Improvement of wall thickness uniformity of thick-walled polystyrene shells by density matching

Meifang Liu [a], Sufen Chen [a], Xiao bo Qi [a], Bo Li [a], Ruiting Shi [a], Yiyang Liu [a], Yongping Chen [b,c], Zhanwen Zhang [a,*]

[a] Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, China
[b] School of Energy and Power Engineering, Yangzhou University, Yangzhou, Jiangsu 225127, China
[c] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, Jiangsu 210096, China

HIGHLIGHTS

- Wall thickness uniformity of PS shells is improved by adjusting density matching.
- The sphericity is much less sensitive to the density matching.
- Mechanisms of density matching affecting wall thickness uniformity are proposed.

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ABSTRACT

The uniformity of wall thickness is one of the hardest specifications to fulfill for thick-walled polystyrene (PS) shells prepared by microencapsulation. To improve the wall uniformity of thick-walled PS shells, both density matching between the inner water phase (W1) and the oil phase (O), and that between the W1/O compound droplets and the outer water phase (W2) were intensively studied. The results showed that the centering of W1/O compound droplets, the location and movement of W1/O compound droplets in the W2 phase were significantly affected by the density matching level, which resulted in the variation in wall thickness. For PS shells with 850 μm inner diameter and 25 μm wall thickness, when the density matching between the W1/O compound droplets and the W2 phase was in the range of -0.007 g cm^{-3} to 0.001 g cm^{-3}, the wall uniformity of the PS shells became better. With the density differences between the W1 and the W2 phases ranging from -0.007 g cm^{-3} to 0.007 g cm^{-3}, the wall uniformity of the PS shells can be further improved. By optimizing the density matching level among the three phases, the batch yields of PS shells with the wall thickness variation less than 5 μm increased from about 15% to above 84%. Compared with the wall uniformity, the sphericity of PS shells was much less sensitive to the density matching level. The relevant mechanisms of how the density matching affecting the wall uniformity and the sphericity of the PS shells were also discussed.

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1. Introduction

Polymer microcapsules (also called as microspheres) with specified diameters and wall thicknesses have been widely used in many fields such as in the pharmaceutical industry, in chromatography, in bioreactors and in inertial confinement fusion (ICF) experiments [1–3]. One technically challenging application of such polymer microcapsules in ICF implosion experiments is the preparation of hollow polymer microcapsules (polymer shell) with further stringent specifications on sphericity, wall thickness uniformity and surface finish [4–6]. Most polymer shells used in ICF implosion experiments, such as polystyrene (PS), poly

(α-methylstyrene) (PAMS), resorcinol–formaldehyde (RF) and divinylbenzene (DVB) foam shells, have usually been made by microencapsulation technique, which includes an inner water phase (W1), an oil phase (O) and an outer water phase (W2) [7,8]. To obtain polymer shells with good sphericity and high uniformity of wall thickness, precise control of the microencapsulation process is critical and has been being a challenge, especially for large diameter and/or thick-walled polymer shells [6]. It has been reported that proper choice of the density matching level among the W1, O and W2 phases is one of the most effective methods to improve the wall uniformity and the sphericity of polymer shells [7–19].

To improve the density matching among the W1, O and W2 phases, the ratios of benzene to 1,2-dichloroethane (DCE) were changed to adjust the density of O phase [7,8]. The density matching between the W1 phase and the O phase was expected to be

* Corresponding author. Tel.: +86 0816 2494151; fax: +86 0816 2493148.
E-mail address: bjzzw1974@sohu.com (Z. Zhang).

controlled by the solvent ratio. However, it has been found that the density of the O phase changed significantly during the solidification process (solvents removal) due to the differing solubility of the two solvents in water [9,10]. Hence, the density matching between the W1 phase and the O phase was difficult to be controlled during the removal of these solvents (solidifying process). Moreover, the diameter of the shells and their wall thicknesses ranged from 100 µm to 1500 µm and 10 µm to 120 µm in that prior work, respectively. For this wide range of microcapsules, it was impossible to obtain a good density matching between the W1/O compound droplets and the W2 phase due to the substantial differences among the average density of the W1/O compound droplets. Later, to obtain mono-dispersion of W1/O compound droplets, a triple orifice droplet generator was developed so as to quantitatively control the inner diameter (ID) and the outer diameter (OD) of a W1/O compound droplet [11]. Consequently, the density matching between the W1/O compound droplets and the W2 phase could be quantitatively controlled. Then, to improve the sphericity and wall uniformity of polymer shells, Overturf et al. [12] and Takagi et al. [13] advised that the density of the W2 phase should be close, but slightly less than that of the W1/O compound droplets. However, Schroen-Carey et al. [11] noticed that the density was affected by the gelation time, polymerization temperature and so on. Therefore, it was difficult to obtain the semi-quantitative relationships between the density matching and the wall uniformity or the sphericity. In 1998, Cook et al. [14] pointed out that for shells with a given diameter, there was an optimum range of density matching. They further emphasized that the optimum range must be corrected by experimental results due to the oversimplified nature of the model used. In 2000, Takagi et al. [15] reported that a slight density difference among the W1, O and W2 phases resulted in non-uniform wall or deformed shape, but there was no clear quantification of the term "slight density difference". In 2003, to study the effects of the density matching on the non-concentricity (NC) of DVB foam shells, Streit and Schroen [16] used deuterated water (D₂O) to control the density of the W1 phase. Their results showed that it was difficult to determine the effects of density matching alone on the NC of DVB shells since some other factors such as temperature and agitation also affected the NC. In 2006, the experimental results of Paguio et al. [17] showed that a slight density mismatch between the inner phase and the middle phase improved the wall thickness uniformity of resorcinol formaldehyde shells. They still did not give the quantitative details of the term "slight density mismatch". In 2009, Bei and Jones [18] used electric fields to form concentric double emulsion droplets. They also emphasized that the density matching still should be controlled within 0.1% to meet high concentricity and sphericity specifications even when using an electric field method. More recently, Lattaud et al. [19] also utilized D₂O to adjust the density matching between the W1 and the O phases. With the density of the W1 phase being slightly higher than that of O phase, foam shells with low NC were obtained in their work. However, for a W1/O compound droplet with a given size, the density matching level between the W1/O droplets and the W2 phase also changes with varying the density of the W1 phase. Therefore, it is difficult to determine whether the improvement of NC results from the density matching between the W1 and the O phase or from that between the W1/O droplets and the W2 phase (or possibly from both).

From these literature results, it is clear that achieving appropriate density matching among the three phases has been being a research focus in the production of polymer shells with uniform wall and good sphericity. However, the densities of the O phase and that of the W1/O compound droplets always change because of the removal of organic solvent in the O phase. The density matching level among the W1, O and W2 phases also changes during the solidifying process. Both the density matching between the W1 and O phases and that between the W1/O compound droplets and the W2 phase probably have an influence on the wall uniformity and the sphericity. Therefore, before optimizing the density matching level between the W1 and O phases, the change of density matching level between the W1/O compound droplets and the W2 phase during the solidifying process must be intensively studied. However, as stated above, the relationships between the density matching and the resulting wall uniformity or the sphericity are not clear enough and the possible mechanism underlying these are also not clear.

To clarify the effects of the density matching on the wall uniformity and the sphericity, the focus of this work is to study the density matching level among the W1, O and W2 phases. The inner diameter and the wall thickness of PS shells were set as 850 µm and 25 µm, respectively. Firstly, the solidifying temperature and the initial PS mass fraction in the O phase were optimized. Then, the density matching levels between the W1/O compound droplets and W2 phase were controlled by adjusting the concentrations of polyvinyl alcohol (PVA) and/or anhydrous calcium chloride anhydrous (CaCl₂) as additives in the W2 phase. Finally, based on the obtained optimum density matching level between the W1/O compound droplets and W2 phase, the density matching levels among the W1, O, and W2 phases were further optimized by regulating the concentrations of ammonium nitrate (NH₄NO₃) added in the W1 phase and the concentrations of CaCl₂ added in the W2 phase at the same time. The mechanisms of how the density matching affecting the wall thickness uniformity and the sphericity of PS shells were also discussed.

2. Experimental

2.1. Materials

PS ($\overline{M}_w$ = 250 kg mol^{-1}, ρ_s = 1.05 g cm^{-3}, Acros Organics Inc.), PVA ($\overline{M}_w$ = 13–23 kg mol^{-1}, 87–89% mole hydrolyzed, Aldrich Company), D₂O (Shanghai Jingchun Reagent Ltd.), CaCl₂ and NH₄NO₃ (Chengdu Kelong Chemical Reagent Factory) were all used as received without further purification. FB (Shanghai Jingchun Reagent Ltd.) was purified by distillation. Distilled, deionized water was used in the preparation of all aqueous phases.

2.2. Preparation of PS shells

Compound droplets (W1/O) were generated by a triple orifice droplet generator (shown in Fig. 1(a)). Pure water, a mixture of pure water and D₂O with different ratios, and aqueous NH₄NO₃ solutions with differing mass concentrations were used as W1 phases of differing densities. The PS/FB solutions with differing PS mass fractions (5.6%, 8.2%, 10.6%, 15.1% and 19.1%) were used as the O phases in this work. Aqueous solutions of PVA and CaCl₂ with differing mass concentrations were used as the W2 phases (of varied density). As shown in Fig. 1(a), the W1, O and W2 phases were delivered into the triple orifice droplet generator by three syringes, which were controlled by three pumps, respectively. The W1 phase left the W1 tube and was surrounded by the O phase. Then, the encapsulated drop of the W1 phase surrounded by O phase was stripped off from the W2 phase, forming the W1/O compound droplets in the W2 phase. The W1/O compound droplets were collected in an 800 ml cylindrical flask filled with 150 ml of the W2 solution.

To limit the possible effects of shell size and wall thickness on the density matching, the ID and wall thickness of the PS shells in this work were set as 850 µm and 25 µm, respectively. With the assumption that the amount of PS and the inner diameter