Macromol. Symp. **151,** *419–425 (2000)*

Characterization of Composite Latex Particles by Positron Annihilation Spectroscopy

B. Lizama*,**, D. Castañeda, R. López-Castañares*, V. Castaño*,** and F. Vazquez*

* Universidad Autónoma del Estado de México, Facultad de Química, A.P. A-20, 50 000 Toluca, Edo. de Méx., E-Mail: fsvm@coatepec.uaemex.mx. ** Universidad Autónoma de Querétaro, Facultad de Ingenieria, Cerro de las Campanas s/n, Querétaro, México.

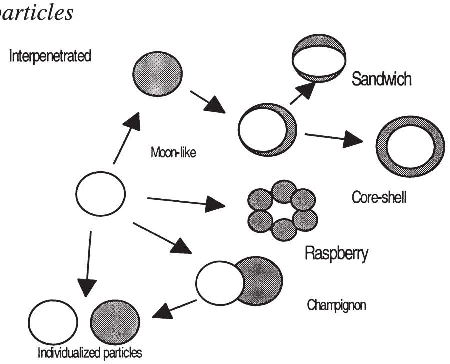
Summary

A series of Polybutylacrylate/Polystyrene composite particles were synthesized through semicontinuous emulsion polymerization. The resulting latex particles were characterized by quasi-elastic light scattering and scanning electron microscopy. Also, these composite particles were irradiated with a Positron source to obtain the so-called mean life time τ_3 *and the formation probability* I_3 *. A dependence of the Positron annihilation parameters with both particle composition and morphology was found.*

1. INTRODUCTION

Aqueous dispersions of submicron latex particles are commonly prepared through two-step emulsion polymerization. In this technique, particles of the polymer 1 act as reaction sites for the polymerization of a monomer 2. This approach allows to produce a wide range of morphologies, ranging from interpenetrated structures, core-shell particles, raspberry-like shapes, etc. (See Figure1).

Figure 1. Phase diagram for composite latex particles



The production of a particular morphology depends on the change of the various driving interfacial energies in the system [1]. The synthesis of these composite particles has produced a growing interest among the specialists because of their potential applications as impact modifiers, varnishes, paints, adhesives, etc. From a practical standpoint, however, the morphology of these composites is routinely

 CCC 1022-1360/00/$ 17.50+.50/0

studied by Transmission Electron Microscopy (TEM). This technique is cumbersome since, in most cases, the polymer samples must be stained with conductive substances which could mask the actual morphology and the whole process, from the sample preparation to the developing of the micrographs, is extremely time consuming. Therefore, alternative techniques, which also allow to establish some parameter for comparing to TEM results, are to be developed, especially for those cases where the polymer phases are similar to each other and the standard contrasting with staining agents is difficult to achieve for an adequate TEM work. In this regard, Hergeth *et al.* [2] have proposed different techniques to characterize this kind of polymeric composites. Small Angle X Ray Scattering (SAXS), Infrared Spectroscopy and Scanning Differential Calorimetry have been thus proposed as potentially useful methods for characterizing the interfaces and the morphology of those particles.

On the other hand, Positron Annihilation Spectroscopy (PAS)has been successfully employed for characterizing spatial structure (mainly porosity) at the nanometer scale in various materials, from semiconductors to metals. In spite that very scarce literature is available on the use of PAS in polymeric materials, it represents an interesting alternative technique for characterizing composite latex particles, as we shall attempt to demonstrate in this present article. Indeed, the Positron is a subatomic particle with the same mass as the electron but with a positive charge. When this subatomic particle is irradiated within condensed matter, it loses all of its kinetic energy by collisions with the electrons and ions naturally present in the sample to be studied. The thermalized positron then can either bound to an electron, to form Positronium (Ps), or becomes part of a chemical complex with a polymer chain. Afterwards, the positron annihilates with an electron, with the resultant conversion of their masses into energetic photons whose energies, momentum and times of emission can be measured with high precision. These observable characteristics of the annihilation process depend upon the state of the positron-many electron system at the time required for the annihilation. Therefore, the specific values of the Positron annihilation parameters (namely, mean life time and probability of formation of the different Ps species) in a particular polymer composite, are closely related to the corresponding morphology [3],[4], since the free spaces in which the Ps can travel without annihilation, depend on the geometrical arrangement, at a quasi-molecular level, of the different phases of the sample.

Of course, it is not simple to deduce the morphology of a particle solely from PAS experiments, but the information provided by this technique constitutes a useful clue on how the free spaces, molecular porosity and free volume are available within the sample, which, along with the data from other characterization techniques, providing a deeper insight into the nanostructure of complex polymeric particles. More specifically, measurements of Positron lifetime (τ_3) and intensity (I_3) give direct information on the dimensions of hole sizes of the free volume in amorphous materials, as we shall see in what follows.

Accordingly, the aim of this work is to study the influence of the morphology and composition of structured latex particles on the Ps annihilation parameters. The materials employed for the characterization were latex particles with Polybutylacrylate (PBuA) as polymer 1 and Polystyrene (PS) as polymer 2.

2. EXPERIMENTAL

The polymerizations were carried out as two stage reactions in a glass reaction vessel, constantly stirred (250 rpm) at 72 ^{o}C. Seed latex were prepared with Butylacrylate (BuA from Aldrich) following a semicontinuous process which has been described elsewhere [3]. In the second step, the seed latex (polymer 1) was covered with polymer 2 by continuous addition of a pre-emulsion containing monomer 2 (Styrene, Aldrich.), ammonium persulphate (Aldrich) as initiator and RAFA (sodium dichloro-hexyl sulphonate from Mexochem) as tensoactive. The second step polymerization was carried out at 72 ^{o} C under starved feeding conditions. The resulting latex, with different polymer 1/ polymer 2 ratios, were characterized by gravimetry, Quasi-Elastic Light Scattering (QELS), with a Coulter nanosizer, and Scanning Electron Microscopy (SEM) in a Philips XL 30 microscope. The composite latex particles were precipitated, washed with warm water and dried. The purified samples were then irradiated with a Positron source ($Na^{22}Cl$, 9 μ Ci radiometric activity) in a degassed glass tube. A fast gamma-gamma coincidences system (i.e. a multichannel ORTEC coupled to a PC) was employed to register the Positron Annihilation Spectrum. The mean lifetime τ_3 and the formation probability I_3 of the ortho-positronium were calculated with the commercial program for PAS analysis known as PATFIT88.

3. RESULTS AND DISCUSSION

The whole series of composite latex particles with different PBuA/PS ratios are described, in terms of their corresponding mean diameters, as measured by QELS, in Table 1.

System	PBuA/PS ratio	Dp_z (nm)
PBuA/PS ($dp_{z,seed}$ =388nm)	80/20	420
	70/30	436
	60/40	460
	40/60	526
PBuA/PS ($dp_{z,seed}$ =580 nm)		
	70/30	653
	60/40	687
	40/60	787

Table 1. Diameter of PBuA/PS composite particles

A rubbery material was obtained, upon precipitation, in all cases where the latex particles had a low thermoplastic content. SEM micrographs of these materials revealed the formation of a continuous film. This leads to conclude that these particles must have a semi-interpenetrated morphology.

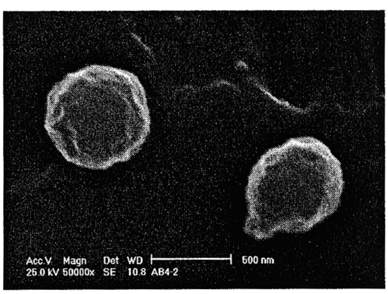


Figure 2. SEM image of a raspberry particle PBuA/PS = 60/40 and Dp_z = 460 nm (obtained by QELS)

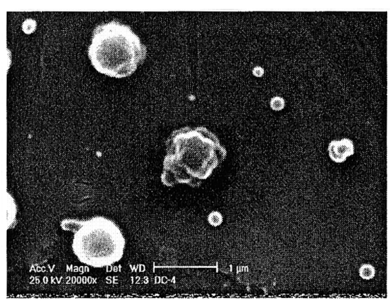


Figure 3. SEM image of a raspberry particle PbuA/PS= 60/40 and DPz= 526 nm (obtained by QELS)

Interestingly, for PBuA/PS ratios higher than 70/30, a raspberry-like morphology was observed by SEM (see Figure 2). Moreover, when the polymer 2 content in the composite particles was increased, the PS lobules around the PBuA seed were expelled and new single particles appeared in the system (Figure 3).

The Ps annihilation parameters (τ_3 and I_3) of the two stage latex particles were plotted as a function of the PS content (Figure 4). A continuous decrease of the mean lifetime as the polymer 2 fraction increases was observed in composites with poor PS content. However, a change in the slope of the resulting curve was detected around a PS content of 30 % wt. On the other hand, the formation probability of the Ps exhibited a similar behavior: a continuous increase of I_3 as the polymer 2 content increases was also detected at PS fractions below 30 % wt. The change in the slope of the Ps functions can only be interpreted, according to the theory, in terms of a morphological phase transition in the composite particles. In fact, it is known that τ_3 depends on the size of the free spaces between the macromolecular chains. Thus, when there exists an interpenetrating process of the rubbery chains of the seed with the more rigid chains of the polystyrene, a decrease of the mean size of the holes which constitute the free volume of the system is expected, revealed by a decrease of the mean life of the Positronium. Similarly, the interpenetrating process produces the formation of smaller holes, where the Positron is formed, and an increase of the experimental value of I_3 is observed. This behavior changes suddenly when the thermoplastic and the rubbery phases separate from each other. The free space between the PBuA increases back again and new holes are formed in the PS. However, when the PS fraction is increased, there is a decrease of the free volume of the system (the PS, a rigid plastic, presents a low free volume fraction). Therefore, smaller holes are formed and produce a decrease in and an increase in I_3. A similar behavior was observed for Pub/PS systems with different initial particle sizes (see Figure 5). In both cases, a change of the Ps parameters, as a function of the particle composition, was detected at the PS fraction where the transition from an interpenetrated to a raspberry morphology was observed by SEM. This neat result implies that the PAS technique may be employed to detect phase transitions and that the values of the Ps parameters may be associated to a specific particle composition and morphology, as a sort of molecular level fingerprint. It is also important to point out that PAS is a non-destructive technique and that the experimental procedure is simple, inexpensive and straightforward.

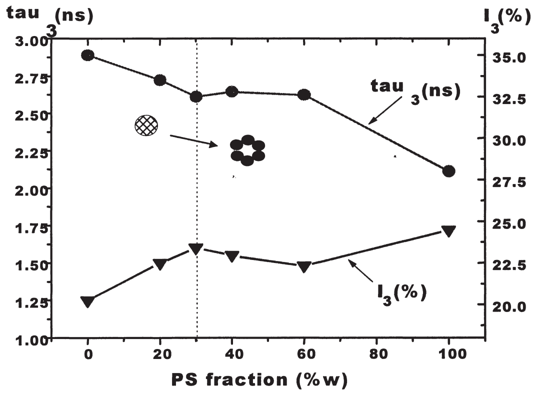


Figure 4. Ps annihilation parameters as a function of the particle composition ($Dp_{z,seed}$ = 580 nm)

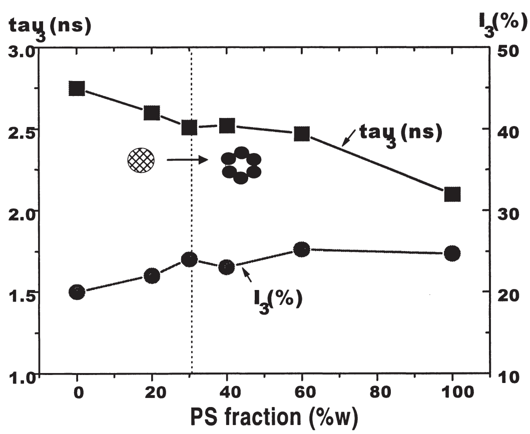


Figure 5. Ps annihilation parameters as a function of the particle composition ($Dp_{z,seed}$ = 388 nm)

4. CONCLUDING REMARKS

A series of PBuA/PS latex particles were prepared by emulsion polymerization techniques. Semi-interpenetrated particles were formed at low PS contents. A transition between the semi-interpenetrated and a raspberry morphology was detected at a composition Pub/PS ≈ 70/30 by SEM. The values of the Ps annihilation parameters τ_3 and I_3 depend on the morphology and composition of composite latex particles.

REFERENCES

(1) Sandbag D.C., Cassias AP, Pantazopoulos, Muscato M. R., *J. Appl. Polym. Sci.* **41**, 1425 (1990)
(2) Hergeth W.D., Steinau U.J., Bittrich H. J., Schmutzler K., Wartewig, S., *Prog. Coll. Polym. Sci.* **85**, 82 (1991)
(3) Kindl P., Puff W., Sormann H., *Phys. Stat. Sol. (a)* **58**, 489 (1980)
(4) Wastlund C., Maurer F.H.J., *Macromol.* **30**, 5872 (1997)
(5) Castañeda D., *Tesis*, UAEM, Toluca, Mexico (1999)