

# Positron annihilation in a rubber modified epoxy resin

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Positron annihilation data is reported on a rubber-modified epoxy resin. Studies of the temperature dependence of the *o*-positronium lifetime indicated the existence of three distinct regions; the associated transition temperatures by comparison with dilatometric data can be ascribed respectively to be glass transition of the epoxy phase and to that of a mixed acrylonitrile-epoxy-butadiene interfacial region.

In the last decade the Positron Annihilation Technique (PAT) has been shown to be a powerful tool in the investigation of hole-type defects in solids. The work done on ice<sup>1</sup> and molybdenum<sup>2</sup> are two examples which demonstrate this fact. Positron annihilation in polymers has been discussed in refs 3 and 4. The lifetime of the free positron (the anti-particle of the electron) in a non-conducting condensed matter is of the order of 0.5 nsec. However, in many non-conducting solids, a hydrogen-like bound state of a positron and an electron, positronium (Ps), is formed by some of the positrons. A detailed discussion of positronium formation is given by Mogensen<sup>5</sup>. The Ps is formed in two different states: *para*-Ps in which the electron and the positron have opposite spin direction, and *ortho*-Ps where the two spins are parallel. The intrinsic lifetime of *para*-Ps and *ortho*-Ps are 0.125 psec and 140 nsec, respectively. However, *ortho*-Ps in condensed matter decays mainly by the pick-off process, i.e. the positron in Ps annihilates with one of the valence electrons which has a spin direction opposite to that of the positron. The pick-off lifetime is about 0.6–10 nsec.

At its formation or during the diffusion in a pretrapped state Ps will have a strong tendency of becoming localized in less dense regions in a molecular solid. After the trapping it will try to increase the size of the cavities in which it is trapped. This is due to the repulsive exchange forces between the bulk molecules and the electron in Ps. Hence, Ps is a 'seeker' and a 'digger'. In one extreme case, the rigid solid, the cavities which trap Ps are the preexisting holes. They are probably enlarged somewhat due to the presence of Ps. The other extreme case is a liquied, where Ps is digging a hole, the Ps 'bubble' (~5 Å in hydrocarbons) which is very large due to the large zero point energy of Ps. The polymer case seems to be inbetween the two extreme cases. The cavities which trap Ps in polymers are probably strongly correlated to the preexisting holes in amorphous regions, which, however, might be appreciably enlarged, after Ps has been trapped, due to relaxation and addition of other diffusing cavities. The larger the cavity the smaller is the positron-

valence electron overlap on the surface of the cavity, and hence the larger is the *ortho*-Ps pick-off lifetime. It is thus possible to obtain information on the preexisting cavities and the softness of the polymers by measuring the *o*-Ps lifetime. The work reported in this communication is a study of positron annihilation in a rubber modified epoxy resin.

## EXPERIMENTAL

### Preparation of polymer sample

The carboxy-terminated acrylonitrile (15%), chain-extended butadiene polymer (M3000) was heated to about 353K with bisphenol A and to this mobile mixture was added 15 parts per hundred of bis-dispropylamine glycol as a curing agent. The resin was cured at 343K for 24h and subsequently annealed at 393K for approximately 3 days. This second annealing process was found from previous studies on these materials to be necessary<sup>6</sup> to aid phase separation and remove internal strain.

### Positron lifetime measurements

The positron source was 40 Ci<sup>22</sup>Na in the form of NaCl sandwiched between two Kapton (Du Pont trade mark) polyimide foils of 1 mg cm<sup>-2</sup>. The positron lifetime was measured as usual by determining the time interval between the detection of the 1.28 MeV photon, emitted simultaneously with the emission of the positron, and the detection of one of the two 0.511 MeV annihilation photons. The positron lifetimes were recorded by a spectrometer using the fast-fast coincidence method<sup>7</sup>. The time resolution of the system was characterized by its full width at half maximum being 400 psec. For each lifetime spectrum at least 5 × 10<sup>5</sup> counts were collected at a count rate of 30 sec<sup>-1</sup>. The positron lifetime spectra were analysed using the POSITRONFIT EXTENDED<sup>8</sup> computer program. A correction for positrons which annihilated in the source and in the Kapton foils (~8.5%) was made. The temperature was controlled with a precision better than ±0.5K.

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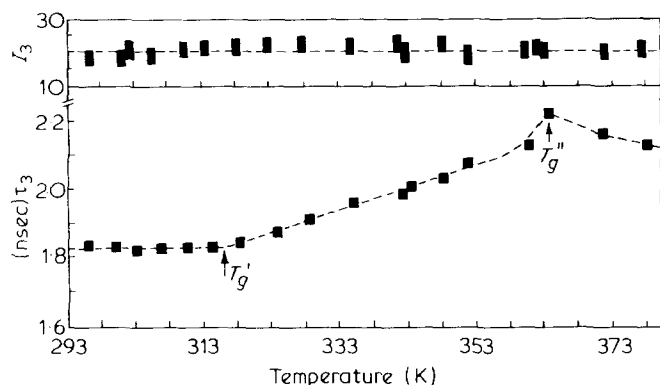


Figure 1 Epoxy  $I_3$  and  $\tau_3$  vs. temperature

### Dilatometric measurements

The volume of the polymer was measured as a function of the temperature using a standard mercury-filled U-shaped dilatometer. The temperature was measured with a precision better than  $\pm 0.1$  K and the height of the mercury column to better than  $\pm 0.1$  mm. A mass of approximately 1.8 g of the polymer was used in this study and corresponded to the same sample upon which the positron lifetime measurements had been performed.

### RESULTS AND DISCUSSION

A positron lifetime experiment was performed on the rubber modified epoxy resin in the temperature range 297 to 178K. All the experimental positron lifetime spectra were analysed in terms of three exponential decaying lifetime components. The two short lifetime components  $\tau_1 \approx 0.35$  nsec and  $\tau_2 \approx 0.7$  nsec with corresponding intensities  $I_1 \approx 70\%$  and  $I_2 \approx 10\%$  were roughly constant in the measured temperature range. The  $I_1$  component is considered to be caused by the decay of *para*-Ps and free positrons. The  $\tau_2$  component equal to  $\approx 0.7$  nsec is larger than the spin average lifetime of free positrons. For this reason it seems necessary to associate the  $\tau_2$  component with the decay of *ortho*-Ps. It is probably caused by pick-off annihilation of *ortho*-Ps trapped in rather dense and rigid region in the polymer. As the  $\tau_2$  value is somewhat uncertain and its intensity low we shall not discuss it further.

The long lifetime component,  $\tau_3$ , of the order of a few nsec and an intensity,  $I_3 \approx 20\%$ , is associated with the decay of *ortho*-Ps in larger cavities. The intensity,  $I_3$ , was fairly constant over the whole temperature range. The lifetime  $\tau_3$  and the intensity  $I_3$  are shown in Figure 1 as a function of the temperature. The value of  $\tau_3$  is constant ( $= 1.83$  nsec) in the temperature region 297 to 336K. This value of  $\tau_3$  is very close to that observed in polybutadiene ( $\tau_3 = 1.90$  nsec).

It is also of interest to note that the lifetime appears to be independent of temperature below  $T_g$  which is contrary to what one would intuitively expect, since the polymer will be expanding in this region. A possible explanation is that the positronium is formed in rubbery phase occlusions dispersed through the epoxy matrix and, since these chains will be well above their  $T_g$ , the positronium lifetime will have apparent independence of the temperature of observation.

When the temperature is increased above  $43^\circ\text{C}$  the lifetime of *ortho*-Ps starts to increase from  $\tau_3 = 1.83$  nsec up to a maximum equal to  $\tau_3 = 2.233$  nsec at  $T = 363\text{K}$ . The rise in the *ortho*-Ps lifetime means that the overlap between

the Ps wavefunction and the outer electrons of the bulk molecules decreases. This suggests that the average size of the cavities in which the *ortho*-Ps is trapped increases. As discussed in the Introduction, two mechanisms can be responsible for this increase: (1) an increase in the number and size of the preexisting cavities which trap Ps; and (2) a decrease in various intermolecular forces in the bulk allowing the trapped Ps to increase the size of a preexisting cavity. The observed increase of the *ortho*-Ps lifetime is probably due to a mixture of both mechanisms. It is difficult to say which of the mechanisms is the most important.

When the temperature is increased above 363K, the *ortho*-Ps lifetime decreases slightly with temperature. The observation of a peak in the *ortho*-Ps lifetime is also observed in tetrafluoroethylene<sup>9</sup>. In the present experiment a plausible explanation of the behaviour of the *ortho*-Ps lifetime is the following. Below 363K the equilibration of the free volume of the rubbery phase is constrained by the acrylonitrile units; above 363K equilibration of the total volume is possible. The net effect being a small reduction in the mean free volume experienced by the positronium above 363K compared with that existing below 363K. The measurements were not performed above 378K since it is known that thermally-initiated rearrangement of the epoxy group can occur above 420K. The rearrangement leads to the formation of an orange-coloured species. No discoloration of the sample was detected for the sample used in this study.

Dilatometric studies of the polymer, Figure 2, indicates that the glass transitions for the resin occur respectively at 328 and 368K. These values are a little higher than those observed in the position annihilation study. The small difference between the two methods can be explained as follows. The dilatometric measurements determine the average volume of the polymer. However, the longest lifetime  $\tau_3$

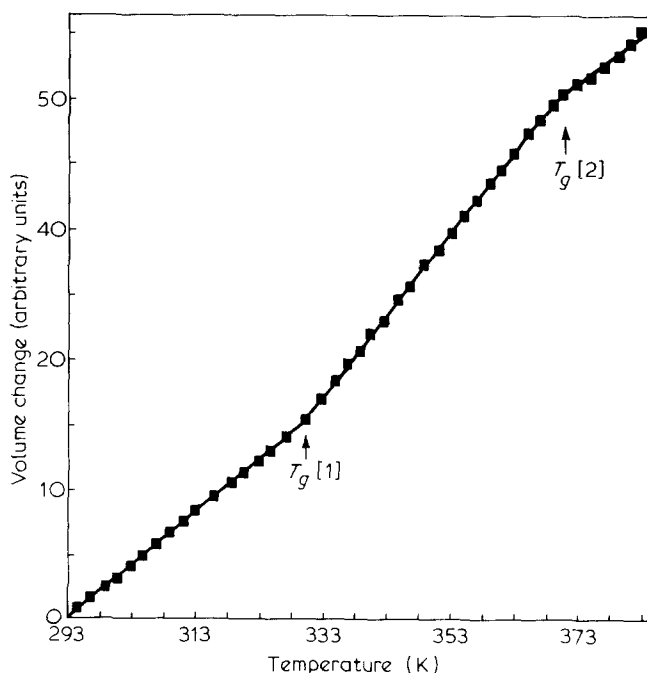


Figure 2 Volume change vs. temperature (K) for rubber-modified epoxy resin

depends on the properties of a selected part of the polymer, namely that part which contains the pre-existing cavities (i.e. probably mainly the less dense, amorphous regions of the polymer) which trap Ps. The 'local' glass transition temperature determined by the  $\tau_3$  measurements can reasonably well be expected to be somewhat lower than that of the average polymer. The fact that  $\tau_3$  is constant below 313K, although the average volume increases with temperature also indicates that  $\tau_3$  and the average free volume need not be directly correlated. Similar effects have been observed in polypropylene and nylon<sup>9-11</sup>.

In conclusion the present work has shown the potential of the positron annihilation technique in the studies of the dynamic properties of a polymer. The obtained glass transition temperatures agreed well with those obtained in dilatometric studies.

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