

Free-Volume, Surface and Interfacial Analysis in Polymers, Thin Films and Nanocomposites Using Positron Annihilation Spectroscopy

Nanoscale properties of polymers and nanocomposites at the surface, interfaces, and the bulk as well as under gas and supercritical fluid treatments have drawn increasing interest in recent years because of their important industrial applications. These include foam forming, membrane separation, synthesis and extraordinary engineering performances as well as biological and environmental issues. Basic understanding of the interaction between nanoparticles or gas molecules and the polymer matrix is fundamentally important for advancing the industrial applications of those systems. Known apparent effects to polymeric performance are the changes of specific volumes, modules and T_g compared with the bulk polymer systems.

While macroscopic effects have been shown to be different from the bulk in thin films and nanocomposite systems, basic understanding on the nanoscale and molecular levels is still limited. Molecular probes, such as AFM, SEM, and TEM, have been employed to provide fruitful information about the structures at the nano- to micrometer scales. However, those methods probe the static properties of polymeric materials, while the polymeric properties depend on the dynamic motion at the molecular levels. Our approach is aiming at the atomic and molecular level free volume properties, which have been known to be important since they provide the molecular dimension at the very origin of the chain motion. Three positron spectroscopies are used in this project: positron annihilation lifetime (PAL) spectroscopy, Doppler broadening energy spectroscopy (DBES), and a variable mono-energetic slow positron beam. The obtained scientific information is: free-volume size and distribution, T_g , depth profiles and structures of nanoscale materials from the surface, interfaces and the bulk, and the depth- and thickness-dependence of T_g . We have performed positron experiments in three polymeric systems: (1) variations of glass transitions in nanocomposites of nanocarbon fibers, silicon oxides, and clays in polystyrene (PS), (2) variations of glass transitions of CO_2 exposed PS, and (3) free volume depth profiles in nanoscale films of PS and CO_2 exposed PS on substrate.

Variations of Glass Transitions in Nanocomposites

We measured positron annihilation lifetime in three series of nanocomposites in polystyrene (PS): PS/carbon nanofibers, PS/silicon oxides, and PS/clays as a function of temperature for different compositions of nanoparticles. The existing data from DSC show that in strong bonding nanocomposites, T_g increases, while in weak bonding composites, T_g decreases due to different surface and interfacial and molecular interactions at the nanoscale. Our results of PS/carbon nanofibers (CNF), which are known to be strong bonding, show a consistent

result of T_g increase. However, in PS/ SiO_2 systems, we also observed a slight increase of T_g . The difference is still under investigation. Fig. 1 shows the results of T_g in one of these series of experiments.

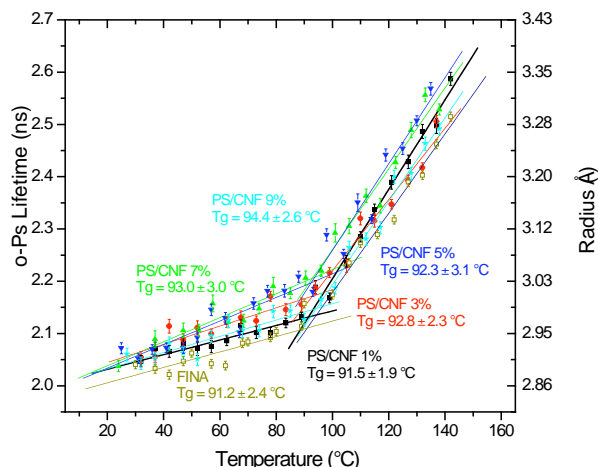


Figure 1. Ortho-Ps lifetimes (free volume radius) vs temperature in different % of carbon nanofiber (CNF) composites in PS. Lines were fitted data below and above T_g . The significant increase of T_g with the CNF indicates a strong effect due to interface bonding between nanoparticles and polymers.

Effect of CO_2 Exposure on Free Volumes in Polystyrene

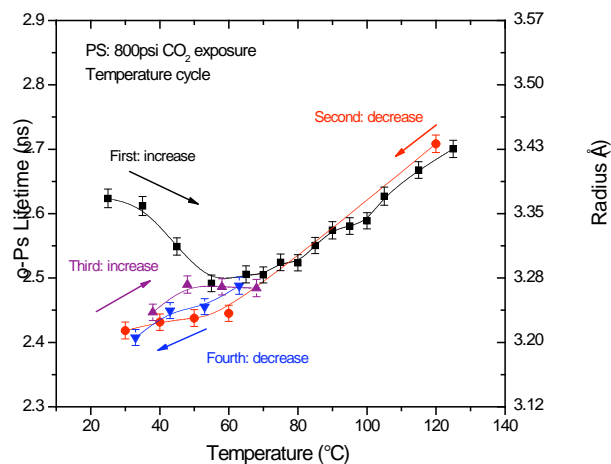


Figure 2. Ortho-Ps lifetimes (free volume radius) vs temperature in 800 psi CO_2 exposed PS. Lines were smoothed lines drawing through the data points for eye-guide purpose. Four runs from low to high and cycle again are as indicated.[1]

We have measured free-volume properties, size and distribution, in amorphous polystyrene exposed to CO_2 as a function of pressure to 800 psi, of time, and of

temperature using positron annihilation lifetime spectroscopy. The free volume increases significantly (Fig. 2) as a function of temperature and its distribution broadens as a function of pressure [Fig.3]. The T_g decreases significantly as a function of CO_2 pressure from the free volume data and is compared with the DSC results (Table 1). The observed free-volume variations as a function of pressure, time, and temperature are interpreted due to hole expansion, creation, free-volume relaxation, plasticization, and hole filling in amorphous polymers, which are important for supercritical fluids.

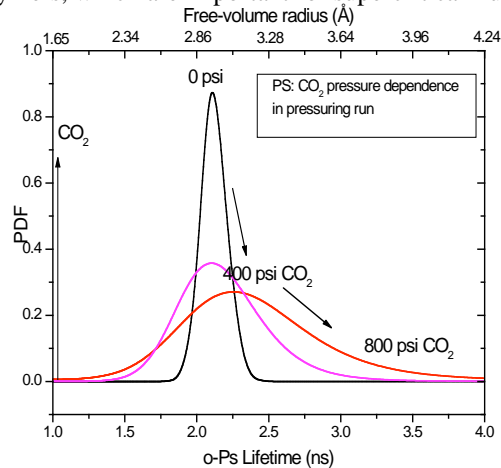


Figure 3. Ortho-Ps lifetime (free-volume radius) density function (PDF) of polystyrene at different CO_2 pressures during pressuring. CO_2 kinetic radius is indicated as an arrow.[1]

PS samples and data	T_g (°C) no CO_2	T_g (°C) 400 psi CO_2	T_g (°C) 800 psi CO_2
o-Ps lifetime first run: heating	90.9±2.5	$T' = 53.1 \pm 1.5$ and $T'' = 82.2 \pm 2.5$ T_g (mid-point) = 67.6 ± 2.0	$T' = 34.8.1 \pm 1.0$ and $T'' = 59.1 \pm 1.7$ T_g (mid-point) = 47.0 ± 1.4
DSC first run only	101.2	73.07	~ 40
o-Ps lifetime second run: cooling	93.0 ± 2.1	87.0 ± 2.0	50.9 ± 1.7
DSC second run	101.2	80.55	---
o-Ps lifetime third run: cooling	91.5 ± 2.8	84.2 ± 2.3	66.3 ± 1.7
DSC third run	101.2	80.49	---
o-Ps lifetime fourth run: heating	----	----	71.0 ± 1.7
o-Ps lifetime all runs except first run data below T_g	91.2 ± 2.4	87.9 ± 3.5	62.9 ± 2.3
DSC all runs	101.2	80.53	---

Table 1 Glass Transition Temperatures in CO_2 exposed polystyrene obtained by positron methods and DSC in various thermal cycles [1].

Free Volume Depth Profile of Nano-scale Films Polystyrene on Substrates

We have performed the free volume depth profile of

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polystyrene thin films on silicon substrates using the DBES of the positron annihilation technique. The thin film thickness at the nanoscale was resolved to a precision of about 1 nm, and the interface thickness was found to be on the order of a few nm to 10 nm for 150 nm PS on Si substrates. In the gold substrate, the interfacial thickness is less than PS/Si interfaces. The obtained densities in interfaces are found to be significantly less than the bulk of PS. Figure 4 shows the variation of free-volume S parameter vs the depth in CO_2 -treated Ps coated on Si substrate at different temperatures and mechanical loading. The resolved layer structures are schematically shown in Figure 5.

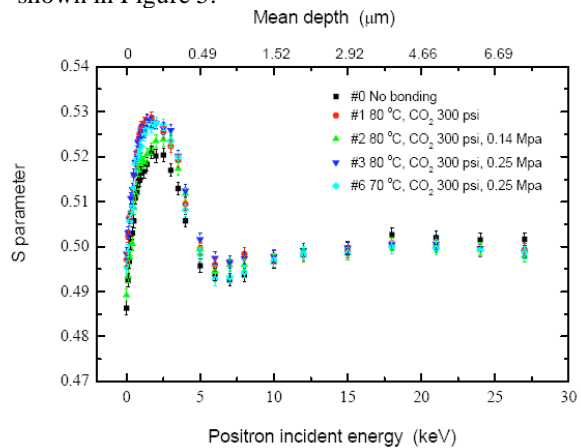


Figure 4. Free-volume S parameter vs positron incident energy (depth) in CO_2 treated PS on Si substrates at different temperature and mechanical loading .

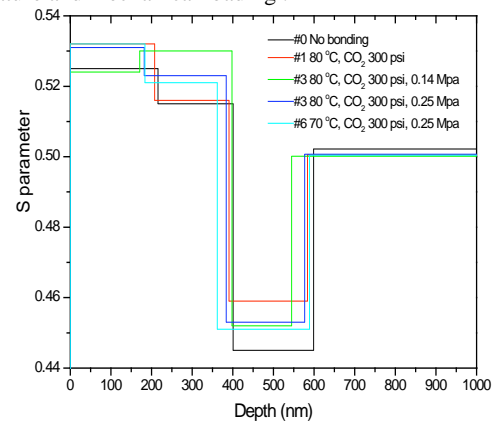


Figure 5. Schematic nanoscale depth structures resolved by the free-volume S parameter data vs positron incident energy (depth) in CO_2 treated PS on Si substrates at different temperature and mechanical loading.

Publications

1. "Effect of CO_2 exposure on free volumes polystyrene studies by positron annihilation spectroscopy," Hongmin Chen, Mei-Ling Cheng, Y.C. Jean, L. James Lee, Jintao Yang , J. Polym. Sci. B: Polym. Phys. **46**, 388-405 (2008).
2. "Positron annihilation lifetime and glass transition temperatures in CO_2 sorption polystyrene" Y.C. Jean, Hongmin Chen, L. James Lee, Jintao Yang. Acta Physica Polonica (submitted).

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