

Free Volume in Layered Organosilicate-Polystyrene Nanocomposites

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Abstract: Experimental studies by Positron Annihilation Lifetime Spectroscopy of free volume in a layered Organosilicate-Polystyrene nanocomposite are reported. Specifically, the intensity (I_3) and lifetime (τ_3) of orthopositronium annihilation were determined for an organically-modified mica-type silicate (OMTS), an atactic polystyrene specimen (M_w), and an OMTS/Polystyrene nanocomposite. The neat OMTS material is produced by a cation exchange reaction between the mica-like silicate and an alkylammonium salt, and has a structure which consists of weakly-cohesive silicate layers connected by galleries with an average spacing of 2.253 nm. The presence of the complexed alkylammonium cations in the galleries between the silicate layers renders the material hydrophobic. On forming the nanocomposite, the interlayer spacing increases to 3.031 nm. PAL analysis of the nanocomposite will be presented and the o-Ps annihilation characteristics, as well as the mean lifetime behaviors, are discussed. Moreover, a comparison of the nanocomposite behavior with the that of the Organosilicate and the bulk polymer is done, in order to unveil the behavior of the confined polystyrene

Introduction: Recently, considerable attention to polymer-layered silicate nanocomposite has been inspired, in part, by the realization that confined polymers often exhibit physical and chemical properties that are dramatically different from their bulk counterpart[1].

A better understanding of the behavior of the confined polymer is needed. This paper describes our initial positron annihilation lifetime measurements in the bulk polymer and the nanocomposite with that of the Organosilicate.

Experimental: The intercalated nanocomposite was synthesized by direct intercalation of atactic polystyrene melts in layered silicate. This involves mixing the 75 wt% organically modified mica-type silicate (OMTS) with a 25 wt% polystyrene ($M_w=152K$) powder, pressing the mixture into a pellet under a load of 7.5 tons, and heating in the vacuum at 170°C for 48 hours. This temperature is well above the bulk glass transition temperature of Polystyrene ($\approx 90^\circ\text{C}$), ensuring the presence of a polymer melt.

The temperature dependence of positron lifetimes in pure Polystyrene, OMTS and intercalated nanocomposite OMTS/Polystyrene were determined from -60°C to 140°C . All materials were subjected to the same thermal history used to form the nanocomposite. The samples OMTS and OMTS/Polystyrene were annealed at 90°C for 1 to 2 hours in the sample holder before the measurement to adsorb organic solvents that exist in the atmosphere. All the spectra were resolved into three components with the longest lifetime attributed to o-Ps annihilation. A search for a free o-Ps component was made by increasing the energy window of the lifetime spectrometer to collect

data on silicate at 20°C, 100°C and 200°C. In the system studied here, no evidence of free Ps atoms are found.

Results and Discussion: The temperature dependence of the o-Ps lifetimes measured in the pure materials (Polystyrene and OMTS) and in the nanocomposite OMTS/Polystyrene are present in Fig. 1. For the bulk Polystyrene,

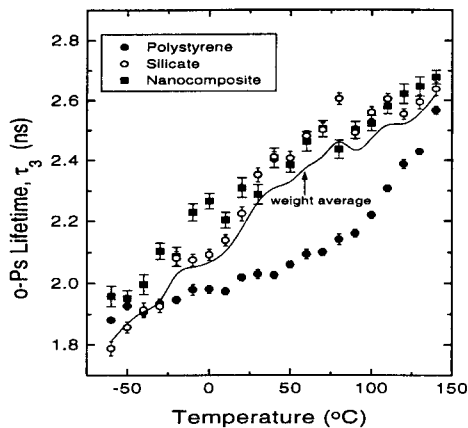


Fig. 1: o-Ps Lifetime (ns) vs. Temperature (°C)

the o-Ps lifetime increases with increasing temperature throughout the entire temperature range studied, with a distinct increase in temperature coefficient at $T_g=87^\circ\text{C}$, corresponding to the glass transition. At low temperature I_3 (assumed to be proportional to the number density of free volume holes) shows a significant variation. Fig. 2 shows that this I_3 variation can be erased after rejuvenating the sample at $T_g+10^\circ\text{C}$, suggesting that it should be associated with chain relaxation and e^+ -irradiation damage. Interestingly, the hole density does not show any significant change at T_g . For the pure OMTS, τ_3 shows a continuous increase with increasing temperature and tends to saturate at 90°C , while I_3 does not vary significantly over this temperature range. Surprisingly, within experimental

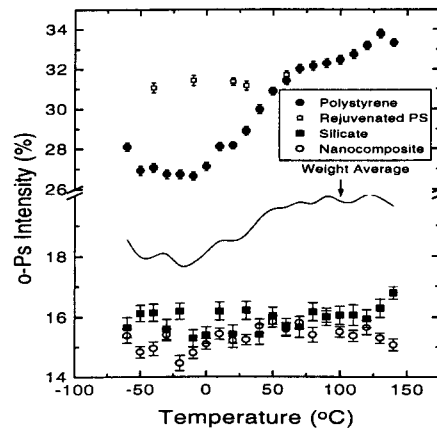


Fig. 2: o-Ps Intensity (%) vs. Temperature (°C)

error, both I_3 and τ_3 for OMTS/PS are very close to the pure OMTS, with I_3 far below the weighted average. Although the weighted average falls just below the lifetimes, a volume average would be even lower, given that the density of Polystyrene is smaller than that of OMTS. These results suggest that no positronium is formed in the confined Polystyrene. A possible explanation is that all the Polystyrene chains are confined to the galleries between the silicate layers with no three-dimensional free volume holes in which o-Ps can reside. X-ray diffraction patterns of OMTS and OMTS/Polystyrene indicate that, on intercalation, the average interlayer distance of silicates are enlarged as much as 0.69nm. This corresponds to a mono-layer of nearly collapsed chains. Since the increase in gallery height is significantly less than the root-mean-square end-to-end distance for a freely-jointed random coil, the confined chain configuration is much more planar compared to the bulk random coil[2]. That is, the intercalated Polystyrene chain adopt a collapsed, two-dimensional conformation. This result is consistent with the PAL measurement. Further evidence for interaction is obtained

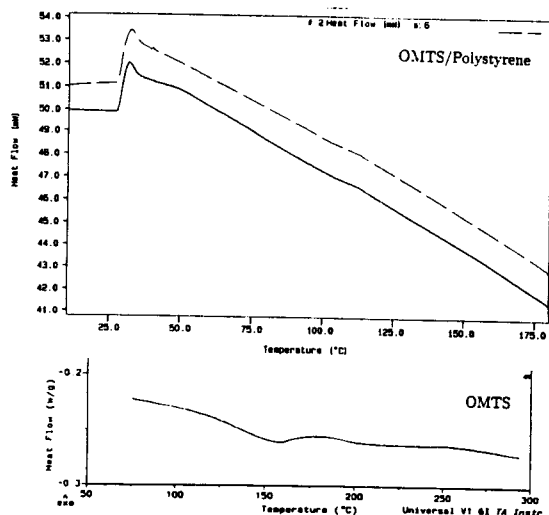


Fig. 3: Differential scanning calorimetry of OMTS and OMTS/Polystyrene

by differential scanning calorimetry (DSC) studies, Fig. 3. Over the temperature range investigated, the silicate exhibits no thermal transitions. Thus, assuming the thermal responses are additive, events observed in the DSC for the OMTS/Polystyrene intercalates are entirely related to the thermal behavior of the polymer. The DSC studies indicate also that the behavior of the intercalated PS is qualitatively different from that characteristic of the bulk polymer. The confined polymer does not exhibit the characteristic 90°C glass transition of the pure bulk polystyrene over the temperature range 50 to 150°C.

References

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