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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 is reported. Specifically, the intensity (I_3) and lifetime (τ_3) of orthopositronium annihilation were determined for an organically-modified fluorohectorite(C18FH), an atactic polystyrene specimen (M_W), and a C18FH/Polystyrene nanocomposite. The neat C18FH material is produced by a cation exchange reaction between the mica-like silicate and an alkylammonium salt with a length of 16 carbon atoms (C18), 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.

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 initial positron annihilation lifetime measurements in the bulk polymer, the organically-modified silicate, and the nanocomposite.

Experimental: The intercalated nanocomposite was synthesized by direct intercalation of atactic polystyrene melts in layered silicate. This involves mixing the 75 wt% organically modified fluorohectorite (C18FH) 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°C), ensuring the presence of a polymer melt.

The temperature dependence of positron lifetimes in pure Polystyrene, C18FH and C18FH/Polystyrene nanocomposite were determined from -60°C to 140°C. All materials were subjected to the same thermal history used to form the nanocomposite. The nanocomposite and C18FH 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 pickoff annihilation. A search for a free o-Ps component in the silicate at 20°C, 100°C and 200°C was made by increasing the energy window of the lifetime spectrometer. 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 C18FH) and in the

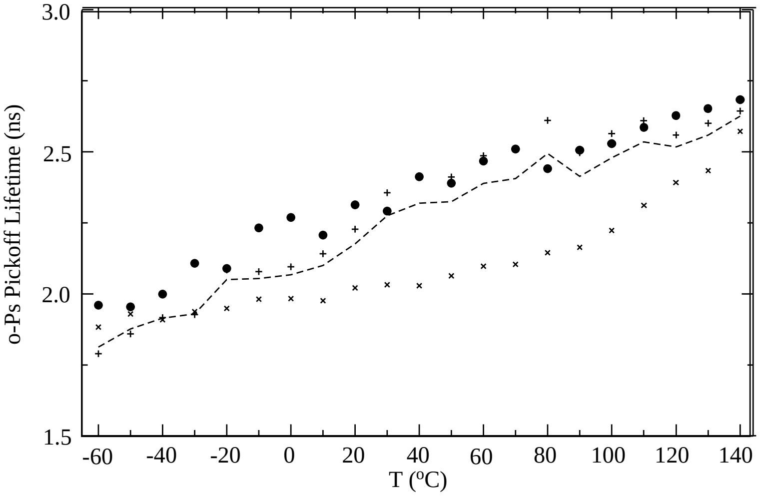

Fig. 1: o-Ps Pickoff Lifetimes for C18FH (+), Polystyrene (×), and 25%/75% Polystyrene/C18FH nanocomposite (●). The dashed line represents the Intensity-Weight average.

nanocomposite C18FH/PS are presented in Fig. 1. For the bulk Polystyrene, 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°C, corresponding to the glass transition. For the pure C18FH, τ_3 shows a continuous increase with increasing temperature and tends to level off at 90°C. Interestingly, the leveling off coincides with a dramatic increase in the gallery height, associated with a transition of the surfactant from a liquid crystal to liquid [3]. Within experimental error, no change in temperature coefficient of τ_3 is observed for the nanocomposite.

In polymer blends, an Intensity-Weight average is used to determine the o-Ps pickoff lifetimes for the composite system. This is based on the idea of addition of free-volume, f, since $f \propto I_3\tau_3$. Assuming this idea is accurate for

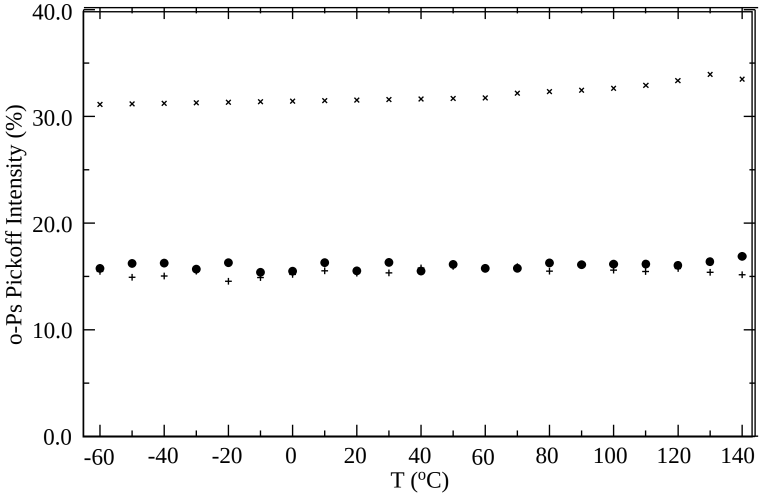

Fig. 2: o-Ps Pickoff Intensities for C18FH (+), Polystyrene (×), and 25%/75% Polystyrene/C18FH nanocomposite (●).

the nanocomposite:

$$I_{3,3}\tau_{3,3} = w_1 I_{3,1}\tau_{3,1} + w_2 I_{3,2}\tau_{3,2} \tag{1}$$

where, w_i is the weight percent, $I_{3,i}$ and $\tau_{3,i}$ are the o-Ps pickoff paramaters with i corresponding to Polystyrene (i=1), C18FH (i=2), and C18FH/PS nanocomposite (i=3). It should be noted that PAL measurements of unmodified Li$^+$-Bentonite (a clay similar in structure to fluorohectorite) shows negligible o-Ps pickoff with intensities of only about 1%. Therefore, the o-Ps pickoff lifetime in the nanocomposite is believed to be due solely to the surfactant and intercalated polymer. The o-Ps pickoff Intensities, shown in figure 2 are related to the number of free-volume sites, for which a weight average can be used to determine the composite value:

$$I_{3,3} = w_1 I_{3,1} + w_2 I_{3,2} \tag{2}$$

Therefore,

$$\tau_{3,3} = \frac{w_1 I_{3,1} \tau_{3,1} + w_2 I_{3,2} \tau_{3,2}}{w_1 I_{3,1} + w_2 I_{3,2}} \tag{3}$$

The dashed line in figure 1 is the corresponding Intensity-Weight average given by equation 3. The fit is consistently lower than the experimental values. One possible explanation is that the confined Polystyrene possesses a slightly larger free-volume than in the bulk.

It is significant that the theoretical calculation of o-Ps pickoff lifetime for the nanocomposite shows essentially a linear increase with temperature. This indicates that the glass transition in the nanoconfined polystyrene occurs at the same temperature as the bulk, but is masked by the transition in C18FH which occurs at about the same temperature.

References

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