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A study of porosity of synthetic polymer nanoparticles using PALS

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Abstract. Positron annihilation lifetime spectroscopy (PALS) has been used to study the free volume in dry synthetic polymer nanoparticles of various sizes. A series of poly(styrene/divinyl benzene) particles with diameters in the range of 100 to 500 nm were synthesized and then carefully chemically treated using the sulfonation process, to increase their porosity. The particles were characterised by Scanning Electron Microscopy (SEM), light scattering and PALS. Light scattering gave larger size for the treated particles, reflecting the hydration effect and therefore the increase in porosity. PALS spectra of untreated and treated particles gave four and three life-time components, respectively. Analysis by PAScual version 1.3.0 program indicated there was a reduction in the intensity and the type of the micropores in the treated particles. The data suggest PALS is a sensitive tool for detecting changes in microporosity in particles. The conflicting results obtained for light scattering compared to PALS for chemically treated particles is difficult to resolve and suggests sample preparation of polymeric materials for PALS is the critical factor.

1. Introduction

The development of drug delivery vehicles and imaging agents using polymeric materials, especially polymer nanoparticles, continues to grow [1-2]. In these systems the free volume sites are important for controlling the uptake, storage, separation and release of the molecules of interest. Thus, in order to optimise their performance, extensive characterisation of their free volume is essential.

Positron annihilation lifetime spectroscopy (PALS) was used to study the microporosity of polymers and polymeric blends/composites [3-7]. PALS is particularly useful as a qualitative tool for measuring the effect of processes on the porosity in materials. However the question whether the sensitivity and resolution of the positron annihilation measurements is affected by the particle size has not been answered. A preliminary investigation into the effect of particle size on the analysis of porosity in synthetic polymer nanoparticles using PALS is presented. A series of monodispersed polymer particles (ranging from 100 to 500 nm in diameter) was synthesized, treated by sulfonation. PALS was used to determine the porosity of particles before and after the treatment.

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2. Experimental procedure

2.1. Synthesis of polymer nanoparticles:

Polymer particles of various diameters (100, 200 and 530 nm by SEM) were synthesized by emulsion polymerisations using the chemicals summarised in Table 1. Reagents were weighed into a round bottom flask. The flask was capped and deoxygenated with nitrogen gas for 15 minutes, and then immersed in a 70°C oil bath with constant stirring for at least 20 hours. The product was dried in a fume hood overnight and then in an 80°C oven for 48 hours to remove water and any free monomer(s).

Table 1 - Recipes and sizes of polymer particles from the emulsion polymerisations

	Particles 1 (100 nm in diameter)	*Particles 2 (200 nm in diameter)*	*Particles 3 (530 nm in diameter)*
Styrene (g)	15.042	23.677	10.080
Divinyl Benzene (g)	0.308	0.378	0.511
Sodium Dodecyl Sulphate (g)	0.115	0.029	0.00
Initiator V-501 (g)	0.116	0.146	0.146
NaOH (g)	0.038	0.045	0.073
Deionised Water (g)	62.210	72.184	40.615

2.2. Modification of porosity for the polymer particles:

A portion of the dry polymer particles was then chemically treated using the sulfonation process from Holboke *et al.* to increase the porosity of the polymer particles [8]. Typically, 0.02 g of silver sulphate was added to concentrated sulphuric acid (15 mL) while stirring and warmed to 90°C. To this mixture was slowly added 1 g of dry polymer particles. The resultant suspension was heated at 90°C for 3 hours with gentle stirring. The mixture was then poured into a 6 M sulphuric acid solution at room temperature (100 ml) with gentle stirring. The particles were centrifuged at 5000 rpm and washed thoroughly with deionised water. The resultant product was dried in an 80°C oven for 48 hours.

2.3. Characterisation of particles:

2.3.1. Scanning Electron Microscopy: (ZEISS, ULTRA *Plus*, 10kV energy): polymer particles were deposited on a 200 mesh carbon coated copper grid. Micrographs of the particles before and after sulfonation are illustrated in Figures 1 and 2.

2.3.2. Light scattering: Zetasizer (ZetaNano, Malvern) was used to measure size distributions of polymer particle suspensions before and after the sulfonation. Data are summarised in Table 2.

2.3.3. PALS: the instrument consists of a fast-fast spectrometer with detectors comprising of a BC418 plastic scintillator coupled to a Burle 8850 photomultiplier tube. A 30 μCi ^{22}NaCl source was used for the collecting spectra. The time resolution of the instrument was determined using a high purity annealed nickel to be approximately 200 ps. Each spectrum has at least $2\text{x}10^6$ counts and was analysed by PAScual version 1.3.0 [9]. Data are given in Table 3.

3. Results and discussion

SEM images in Figure 1 show that the polymer particles obtained from the emulsion polymerisations (untreated particles) are monodispersed and have mean diameters of 100, 200 and 530 nm. The particles after the sulfonation (treated particles) (Figure 2-B) retain their original shape and size (Figure 2-A). The SEM technique measures particles in their dry form (i.e. free of water and unreacted monomers).

The light scattering measures the diameters of the particles suspended in the aqueous solution. It is important to note that particles become hydrated in the aqueous solution and if there is any unreacted monomer it can influence the radii obtained. As expected particle diameters obtained by the light scattering were consistently higher than those given by SEM (see Table 2). For the Particles 1 and 3, diameters given by the light scattering appear to be increased by 1.3 to 1.5 fold, while the variation in the Particles 2 is only by 1.03 fold. This is mostly likely due to the presence of unreacted monomer remaining in the former particles.

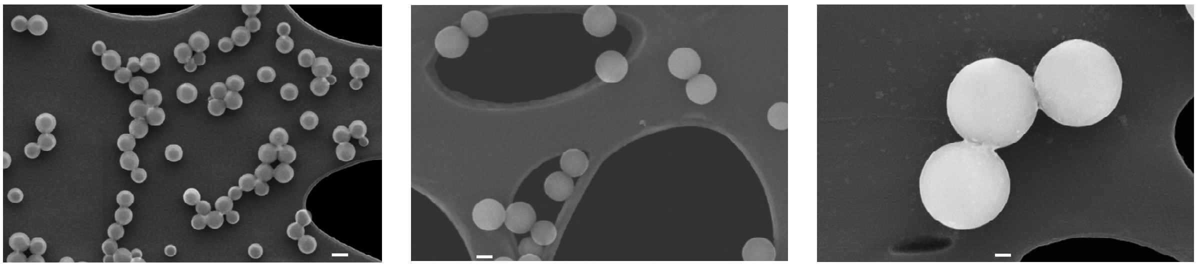
100 nm particles 200 nm particles 530 nm particles

Figure 1 - SEM micrographs of untreated particles. Scale bar: 100 nm

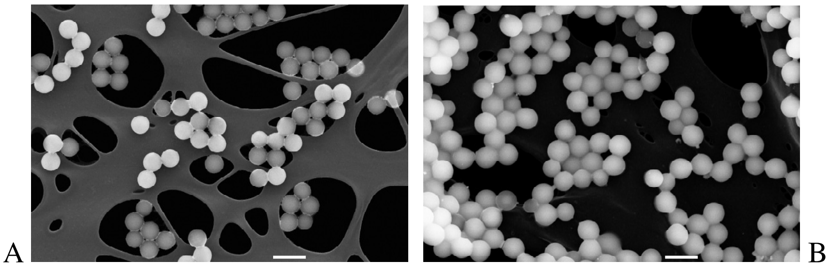

Figure 2: SEM micrographs for 530 nm particles: untreated (A) and treated (B). Scale bar: 1 μm

The light scattering data revealed that the diameter of treated particles increased by 2 fold compared to untreated particles. Such an increase confirmed the treatment by sulfonation was successful (See Table 2).

Table 2 – Summary of the colour and average diameter of untreated and treated particles

Particles	*Colour*		*Diameter by SEM of dry particles (nm)*	*Diameter by Light Scattering of hydrated particles (nm)*	
	Untreated	*Treated*		*Untreated*	*Treated*
1	White	Light brown	100	153	320
2	White	Grey	200	216	-
3	White	Creamy grey	500	665	1329

Prior to lifetime measurements the samples were heated at 80°C (close to the glass transition temperature of polystyrene of 100°C) for 24 hours to remove remaining moisture. The o-Ps lifetimes and intensities are given in Table 3.

Table 3: Ortho-positronium lifetimes and intensity for particles

Particles	**D (nm)**	**τ_3 (ns)**	**I_3 (%)**	**τ_4 (ns)**	**I_4 (%)**	**d_3 (nm)**	**d_4 (nm)**
1 untreated	100	2.03 (0.01)	30.7 (0.1)	29.4 (0.1)	1.5 (0.1)	0.65	2.54
2 untreated	200	2.01 (0.01)	33.1 (0.1)	15.0 (0.9)	0.8 (0.1)	0.65	1.75
1 treated	100	1.58 (0.01)	11.6 (0.1)	-	-	0.56	-
2 treated	200	1.69 (0.01)	11.8 (0.7)	-	-	0.58	-
3 treated	530	1.57 (0.01)	10.2 (0.8)	-	-	0.55	-
particle diameter (D), o-Ps lifetimes (τ), intensities (I) and pore diameters (d) Colours of particles: white (untreated), light brown (1, treated), grey (2, treated) and creamy grey (3, treated)							

Spectra of 100 nm and 200nm untreated particles could be deconvoluted into four discrete components. Two of these components (less than 0.5 ns) are associated with p-Ps and free positron annihilation, as well as annihilations in the source material and supporting foil. The longer components (more than 1 ns) are of higher interest for the present study. They are associated with o-Ps pick-off annihilation in the free volume of the polymeric particles. The τ_3 values (approximately 2 ns, using the RTE model [10]) for untreated Particles 1 and 2 correspond to a pore diameter d_3 of 0.65 nm. The intensity of this component (I_3) exceeds 30%, indicating that these materials contain significant nanoporosity. Their lifetime τ_4 components (29.4 and 15 ns, respectively) correspond to larger pores with diameters d_4 of 2.54 and 1.75 nm, respectively. However, this component could be due to annihilations in the space between the particles or at free surfaces and the chemical and preparation processes for forming these particles are unlikely to generate to distinct type of pores.

For the treated particles the spectra could be deconvoluted into only three discrete components. Very close values for lifetimes τ_3 observed for treated Particles 1 and 3 correspond to a pore diameter of 0.56 nm. A slightly larger τ_3 of 1.69 ns for treated Particles 2 corresponds to a slightly larger pore diameter of 0.58 nm. I_3 values for these samples were in the range of 10.2-11.8%.

The light scattering measurements suggest that the microporosity of these particles is increased after sulfonation. However there was a conflict between the results given by light scattering and by PALS. Measurements by light scattering indicated the hydration of treated particles increased due to an increase in the porosity. In contrast, the PALS results suggest the treated particles have significantly lower free volume in comparison to the treated particles. The τ_3 values indicate that the average pore diameter of the treated particles decreased by around 1 Å. The intensity of this component also decreased significantly.

While the particles were washed extensively after the sulfonation process, their colour changed from white to cream and brown as the particles decreased in size. Hence the PALS results could reflect the presence of silver ions inside the particles. The different observations from light scattering and PALS could also be due to the sample preparation and drying processes deployed for particles prior to PALS measurements. As the particles have polymer chains at low cross-linker (divinylbenzene) concentration, drying at 80°C (close to their glass transition temperature) could have resulted in the collapsing in the nanostructure of the particles.

Future experiments will be directed toward the effect of sample preparation (i.e. drying conditions) and cross-linking agent used to synthesize the polymer particles on PALS analysis.

4. Conclusion

PALS was proved to be a sensitive technique to measure the free volume in the synthetic polymer particles of a range of particle sizes. The results show that the untreated polymer particles have comparable τ_3 values but there is a significant difference in respective τ_4 values. The size of the nanopores for the treated particles is similar but there is no evidence of τ_4. There appears to be an effect of particles size on the PALS analysis, however the results are inconclusive and further work is warranted. The light scattering data indicate an increase in porosity for treated particles however PALS show a reduction in free space. Future experiments will investigate the effects of particle size and sample preparation on the PALS measurements.

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