Supporting Information

Investigation of free volume characteristics of interfacial layer in Poly (methylmethacrylate) PMMA-alumina nanocomposite and its role on thermal behaviour

S. K. Sharma[†], K. Sudarshan[†], M. Sahu[‡] and P. K. Pujari[†,*]
[†]Radiochemistry Division and [‡]Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085
*puajri@barc.gov.in

1. *Determination of crystallite size of alumina using Scherrer formula*

The crystallite size of alumina has been calculated using the following equation (S1), where D (nm) is the volume average crystallite size assuming their shape to be spherical, λ is the X-ray wavelength (nm), β is the FWHM (radian) of the diffraction peak corrected for the intrinsic broadening and θ is the Bragg angle of diffraction.

$$D = 0.9\lambda/\beta\cos\theta \quad \textbf{(S1)}$$

Two prominent peaks (2θ = 46.03 and 67.13 degree) were fitted to Lorentzian distribution for evaluating the broadening (FWHM) of the peaks. The calculated average crystallite size from the two peaks is 4.32±0.26 nm.

2. *PALS results in nanosized alumina*

Table S1: *Positron lifetime and intensity in alumina nanoparticles*

sample	τ_1(ps) / I_1(%)	τ_2(ps) / I_2(%)	τ_3(ns) / I_3(%)
Nanosized alumina	234.9±3.2 / 66.5±2.0	454.8±9.2 / 31.0±2.0	8.44±0.19 / 2.43±0.03

3. *Three component PALSFIT analysis results in PMMA-alumina nanocomposites*

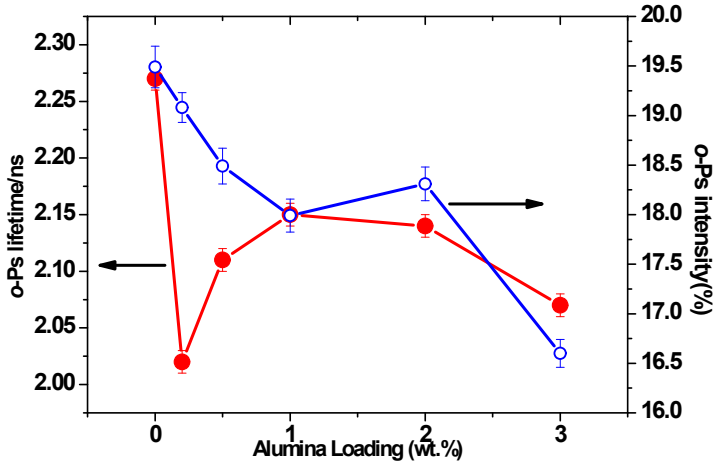


Figure S1. Variation in *o*-Ps lifetime and Intensity as a function of alumina loading as determined from the three discrete component analysis of PALS spectra.

4. *o-Ps lifetime and Intensity calculated from admixture rule:*

The *o*-Ps lifetime and intensity are calculated assuming that loading of alumina will not affect the free volume characteristics of PMMA. In such a case, *o*-Ps lifetime and intensity values in the nanocomposite would follow the admixture rule. According to this rule, *o*-Ps lifetime corresponding to larger nanoholes i.e. τ_4 and intensity, I_4 can be calculated according to following equations:

$$\tau_{4,cal} = \tau_{4,pmma} * \Phi_{pmma} + \tau_{3,alumina} * \Phi_{alumina} \quad \text{(S2)}$$

$$I_{4,cal} = I_{4,pmma} * \Phi_{pmma} + I_{3,alumina} * \Phi_{alumina} \quad \text{(S3)}$$

where Φ correspond to volume fraction of PMMA and alumina as per the subscript. The volume fractions of PMMA and alumina in nanocomposites have been calculated considering the densities of PMMA and alumina as 1.18 and 3.5 g/cc, respectively. Thus calculated *o*-Ps lifetime and intensities are plotted in figure S2. It is observed from the figure that due to low wt.% of alumina and very low amount of Ps formation in nanosized alumina (table S1), the *o*-Ps lifetime and intensity do not vary significantly.

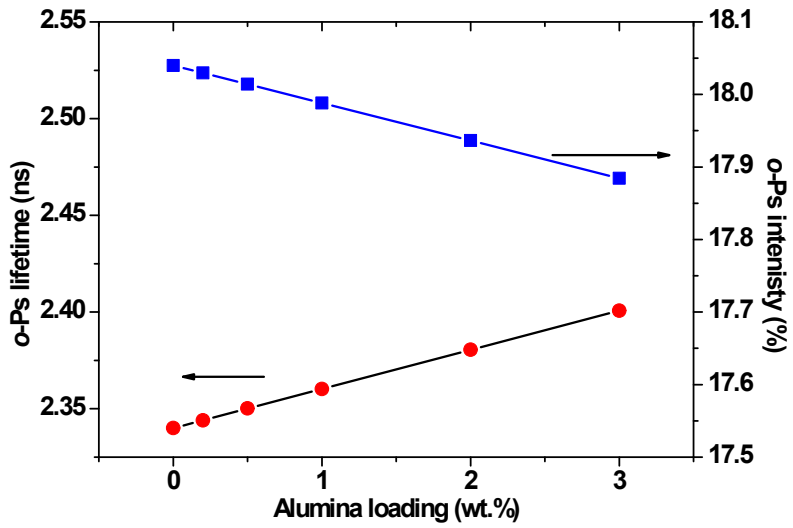


Figure S2: Variation in *o*-Ps lifetime (τ_4/ns) and intensity (I_4) calculated from the admixture rule in PMMA nanocomposite

5. *FTIR of alumina nanoparticles:*

FTIR of alumina nanoparticles has been carried out and shown in figure S2. The hump around ~ 3400 cm^{-1} indicate the presence of –OH functionalities at alumina surface which can undergo hydrogen bonding with PMMA molecules.

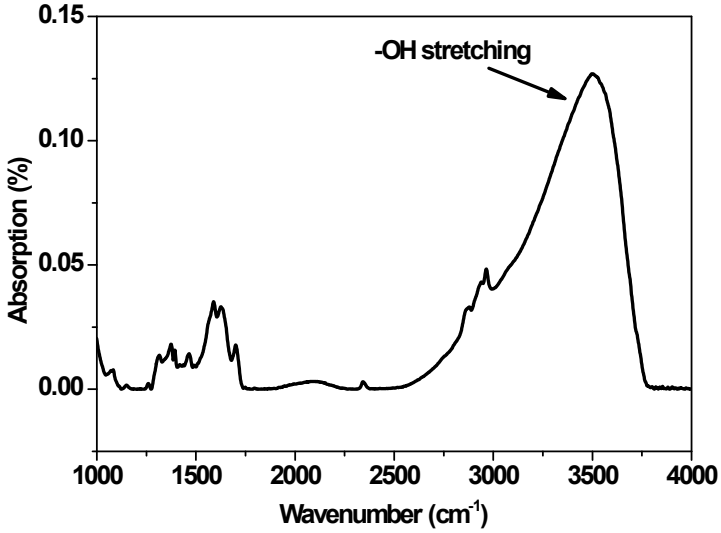


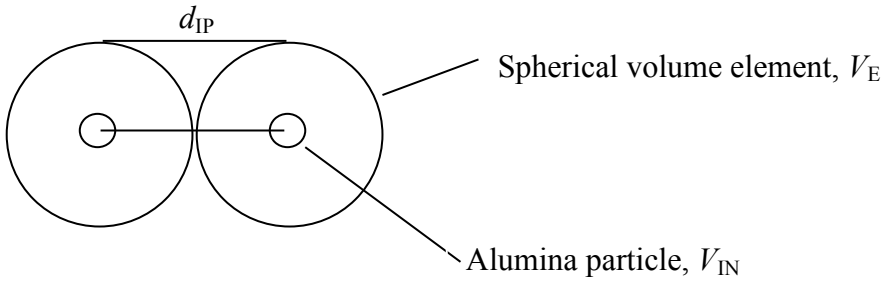
Figure S3: FTIR of alumina nanoparticles

6. Interparticle distance between alumina nanoparticles in PMMA matrix.

Interparticle distance between alumina nanoparticles in PMMA nanoparticles is calculated assuming the fine dispersion of nanoparticles of diameter ~ 5 nm (least value possible as determined from XRD peak broadening). Assuming a closed packed density model (Scheme 1 and scheme S1), where all the alumina particles are situated at equal distance (d_{IP}) and associated with a spherical volume element in polymer matrix, the interparticle distance can be calculated using the following equation;

$$\frac{V_{NC}}{V_E} = \frac{V_{TN}}{V_{IN}} \qquad \text{(S4)}$$

where V_{NC} and V_{TN} represent the total volume of polymer nanocomposite and nanoparticles loaded into the polymer matrix, respectively. $V_E = 4\pi(d_{IP}/2)^3/3$ is the volume of a spherical volume unit of diameter d_{IP} which has an alumina nanoparticle of 5 nm diameter (as determined from XRD) with its volume V_{IN} at its centre. Thus calculated interparticle distance is ~ 114 nm.



Scheme S1. 2D Schematic representation for calculation of interparticle distance

7. Determination of Glass transition temperature

The T_g value is taken as the onset temperature of the glass transition process which is determined from the intersection of the tangents from the low temperature base line and from the inflection point. The intersection of the tangents from the inflection point and the high temperature base line is taken the end of the glass transition process and the corresponding value is taken as T_{end}.

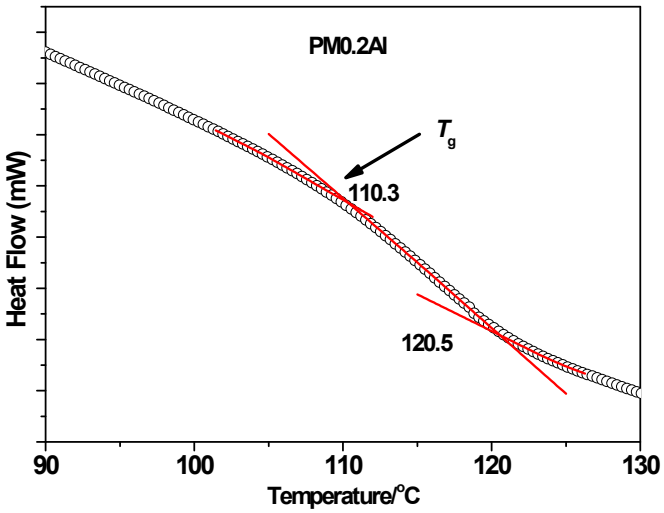


Figure S4. Determination of glass transition temperature for PM0.2Al from the DSC 2nd heating cycle thermogram.