INFLUENCE OF FEEDING CONDITIONS ON THE SYNTHESIS OF CORE-SHELL PARTICLES OBTAINED BY SUSPENSION POLYMERIZATION

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Abstract - In this work, core-shell particles with diameters up to 1500 micrometers were obtained by seeded suspension polymerization, composed by a core of polystyrene and a shell of poly(methyl methacrylate). The amount of PMMA deposited on the seed particles were determined by ¹H Nuclear Magnetic Resonance and the formation of secondary particles were confirmed by Scanning Electron Microscopy - SEM. Transmission Electron Microscopy – TEM, was used to evaluate particle morphology, demonstrating that the internal microstructure is composed by micron-sized clusters of poly(methyl methacrylate) dispersed in the polystyrene phase and that their size varies along the particle radius. The obtained particles were characterized in respect of their solubility in substances that readily dissolve polystyrene or poly(methyl methacrylate) (cyclohexane and acetic acid, respectively), demonstrating that the incorporation of poly(methyl methacrylate) to the seeds improved their chemical resistance.

Introduction

The synthesis of particles with more complex morphologies (core-shell structures and phase separated structures) have been studied in the last years mainly in emulsion polymerization systems as they have a major influence on the properties of the latex as, for example, impact modification and toughening of polymer matrices¹. The core-shell structure, in which two or more polymers form particles with concentric core and shell (or shells) are obtained mainly by seeded emulsion polymerization²⁻⁵. Nevertheless, this technique may generate particles with a variety of morphologies. According to Rajatapiti et al.⁶ (1997), the composite particle morphology depends on many parameters, such as viscosity of the reaction medium, mode of monomer addition, polymer molecular weight, polymerization temperature, hydrophilicity of each phase, particle surface polarity, interfacial tensions and particle size distribution. Several works discuss how these factors affect the morphology of core-shell particles obtained by emulsion polymerization⁷⁻¹¹. However, there is a lack of information about producing core-shell particles by suspension polymerization, which is an important technique in polymer foams industry, for instance¹²⁻¹⁴. The size of particles produced by emulsion and suspension polymerization differ greatly, as emulsion polymerization usually leads to particles with diameters of 100-500nm and suspension polymerization to particles with 300-1500µm. It means that, the volume / superficial area ratio of the particles produced by suspension polymerization is much larger than the ratio obtained for emulsion polymerization particles. Therefore, one would expect that the parameters affect particle morphology in a different extent when comparing suspension and emulsion polymerization systems. This work presents the efforts on obtaining core-shell particles through seeded semi-batch suspension polymerization, yielding micrometric particles with complex microstructure.

Experimental

Polystyrene Seeds:
Polystyrene seeds were obtained by batch suspension polymerization at 90°C, using di-benzoil peroxide (BPO) (0.33%wt) as initiator and poly(vinyl pyrrolidone) - PVP k-90 (1.0%wt) as stabilizer. Polymer beads were washed and dried before granulometric separation; beads retained between Tyler Standard sieves (nominal aperture of 1180 to 1680 micrometers, respectively) were used as seeds.

Core-shell synthesis:
Core-shell syntheses were carried out in a one-liter jacketed reactor; the formulation employed in all reactions is presented in Table 1. The initial charge in all reactions consisted in polystyrene seeds and, as the continuous phase, distilled water, poly(vinyl pyrrolidone) k-90 and ascorbic acid. The seeded suspension polymerizations differed only in the mode of monomer addition to the reactor.

Procedure 1. After the addition of the initial charge to the reactor the reaction medium was heated to 50°C. The solution of monomer (MMA) and initiator (BPO) was then added to the reactor under vigorous stirring (900 rpm) at 0.9 grams
per second. As the MMA feed was finished, temperature was increased to 70°C and the system was allowed to react for four hours. After that, the reactor was cooled, the particles were washed and dried.

**Procedure 2.** The initial charge was fed to the reactor; meanwhile, BPO was dissolved in MMA. The reactor was heated to 70°C and the solution of monomer and initiator was added to the reactor under vigorous stirring (900 rpm) at 0.9 grams per minute; after the end of the monomer feeding, the system was allowed to react for four hours. After that, the reactor was cooled, the particles were washed and dried.

<table>
<thead>
<tr>
<th>Table 1. Recipe used for core-shell synthesis.</th>
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<tbody>
<tr>
<td>water (g)</td>
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<tr>
<td>polystyrene seeds (g)</td>
</tr>
<tr>
<td>methyl methacrylate (g)</td>
</tr>
<tr>
<td>di-benzoyl peroxide (g)</td>
</tr>
<tr>
<td>poly(vinyl pyrrolidone) (g)</td>
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<td>ascorbic acid (g)</td>
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**Characterization:**
Tyler Standard sieves were used in granulometric separation. Particle composition was determined by $^1$H NMR spectroscopy; particles samples were dissolved in deuterated chloroform, CDCl₃; the spectra were recorded at 20°C using a Bruker Avance spectrometer (500 MHz). The molar percentage of PMMA in the sample was determined using the peak of CH$_3$-O group, while the peaks correlated to the aromatic ring were used for polystyrene. The peaks correlated to the CH$_2$ and CH groups were used to verify the integration error.

Transmission Electron Microscopy (Hitachi 7000 at 75 kV) was used to study the morphology of the particles; the images were taken at 6000x magnification. Particles were sliced using an ultramicrotome and deposited on a copper grid; then, the samples were stained by ruthenium tetroxide (RuO$_4$) vapour for 1 hour (PS appears dark whereas PMMA appears light). Scanning Electron Microscopy-SEM, (Philips XL-30) was used to evaluate the core-shell particles surface and the morphology of the secondary particles; images were obtained from gold coated samples at 15kV.

Micron-size particles were separated from the aqueous phase by centrifugation. A sample from the reaction was centrifuged until no particles were detected in the aqueous phase in an optical microscopy at 10x magnification; for all samples, centrifugation at 1000 rpm for 12 min was enough to assure an efficient separation.

**Results and Discussion**

**Shell Formation:**
Shell formation is determined in a large sense by the amount of methyl methacrylate effectively incorporated in the seeds. The ideal situation is the one in which all monomer enters the seeds to form the shell, maintaining the mass proportion given by the initial recipe.

Table 2 presents the values of mass percentage of PMMA in the seed particles, determined by $^1$H NMR. The efficiency of incorporation was defined as the relation of MMA fed to the reactor and the MMA effectively incorporated in the seed particles (called here primary particles).

<table>
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<th>Table 2. Particles composition and efficiency of incorporation.</th>
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<tr>
<td>Sample</td>
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<tr>
<td>Procedure 1</td>
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<td>Procedure 2</td>
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The procedure employed to fed the monomer to the reactor strongly affected the final particle composition. In Procedure 1, since monomer was fed at a temperature in which the initiator decomposition was negligible, a great part of the methyl methacrylate was able to diffuse into the seeds before polymerize, increasing the amount of PMMA at the seed particles. In Procedure 2, methyl methacrylate was added at 70°C, and the polymerization started immediately during monomer feeding. Therefore, new polymer particles were formed before monomer and initiator could diffuse into the seed particles. The result is that a lower quantity of PMMA was formed at the seeds.

In both procedures, a certain amount of methyl methacrylate added to the system entered the seed particles while another formed new particles. The aqueous phase (separated from micron-size particles as described above) was observed by Scanning Electron Microscopy, as one can be seen in Figure 1(a).
These secondary particles (formed after monomer addition) were produced in both reaction procedures; also, their sizes (around 400 nanometers) do not vary significantly. They are also adhered to the primary particles, as shown in Figure 2 below. Besides these nano-size particles, some agglomerates can also be found, clearly formed from the agglomeration of the small particles (as in Figure 1(b)).

The composition of both secondary particles and agglomerates were determined by $^1$H NMR, showing that they are composed solely by poly(methyl methacrylate). It suggests that their site of polymerization is somewhere out of the polystyrene seeds. The mechanism responsible for secondary particles formation and stabilization will be subject of another work.

**Core-shell Morphology:**
In order to evaluate the internal microstructure of the core-shell particles, TEM images were taken at a cross section of the particle at various points. Figure 4 presents the TEM images for a typical particle obtained through *Procedure 1* and *Procedure 2* while Figure 3 shows a representation of the cross section and the points at which each image was taken.
Figure 3: Representation of the cross-section of the particle obtained by (a) Procedure 1 (b) Procedure 2.

Figure 4: TEM images of the cross section of a core-shell particle obtained through (a) to (e) Procedure 1 and (f) to (i) Procedure 2. Points A to E are indicated at Figure 3 above (Magnification: 6000x).
One can see that PMMA (which appears light while PS appears dark) is distributed as domains in the PS matrix. It occurs because PS is soluble in methyl methacrylate but PS and PMMA are immiscible in each other; at the beginning, MMA swells the seeds and, as polymerization takes place, phase segregation occurs and PMMA forms separated clusters.

It can also be seen that the size of the PMMA clusters and the concentration of PMMA in the polymer seeds decrease along the radius of the particles. At a certain point, no clusters can be seen. One can conclude that the particles have a shell composed of small clusters (approximately 3 micrometers) of PMMA dispersed in a polystyrene matrix and a nucleus composed solely by polystyrene.

For the core-shell particle obtained by Procedure 2, TEM images shows that the thickness of the PMMA/PS shell is lower than the obtained in the first procedure; it can be explained by the fact that, since MMA was fed to the reactor at a temperature in which the reaction rate is considerable, there was less time available for MMA to swell the seed particles before polymerization takes place. Moreover, one can note that clusters sizes and shape do not change significantly when changing the reaction procedure.

Behaviour on Solvents:
The behavior of the core-shell particles under substances that selectively dissolves polystyrene and poly(methyl methacrylate) were qualitatively evaluated, Figures 5 and 6. Core-shell particles, pure polystyrene and pure poly(methyl methacrylate) particles were immersed in ciclohexane and acetic acid. The former is solvent for PS and not for PMMA, while the later readily dissolves PMMA but not dissolves PS.

![Image](image1.png)

(a) Pure polystyrene on ciclohexane, zero minute.  
(b) Pure polystyrene on ciclohexane, 120 minutes.

![Image](image2.png)

(c) Core-shell Procedure 1 on ciclohexane, zero minute.  
(d) Core-shell Procedure 1 on ciclohexane, 120 minutes.

![Image](image3.png)

(e) Core-shell Procedure 2 on ciclohexane, zero minute.  
(f) Core-shell Procedure 2 on ciclohexane, 120 minutes.

![Image](image4.png)

(g) Core-shell Procedure 1 on ciclohexane, six months.

Figure 5: Images of the particles immersed in ciclohexane (without scale).
As one can observe in Figure 5, the behaviour of the core-shell particles, obtained by both reaction procedures, were completely modified from that of PS. At the same time scale, core-shell particles do not dissolve in polystyrene-solvent. Core-shell particles are also resistant to the attack of acetic acid, as demonstrated in Figure 6. While pure poly(methyl methacrylate) particles dissolve in this acid at approximately 5.5 hours, core-shell particles remains unaltered, even for several months.

When immersed in ciclohexane for several months, core-shell particles have swollen, Figure 5 (g). This is in accordance with TEM images, which show that PMMA clusters are dispersed in a continuous polystyrene matrix. For long times, ciclohexane diffuses through the polystyrene matrix, swelling the particles. When immersed for long times in acetic acid, core-shell particles remains unaltered, which is also expected considering the microstructure showed by the TEM images.

**Conclusion**

Seeded semi-batch suspension polymerization was implemented to produce core-shell particles. $^1$H Nuclear Magnetic Resonance and Transmission Electron Microscopy have demonstrated that the particles are formed by a nucleus composed solely by polystyrene and by a shell composed by PMMA clusters distributed along a PS matrix.

Increasing the time available for methyl methacrylate to swell the polystyrene seeds increased the shell thickness and the amount of poly(methyl methacrylate) effectively incorporated in the seeds. An amount of the MMA fed to the system formed secondary particles and small agglomerates; they are composed solely by PMMA, suggesting that their site of polymerization is other than the polystyrene seeds.

Qualitative observation of pure PS, pure PMMA as well as core-shell particles when in contact of different solvents corroborates the microstructure showed by TEM images.
Acknowledgements

Authors would like to thank CNPq and FINEP for the financial support, as well as the Programme Alban, the European Union Programme of High Level Scholarships for Latin America, scholarship no. E06D101711BR.

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