SUSPENSION MADE CORE-SHELL PARTICLES: STRATEGIES FOR SYNTHESIS AND CHARACTERIZATION

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This work describes the synthesis and characterization of core-shell structured particles suitable for applications as rigid foams. A seeded suspension polymerization approach was implemented resulting in particles composed by a polystyrene core and a shell composed by poly(methyl methacrylate) (PMMA) domains densely dispersed in a polystyrene matrix. Particle morphology showed to be largely controlled by the limitations to the diffusion of the methyl methacrylate through the polymer particle. However, the formation of secondary particles (formed only by PMMA) was relevant depending on the operation conditions. The mechanism of secondary particles formation during seeded suspension polymerization was also investigated using monomers with different water solubility. The results were consistent with the formation of secondary particles by both homogeneous nucleation and monomer droplet nucleation.

Keywords: Seeded suspension polymerization, core-shell, secondary particles.

Introduction

Core-shell morphology is of particular interest in polymer engineering because particles with a composition profile along their radius could present unique properties. The implementation of a synthesis procedure to obtain core-shell particles by seeded suspension polymerization has been studied by our group in the last years (GONÇALVES et al., 2008; GONÇALVES et al., 2009a; GONÇALVES et al., 2009b).

One of our objectives is to obtain particles with improved properties to be used as rigid foams, in particular chemical resistance and mechanical strength. A core-shell morphology of the polymer beads could be a suitable strategy to improve the properties of the foam because a shell composed by a resistant polymer could improve the resistance of the entire foam sheet. These particles should have a particle size of 400-1600 micrometers, a spherical shape (SCHEIRS e PRIDDY, 2003) and an external shell more resistant than the conventional material (usually polystyrene). The idea is to form a poly(methyl methacrylate) shell on suspension-made polystyrene particles. Although there is plenty of information regarding the mechanisms involved in the development of the core-shell morphology of emulsion particles (GONZÁLEZ-ORTIZ e ASUA, 1995, 1996a,b; HERRERA et al., 2006; KEUSCH e WILLIAMS, 1973; LEE e ISHIKAWA, 1983; MORGAN, 1982), the difference in size between emulsion and suspension particles (about 4 orders of magnitude) introduces aspects that make of limited use the information
available (diffusional limitations to monomer mass transfer; much lower number of particles, which favours the nucleation of secondary particles; much smaller polymer-water interfacial area). Just a few works can be found on suspension polymerization (KASAI et al., 1989; KAWAGUCHI et al., 2005; LENZI et al., 2003; BYUN et al., 2004) but the resulting particles are not suitable for foam production.

In order to properly control the production of such particles, the influence of experimental conditions as monomer feed policy, monomer and initiator types and concentrations on particle morphology and composition must be well understood. Another challenge is to identify the most suitable characterization procedures to correctly determine how polymer phases are distributed inside the particles. Furthermore, seeded polymerization systems are prone to form secondary particles during the core-shell synthesis so their mechanism of formation must be determined.

This work presents our efforts in the production and characterization of suspension-made core-shell particles. Polystyrene particles were used as the core polymer and the use of different monomers were evaluated. Particle morphology were determined as well the mechanisms involved in the formation of secondary particles during the synthesis.

**Experimental**

Technical grade styrene, methyl acrylate and methyl methacrylate were used as monomers and benzoyl peroxide (BPO, Sigma-Aldrich) was used as initiator. Distilled water was used as continuous phase and poly(vinyl pyrrolidone) (PVP, 360,000g/mol, Sul Polímeros Ltda) as stabilizer. Ascorbic acid (Sigma-Aldrich) was used to avoid inhibition caused by oxygen. All chemicals were used as received. Polystyrene (PS) seeds were obtained by batch suspension polymerization at 90ºC, using BPO (0.36%wt/monomer wt) as initiator and PVP (1.0%wt/water wt) as stabilizer. Polymer beads were washed and dried. Beads retained between Tyler Standard sieves with nominal apertures of 710 and 1180 micrometers were used as seed particles.

The synthesis of core-shell particles were carried out in a one-liter jacketed reactor with a three-bladed propeller stirrer as presented in details by Gonçalves et al. (2008). Briefly, three strategies were implemented differing in the way in which the monomer was fed into the system. In all of them, the initial charge was composed by distilled water, polystyrene seeds, PVP and ascorbic acid and the monomer feed was composed by initiator and monomer (fed to the reactor at a constant rate of 0.9 g/min). They differ only in the time the system was kept at low temperature in order to the monomer to diffuse into the polystyrene particles. In the first strategy the swelling time was zero and in the other two

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strategies the respective swelling times were 90 and 130 minutes. Batch and semi-batch methyl methacrylate suspension polymerization were implemented as discussed by Gonçalves et al. (2008).

Polymer composition was determined by $^1$H NMR (Bruker Avance spectrometer at 20ºC and 500 MHz). The efficiency of incorporation was defined as the ratio of the MMA fed to the reactor and the MMA effectively incorporated to the particles. Transmission Electron Microscopy (Hitachi 7000 at 75 kV) was used to study the morphology of the particles. Composition mapping was carried out with Fourier Transform Infrared Spectroscopy – FTIR (Nicolet 5DXC Spectrometer with an optical microscope). The particles were sliced with an ultramicrotome to obtain cross-section with 1 micrometer thickness. They were deposited on KBr tablets before analysis and the peak at 1740 cm$^{-1}$ was used to determine the presence of PMMA. Scanning Electron Microscopy (SEM, Philips XL-30) was used to evaluate the core-shell particle surface and the morphology of the secondary particles; images were obtained at 15kV from gold coated samples. The procedures used for polymer separation and purification were described by Gonçalves et al., (2009).

Results and Discussion

Shell formation

The total amount of MMA incorporated into the seed particles with 0.23% of BPO is presented in Table 1. In addition, Figures 1 – 3 present the particle morphology obtained when the swelling time was increased from 0 to 130 min. These figures combined TEM micrographs with IR data of the cross-section of the particles. Each image in TEM micrographs corresponds to the approximate position in the particle diameter as indicated in Figures 1(a), 2(a) and 3(a). In Figure 1(b), the cross-section of the particle was scanned with IR starting in position P1, which is near the particle surface, passing through the center of the particle (at P4 and P5) and reaching the other side of the cross-section at P8; the same is valid for Figures 2(b) and 3(b). Figure 4 presents the evolution of monomer conversion in the bulk polymerization carried out with the same monomer/initiator/seed ratio.

<table>
<thead>
<tr>
<th>Swelling time (min)</th>
<th>PMMA – shell polymer (mol%)</th>
<th>Efficiency of incorporation (%)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>3.0</td>
<td>11</td>
</tr>
<tr>
<td>90</td>
<td>9.0</td>
<td>38</td>
</tr>
<tr>
<td>130</td>
<td>23.0</td>
<td>97</td>
</tr>
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Figure 1. TEM images and IR spectra of a typical core-shell particle obtained with swelling time of 0 minute and 0.23 mol% of BPO (PMMA appears as light gray and PS as dark gray; 6.000X).

Figure 2. TEM images and IR spectra of a typical core-shell particle obtained with swelling time of 90 minutes and 0.23 mol% of BPO (PMMA appears as light gray and PS as dark gray; 6.000X).
TEM images and the approximated representation of the cross section of the particle (6.000X).

Figure 3. TEM images and IR spectra of a typical core-shell particle obtained with swelling time of 130 minutes and 0.23 mol% of BPO (PMMA appears as light gray and PS as dark gray; 6.000X).

Analyzing these data is worthwhile reminding that the solubility of BPO in water is very small ($3 \times 10^{-4} \text{g}/100\text{g}_{\text{water}}$, ALDUNCIN et al., 1994) and that it was fed dissolved in the monomer. Comparison of TEM and IR results showed that TEM morphologies agreed very well with those determined by IR mapping. IR spectra confirmed that PMMA concentration was not uniform along the particle radius. PMMA concentration, denoted by the intensity of carbonyl absorption bands at 1740 cm$^{-1}$, reached maximum values near the particle surface and decreased along the particle radius. TEM images show that the PMMA was distributed forming domains within the polystyrene matrix. These domains resulted from the phase separation of the PS and the newly formed PMMA, because these two polymers are incompatible.

When no swelling time was allowed, Figure 1 shows that a sharp core-shell morphology was obtained, namely only the outer layers of the particle contained PMMA. When the swelling time was increased to 90 minutes, the shell became thicker but still the
core of the particle was essentially free from PMMA. 130 minutes of swelling led to a less defined morphology with a continuous decrease of the PMMA concentration from the surface to the center of the particle. After initiator and monomer enter the seeds, diffusion toward the center of the particle and polymerization occur simultaneously. With increasing swelling time, more time is available to monomer/initiator to diffuse before polymerize resulting in a thicker shell.

Table 1 shows that the swelling time severely affected the fraction of PMMA incorporated into the polymer particles and that long swelling times (130 minutes) were required to achieve the incorporation of almost all the MMA. When no swelling time was used (meaning that the monomer was added at the polymerization temperature) only a thin shell was obtained and most of the monomer polymerized before entering the seeds forming secondary particles.

In Figure 4 it can be seen that monomer conversion reached high conversion in 40-50 min. The combination of this piece of information with the particle morphologies shown in Figures 1-3 leads to the conclusion that the rate of diffusion of the monomer through the polymer particles played a critical role in determining the morphology of the particles. As the polymerization was faster than monomer diffusion, well defined core-shell structure (high concentration of PMMA at the shell and no PMMA at the core) were obtained when no or short swelling times were used. However, this resulted in a substantial polymerization in the aqueous phase namely in a less efficient incorporation.

It is also worth noting that in all cases it was not obtained a well-defined core-shell morphology as the surface of the particles was composed by polystyrene with PMMA domains below the surface. This kind of morphology was obtained because the system was not under thermodynamic equilibrium as the polymerization rate is much faster than the diffusion of PMMA/MMA in the swollen seed particles. This resulted in the formation of PMMA domains close to the surface of the particle instead of a continuous PMMA shell.

Secondary particles formation

The reaction products were separated in three distinct fractions: core-shell particles, “agglomerate-like” particles (sizes from a few micrometers to one millimeter) and the aqueous phase. One drop of the aqueous phase was deposited on a copper grid to be evaluated by TEM, demonstrating the presence of secondary submicron particles (Figure 5(a)). Figure 5(b) presents SEM images of the agglomerates. The $^1$H NMR spectra of the submicron particles and the agglomerates are presented in Figures 6(a) and 6(b), respectively.
TEM and SEM images showed the presence of particles with an average size of 300 nanometers in the aqueous phase, which explains the changes of the water phase from transparent to opaque. These submicron particles formed the agglomerates of irregular shape with sizes from a few micrometers to one millimeter (Figure 5(b)). In all cases the weight fraction of agglomerates was much higher than the fraction of submicron particles. Actually, only less than 2 wt% of the total of secondary particles was found as submicron particles.

The spectra presented in Figures 6(a) and (b) demonstrated that the agglomerates and the submicron particles were composed only by PMMA because of the presence of peaks at 0.8 and 1.3 ppm (characteristic of C-CH\textsubscript{3} group) and 3.6 ppm (characteristic of O-CH\textsubscript{3} group) and because there was no peaks at the region characteristic of polystyrene aromatic ring (between 7.2 and 6.2 ppm).

The formation of the agglomerates can be explained by the fact that no surfactant was added to the system and the amount of PVP employed was not enough to guarantee the
stabilization of the large surface area generated by the nucleation of submicron particles during the reaction. Therefore, as the submicron particles were formed, most of them coagulated. These newly formed agglomerates continued to coagulate with submicron particles and other agglomerates until sizes large enough to be stabilized by the suspension stabilizer (PVP) were reached.

The small diameters of the secondary particles suggest that they could not be formed through a conventional suspension polymerization mechanism. Suspension polymerization systems generate particles in the micrometric scale, i.e., at least 2 orders of magnitude larger than the submicron particles produced here (CHATZI e KIPARISSIDES, 1994; TANAKA, 1985; YUAN et al., 1991; ZERFA e BROOKS, 1996; KONNO et al., 1982). In addition, they could not be formed by the erosion of the monomer swelled seed particles, since there was no polystyrene in their composition.

**Secondary Particle Formation – Influence of monomers**

Taking into account the results presented above, the formation of secondary particles was investigated by using monomers of different water solubility. Experiments were carried out using the same reaction procedure and 90 min swelling time. Styrene, methyl methacrylate and methyl acrylate were used to prepare the shell (BPO as initiator at 0.23 mol%). The water solubility of these monomers are 0.0271 (25ºC), 1.59 (20ºC) and 5.2 (20ºC), respectively (ZHANG e RAY, 1997; MIN e RAY, 1974).

The fraction of secondary particles formed in each case were 3%, 60% and 88%, respectively. It may be observed that the water solubility of the monomer strongly influenced the formation of secondary particles. Although many factors are known to influence the secondary particle formation in dispersed polymerization systems (such as the type and concentration of the surfactant, feed conditions in semibatch systems and reaction conditions) the increase in the fraction of secondary particles formed is closely related to the monomer used since all other experimental conditions were kept constant and the main difference between the monomers is their water solubility. Styrene, which is rather water insoluble, was almost totally incorporated in the seeds, while a large fraction of MMA and methyl acrylate polymerized outside the seed particles. The results obtained with MMA and MA are at first sight surprising, because considering the particle / water partition coefficients of these monomers (K_{MMA}= 38; K_{MA} = 11) under equilibrium conditions, only 7 % of MMA and 19 % of MA were in the aqueous phase, the rest being in the seed particles. In addition, a rather water insoluble initiator (BPO) was used in these experiments, which under thermodynamic equilibrium conditions should be mostly in the
organic phase. This would result in a much lower fraction of secondary particles. Therefore, the system could not be under thermodynamic equilibrium conditions, namely, the process was mass transfer limited.

A mechanism that may explain these results is as follows. A fine dispersion of monomer droplets containing the initiator was fed into the reactor containing a dispersion of polystyrene suspension particles. Monomers could diffuse relatively fast to the seed particles but diffusion within the hard seed particles may be slow. The initiator, which is rather water insoluble, diffused slowly to the aqueous phase and then to the polymer particles. Some of the initiator decomposed in the aqueous phase forming radicals. These radicals may react with the monomer dissolved in the aqueous phase. Because of its low water solubility this was not a likely process for styrene, but the likelihood substantially increased for MMA and even more for MA. The oligoradicals formed precipitated when they reached a critical length, and the precipitated polymer was stabilized by the poly(vinyl pyrrolidone) present in the reactor, forming secondary particles. These particles correspond to the so-called submicron particles. According to this mechanism, it is expected that the number of secondary particles increased with the water solubility on the monomer, i.e., with the likelihood of occurrence of polymerization in the aqueous phase. From the instant of their formation, newly formed particles were plasticized by absorbed monomer, therefore no limitations to the monomer mass transfer within the secondary particles occurred and polymerization was relatively fast in these particles. Another factor that may accelerate the polymerization rate in the secondary particles as compared with the seed particles was radical compartmentalization. Poly(vinyl pyrrolidone) is a polymeric stabilizer that does not diffuse fast through the aqueous phase and hence it is not efficient stabilizing newly formed particles. Therefore, massive coagulation of the submicron particles occurred yielding micrometer aggregates.

Conclusions

Core-shell particles with sizes suitable for rigid foams were obtained by seeded suspension polymerization of methyl methacrylate using polystyrene particles as seeds. The particles presented a complex morphology with a polystyrene core and a shell composed by PMMA domains distributed in the polystyrene matrix. Shell thickness and the amount of MMA incorporated as a polymeric shell to the seed particles were strongly influenced by the strategy adopted for monomer feeding into the system: the higher the swelling time, the higher both the shell thickness and the fraction of PMMA formed inside the seeds as a shell. However, the less sharp the interface between the core and the shell.
The formation of secondary particles during seeded suspension polymerization was investigated. Images from SEM and TEM demonstrated that these secondary particles, presenting diameters of a few hundred nanometers, are dispersed in the water phase or are present as micrometric, irregular agglomerates, since no surfactant was added to the system in order to stabilize them. \(^1\)H NMR did not detect the presence of polystyrene in the secondary particles, indicating that they were not formed by erosive breakage of the swollen primary particles. The fraction of secondary particles formed increased when monomers with higher water solubility were used. These results were in agreement with a mechanism in which secondary particles were formed by homogeneous nucleation as well as the nucleation of the monomer droplets depending of the experimental conditions.

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Referências Bibliográficas

O. H. Gonçalves; J. M. Asua; P. H. de Araújo; R. A. F. Machado Polymer, 2009a, 50, 375.