2 and 4

from 20 to 200°C at 5°C h⁻¹, kept for 1 h at 200°C and then cooled to 20°C at the same rate. The values of τ_3 and I_3 during this process are shown in Figure 5. The glass transition temperature (T_g) is clearly seen around 116°C on the curve of τ_3 . However, I_3 increases or decreases monotonically with temperature without showing any special change at T_g . The value of T_g thus obtained is slightly lower than T'_g (126°C) determined by thermomechanical analysis (t.m.a.). The difference can be explained as follows. The T_g is related to the onset of micro-Brownian motion. Regions around cavities, in which positronium are trapped, are distorted because of defects. Hence, molecules situated in these regions become mobile at temperatures slightly below T'_g . T'_g determined by t.m.a. is connected with macroscopic movement of molecules, which requires more energy than the motion of a few molecules. The *o*-Ps state can be affected by motion on a molecular level and thus T_g can become smaller than T'_g .

Figure 6 shows the variation of volumes calculated from τ_3 shown in Figure 5 using equation (1). It is seen that the rate of increase of volume below $T_g = 116^\circ\text{C}$ is smaller than that above T_g . Linear expansion coefficients are calculated from the rate of increase as $6.8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ at 50°C and $2.3 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ above T_g . These coefficients are one order larger than those determined by t.m.a., which are about $8.6 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ below T_g and $1.8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ above T_g . The large coefficients determined by PAL show the expansion of cavities created among polymer chains, where the polymer structures are distorted and easily mobile with increasing temperature.

Curing at temperatures higher than T_g

As discussed above, when the sample is heated above 100°C, I_3 and τ_3 start to increase around 115°C, which corresponds to T_g , and then I_3 shows a sharp increase around 135°C. The sharp increase of I_3 above T_g may be related to the formation of further three-dimensional networks, since molecules in the polymer structure can move easily in a rubbery state. Normally, thermosetting plastics are cured at several different temperatures. Hence, from the results of I_3 and τ_3 , it is deduced that after curing, the size of cavities is restored to the size determined at the precuring temperature, and the number of cavities increases if resins are cured at temperatures higher than T_g , which reflects the formation of complicated three-dimensional networks by further reactions.

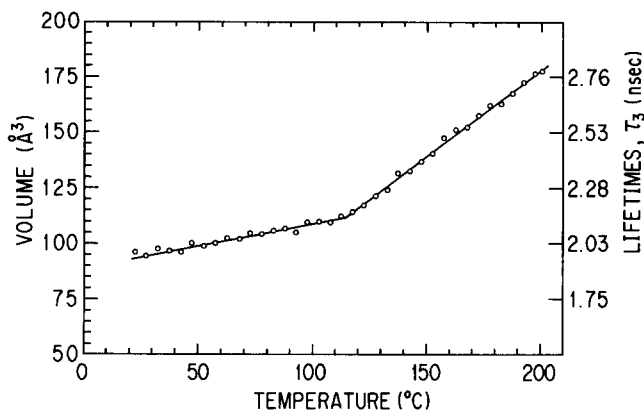


Figure 6 Sizes of cavities versus temperature calculated from lifetimes of the long-lived component during the heating process shown in Figure 5

CONCLUSIONS

A positron annihilation lifetime method has been employed to study polymerization of epoxy resins. During the precuring polymerization, there is a mixed state of liquid and solid. Although, at the first stage, τ_3 is constant, i.e. no change in the size of cavities is observed, I_3 increases, which suggests that polymerization is in progress. The increase of I_3 can be explained by consumption of hardener monomers which has the effect of reducing Ps formation. Then, τ_3 starts to decrease sharply, which is related to the decrease of specific volume. The gel time is defined as the point of the greatest rate of change of τ_3 . When the variation of τ_3 and I_3 becomes constant, the polymerization terminates.

Epoxy resins are normally cured at several different temperatures. From the variation of I_3 , the development of polymer structures can be understood as follows. When they are subsequently heated at a higher temperature than the first curing temperature, three-dimensional networks are developed by additional reactions. A sharp increase in I_3 is observed when curing is conducted at temperatures higher than T_g and this reflects the development of the extended three-dimensional networks.

When the linear expansion coefficient and T_g are determined by the variation of τ_3 , T_g is slightly lower and the linear expansion coefficient is one order larger than the values determined by thermomechanical analysis.

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REFERENCES

- 1 Ito, Y., Kaji, H., Tabata, Y. and Yoshihara, K. 'Chemistry of Elementary Particles', Gakkai Shuppan Center, Tokyo, 1985 (in Japanese)
- 2 Schrader, D. M. and Jean, Y. C. (Eds) 'Positron and Positronium Chemistry', Elsevier, Amsterdam, 1988
- 3 Serna, J., Abbe, J. Ch. and Duplatre, G. *Phys. Stat. Sol. (A)* 1989, **115**, 389
- 4 Okamoto, K., Tanaka, K., Katsube, M., Sueoka, O. and Ito, Y. *Radiat. Phys. Chem.* in press

- 5 Nakanishi, H. and Jean, Y. C. in 'Positron and Positronium Chemistry' (Eds O. M. Schrader and Y. C. Jean), Elsevier, Amsterdam, 1988, p.159
- 6 Jean, Y. C., Sandreczki, T. C. and Ames, D. P. *J. Polym. Sci.* 1986, **B24**, 1247
- 7 Jean, Y. C. *Microchem. J.* 1990, **42**, 72
- 8 Suzuki, T., Ito, Y., Endo, K., Fujita, S., Masuda, Y. and Egusa, T. *Int. J. Appl. Radiat. Isot.* 1988, **39**, 53
- 9 Eldrup, M., Pedersen, N. J. and Sherwood, J. N. *Phys. Rev. Lett.* 1979, **43**, 1407
- 10 Kindl, P. and Sorman, H. *Phys. Stat. Sol. (A)* 1981, **66**, 627
- 11 Reiter, G. and Kindl, P. *Phys. Stat. Sol. (A)* 1990, **118**, 161
- 12 Shinpo, M. 'Handbook of Epoxy Resins' (Ed. M. Shinpo), Nikkann Kougyou, Tokyo, 1987, (in Japanese)
- 13 May, C. A. 'Epoxy Resins' (Ed. C. A. May), Marcel Dekker, New York, 1988
- 14 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2567
- 15 Suzuki, T., Ito, Y., Endo, K. and Fujita, S. *Int. J. Appl. Radiat. Isot.* 1989, **40**, 397
- 16 Kirkegaard, P. and Eldrup, M. *Computer Commun.* 1972, **3**, 240