

Positron Annihilation Lifetime Spectroscopy

Characterization of Polymers: Free Volume Effects

Probed by PALS

Positron annihilation lifetime spectroscopy (PALS) can provide an atomic scale probe of the free volume in polymers. The free volume model applied to PALS data interprets the lifetime of orthoPositronium (oPs) localized in inter- and intra-molecular spaces as a measure of the size of those spaces. Typical oPs lifetimes in polymers range from 1 nanosecond (ns) to 3 ns corresponding to free volume cavity diameters ranging from 0.3 nm to 0.7 nm. These distances compare well with nonbonded interatomic distances in polymers and the root mean square end-to-end distance of an average polymer repeat unit.

PALS gives a measure of the positron lifetime which is related to the electron density at the annihilation site. Changes in chemistry, temperature, pressure or some other variable which affect the electron density at the oPs localization (annihilation) site are reflected in the oPs pickoff lifetime τ_3 . The oPs localizes in regions of reduced electron density such as free volume sites in polymers. Hence the variations in the lifetime, τ_3 , and intensity, I_3 , of the oPs pickoff component are frequently related to free volume behavior. The sensitivity of the PALS probe to the free volume that affects physical, diffusional, and mechanical properties indicates that the PALS technique provides a useful characterization tool.

Numerous properties of importance to the performance of polymers are related to the polymeric free volume. PALS can provide a direct probe of the free volume sites which are used to model phenomena such as the glass transition, blend miscibility, plasticization, stress relaxation, physical aging, yield behavior, permeability, and diluent diffusion. In addition to examination of the above phenomena, PALS has been used by researchers to investigate the following effects: degree of cure, degree of crystallinity, crystalline constraint of the amorphous phase, crazing, moisture uptake, orientation and drawing, phase separation, sub- T_g transitions, and phase transitions. Examples of detection of the glass transition and physical aging in a polyester are given in this application note.

THE GLASS TRANSITION

Usually the third lifetime component (τ_3 , I_3) is associated with free volume related phenomena in polymers where τ_3 is related to the mean radius of the free volume sites and I_3 is related to the concentration of free volume sites. PALS free volume measurements as a function of temperature can be used to study the glass transition T_g as illustrated by the dependence of the oPs pickoff annihilation parameters, τ_3 and I_3 , on temperature. The glass transition is indicated as a change in slope of τ_3 versus temperature similar to specific volume - temperature behavior as shown in Figure 1a. The I_3 parameter, shown in Figure 1b, also is sensitive to T_g and indicates a change in the relative number of free volume cavities rather than a change in their mean size. The glass transition indicated by PALS is usually evident at a lower temperature than that found by differential scanning calorimetry or dynamic mechanical thermal analysis. It is postulated that the oPs free volume probe detects the changes in electron density due to molecular motion that occur at temperatures lower than the cooperative motion of chains measured by other techniques.

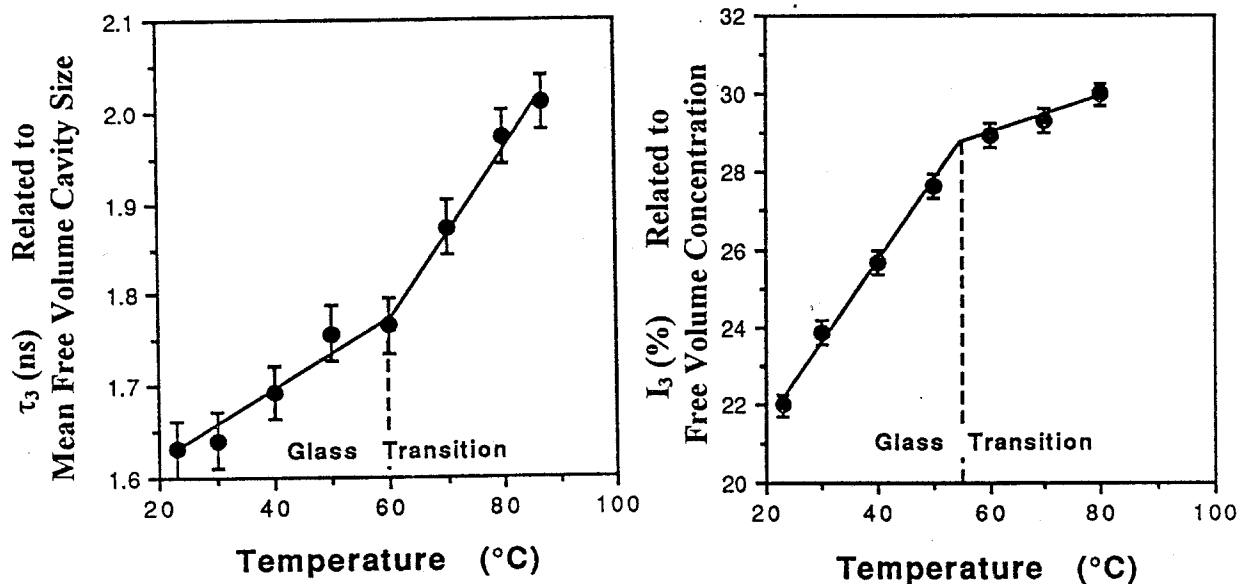


Figure 1 The variation in oPs pickoff lifetime τ_3 (a) and intensity I_3 (b) with temperature in a polyester.

PHYSICAL AGING

As polymers are cooled through T_g , the inability of molecular relaxations to occur on the time scale of cooling creates a nonequilibrium state, the glassy state. In the glassy state, thermodynamic properties change at constant temperature and pressure as a function of time. The gradual approach of polymer properties toward a quasi-equilibrium below T_g is termed physical aging. The extent of physical aging is a function of aging time and temperature and is reflected in physical property changes, such as an increase in density and T_g , and in mechanical property changes, such as an increase in tensile yield strength and a decrease in fracture toughness. PALS measurements of the free volume change due to physical aging on cooling from above T_g to the aging temperature are shown for the polyester in Figures 2a and 2b. The PALS parameters for the unaged material are marked as dotted lines in Figures 2a and 2b. The decrease in relative free volume concentration as indicated by I_3 can occur due to a temperature jump without the occurrence of physical aging (termed a 'contraction experiment'); however, the effect of physical aging is evident in these data from the decrease in I_3 to a value below that characteristic of the unaged material at the same temperature.

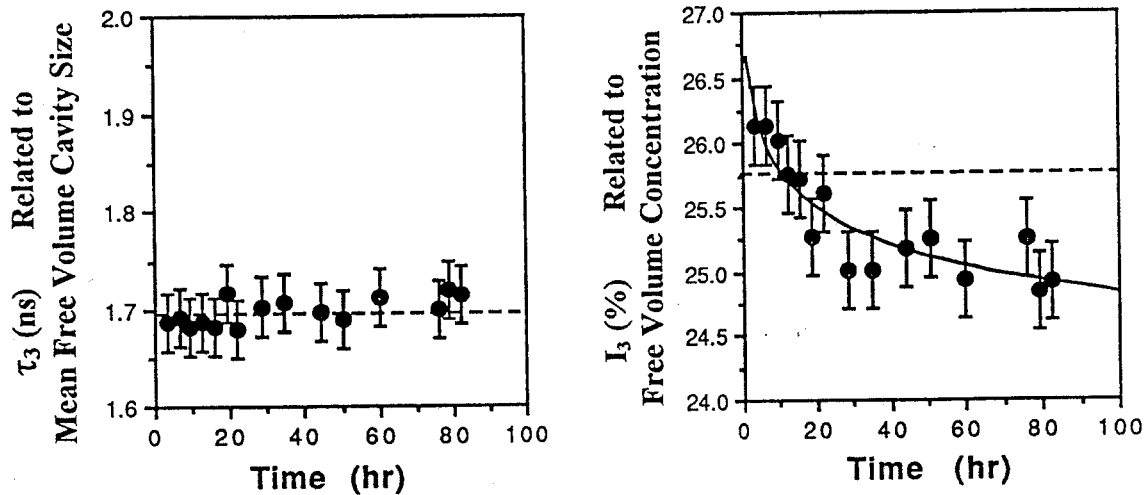


Figure 2 The variation in oPs pickoff lifetime τ_3 (a) and intensity I_3 (b) with aging time for a polyester.

As mentioned previously, PALS has been used to study numerous polymers in order to understand free volume-related phenomena. Whilst PALS is not a conventional technique such as differential scanning calorimetry or dynamic mechanical thermal analysis, it can give unique information about the free volume in polymers which is complementary to conventional characterization and often critical for the development of a molecular understanding of polymer properties.

This application note was adapted with permission from the work of Dr. A. J. Hill.