

Response Surface Methodology for Design of Porous Hollow Sphere Thermal Insulator

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Abstract. In this study, response surface method is used for synthesizing polystyrene (PS) as sacrificial templates and optimizing the particle size. Three factors of initiator, stabilizer concentration and also stirring rate were selected as variable factors. Then, three different concentration of tetraethyl orthosilicate (TEOS) added to reaction media and core-shell structure with PS core and silica shell was developed. Finally, core-shell structure was changed to hollow silica sphere for using as thermal insulator. We observed that increased initiator concentration caused to larger PS particles, increase the stirring rate caused the smaller PS and also with increased the stabilizer concentration obtained that particle size decrease then after 2.5% began to increase. Also the optimum amount of TEOS was found.

1. Introduction

Recently, the synthesis of inorganic spheres with hollow structures such as TiO₂, SiO₂, ZnO, calcium silicate [1-4] and etc. had attracted a lot of attention because of many extraordinary properties such as low density, low toxicity, good chemical, thermal stability and large surface area. Sacrificial templates such as polystyrene [5] were commonly used to prepare hollow spheres. Silica hollow spheres have a wide range of application for thermal insulation [6]. Polystyrene due to easily synthesis and uniform particles is attractive as a template. In many cases, spherical polymeric micro particles are synthesized by suspension polymerization as a template for core-shell structure [7].

For preparing silica shell sol-gel process was usually used. Sol-gel polymerization of TEOS, involves hydrolysis and condensation reaction. The pH of the reaction media, type of catalyst and proportion of solvent to precursor are important and effective parameters on preparation of silica particles [8]. In a research, mineral insulators in paint for wall coatings has been simulated for flow field and temperature distribution in a room [9, 10]. The results showed that the coating with mineral particles has leads to a 17% decrease in energy consumption.

In this research, response surface experimental design as an efficient way [11, 12] was used in suspension polymerization for synthesizing of polystyrene template and the effect of initiator concentration; stabilizer and stirring rate on polystyrene particle size were investigated. Then, the best sample was selected and core-shell structure with polystyrene core and silica shell with different shell thickness were synthesized by sol-gel process. Finally, silica hollow spheres were obtained by calcinations process and pouring it into THF solvent.



2. Experimental

2.1. Materials

Styrene as a monomer, poly(vinyl alcohol) (PVA, $M_w \sim 128000$) used as a stabilizer, tetraethyl orthosilicate as a precursor, ethanol and HCl (37%) for sol-gel process and tetrahydrofuran (THF) were purchased from Merck company (Germany). Benzoyl peroxide as an initiator was purchased from Alfa Aesar Company (USA). Styrene was distilled before using and other chemicals used without any purification. Also deionized water (DI water) was used throughout all of the experiments.

2.2. Synthesis of PS template and preparation of hollow silica spheres

Polystyrene templates with various sizes were synthesized by suspension polymerization. Amount of initiator, stabilizer and stirring rate were investigated in 1-3 wt%, 1-4 wt% of monomer and 550-750 rpm, respectively. Table 1 shows experimental conditions for the synthesis of polystyrene. Suspension polymerization was carried out in 500 ml three-necked flasks equipped with a condenser styrene monomer (20gr) and benzoyl peroxide was poured in the reactor and nitrogen was purged for 20 minutes to remove dissolved oxygen. The vessel was heated to 90 °C and PVA was added to reactor after 10 minutes then the polymerization was continued for 8 hours under a stirring according to the condition of the table 1.

Table 1. Preparation conditions for polystyrene synthesis.

Sample	Initiator concentration (wt%)	Stabilizer concentration (wt%)	Stirring rate (rpm)
S-1	1	1	550
S-2	3	1	550
S-3	1	4	550
S-4	3	4	550
S-5	1	1	750
S-6	3	1	750
S-7	1	4	750
S-8	3	4	750
S-9	0.48	2.5	650
S-10	3.52	2.5	650
S-11	2	0.21	650
S-12	2	4.8	650
S-13	2	2.5	500
S-14	2	2.5	800
S-15	2	2.5	650
S-16	2	2.5	650

To achieve uniform shells, smooth and spherical cores silica spheres were prepared via a sol-gel process in a Stöber method [13]. At first, prepared PS templates were ultrasonically treated with 20 ml of ethanol for 15 minutes to obtain a well dispersed suspension. The suspension was transferred into a 250 ml flask and heated to 70 °C in a water bath and kept stirred for 90 minutes. Then, tetraethyl orthosilicate (TEOS) and ethanol solution was added drop wisely to the suspension in 180 minutes and stirring (250 rpm) was kept for 5 hours. The pH of reaction was adjusted to value about of 1.5 by adding HCl solution. The pH value of the reaction solution was kept at about 1.5 during the coating process by adding of the HCl. In table 2 the values of the synthesis conditions for the experiment were shown.

Table 2. Preparation conditions for SiO₂-coated PS templates.

Sample	PS (gr)	TEOS (mol)	Ethanol (ml)	pH
CS-1	2	0.024	20	1.5
CS-2	2	0.033	30	1.5
CS-3	2	0.043	45	1.5

Calcination is one of the methods for removing polystyrene cores from core-shell particles. Therefore, a drop of suspension in ethanol was placed on an aluminum sheet and dried. It was then placed in furnace and heated at a rate of 1 °C/min to 500 °C with air flow and kept at 500 °C for 3 hours. After this time, it was cooled to room temperature. For completely removal of polystyrene, hollow silica spheres were kept in THF solvent for 14 days to extract the residue polystyrene.

2.3. Characterization

The Malvern Master Sizer 2000 dynamic light scattering (DLS) was used to measure particle sizes in this study. Scanning electron microscopy (SEM) Leo 1455VP and field emission scanning electron microscopy (FE-SEM) Mire 3-XMU were used to investigate the morphologies of the polystyrene templates, the silica-coated latex template core-shell composites and the hollow silica spheres.

3. Results and discussion

3.1. Effect of different synthesis parameters on particle size

The particle size of polystyrene synthesized by suspension polymerization was obtained are between 100-320 μ . Effect of initiator concentration on particle size is shown in figure 1.a. It was found that by increasing the initiator concentration, larger polystyrene particle are obtained. This event can be attributed to balance the system and polymerization rate at the beginning of the reaction. When the initiator concentration increase in system, activated site and rate of polymerization were increased too.

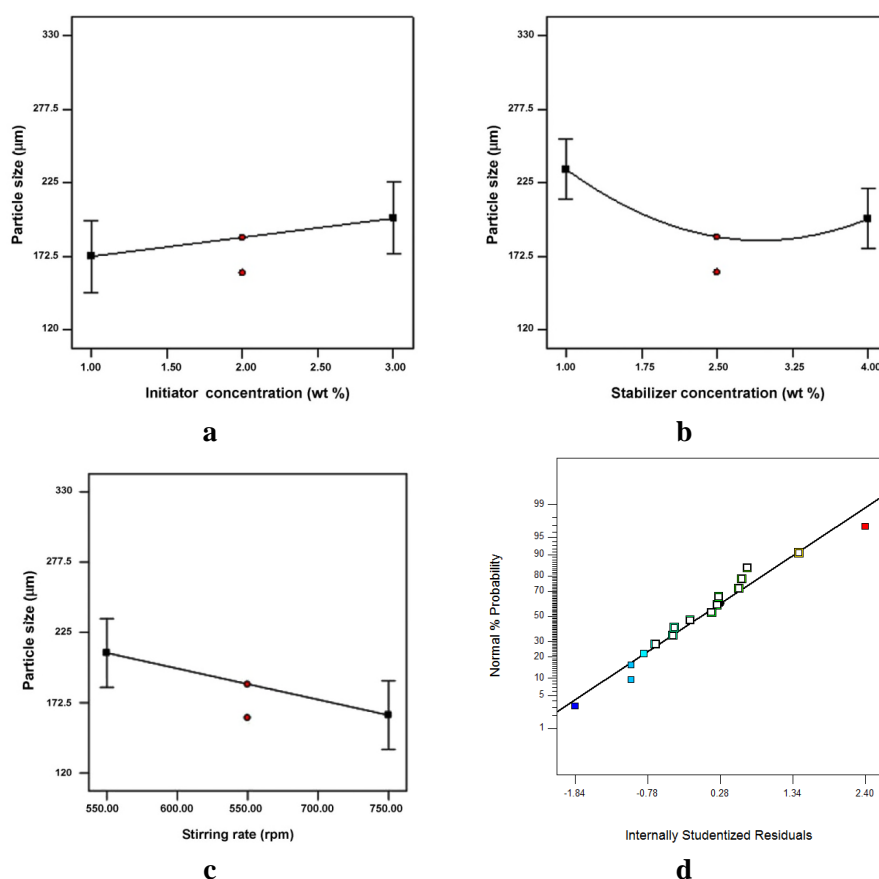


Figure 1. a) Initiator concentration (wt%)-particle size curve by constant value for stabilizer concentration (wt%) and stirring rate (rpm), b) Stabilizer concentration (wt%)-particle size curve by constant value for initiator concentration (wt%) and stirring rate (rpm), c). Stirring rate-particle size curve by constant value for initiator concentration (wt%) and stabilizer concentration (wt%) and d) Normal distribution curve.

The next parameter affecting is stabilizer concentration. The effect of this parameter on polystyrene particle size in range of investigating is shown in figure 1.b. Stabilizer creates a film around monomer droplets, so it causes droplets not to coagulate. Stabilizer leads to decreasing interfacial tension, then the possibility of colliding the droplets is decreased. As a result, smaller particles are obtained. However, it must be noticed that with increasing the stabilizer concentration to about 2.5 wt%, the particle sizes are increased. The reason of this phenomenon, stabilizers coagulate, deactivate in the media and the bridging effect is included.

As it can be seen in figure 1.c, in range of 550-750 rpm with enhancing the stirring rate, decreasing in the sizes of polystyrene particles can be observed. In suspension polymerization, each monomer droplet acts as a bulk reactor; therefore, final size of polymer was influenced by the size of initial monomer droplets. The monomer droplets sizes are decreased by increasing stirring rate because of the stress is created by stirrer.

According to sum of squares and P value, that amount of P factor is lower than other modeling, the linear model was selected as a selective model and all of curves and results were studied by this model. In the linear model, the amount of P value was 0.0134.

In this work, the normal distribution investigated to ensure the integrity of the chosen model. According to all of experimental results are around the line (figure 1.d), it can be conclude that suitable model was selected.

3.2. Morphology of particles

SEM images of polystyrene particles have spherical shape. The SEM images and DLS results were in the same manner about the particle size of this sample which was 100 μ and monodisperse in distribution. According to figure 2, When TEOS with amount of 5 (0.024 mol) was used, the shell created incompletely around the polystyrene template and after the calcinations process, the strength of shell was low and it was fractured. The amount of TEOS was increased to 7 gr (0.033 mol) in order to improve the strength of the shell. As can be seen in figure 3, with increasing amount of TEOS, more uniform and completely shell obtained. Also after calcination, broken hollow sphere was not observed. For 0.043 mol of TEOS, the thickness was not changed significantly and the silica particles were agglomerated.

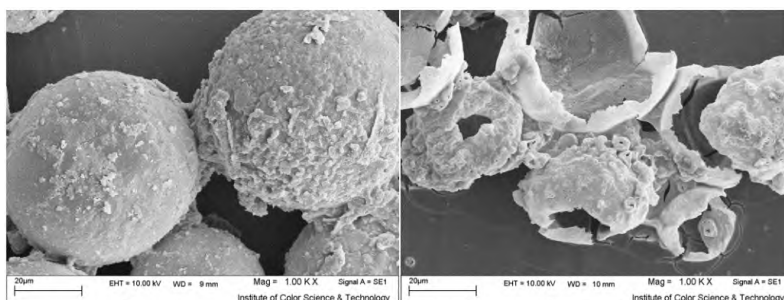


Figure 2. SEM image of CS-1 (left) and hollow sphere of CS-1 after calcination (right).

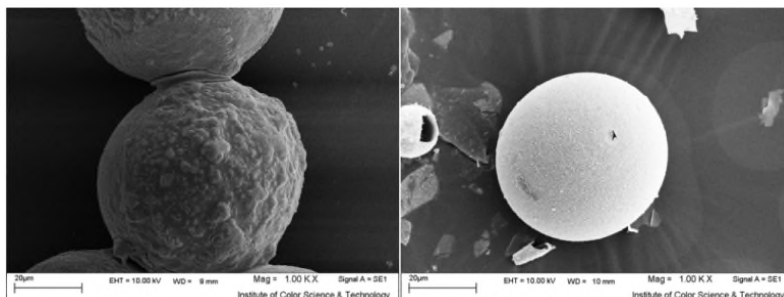


Figure 3. SEM image of CS-2 (left) and hollow sphere of CS-2 after calcination (right).

4. Conclusion

Different sizes of polystyrene particles were prepared by suspension polymerization. It was found out that particle size was increased by increasing the amount of initiator, decreasing the speed of stirrer and increasing stabilizer concentration up to certain level (2.5 wt%). For synthesis of PS/silica core-shell, three levels of TEOS for controlling of shell thickness and strength was investigated. We obtained that, when 0.033 mol TEOS was used, silica shell was created completely and after calcinations hollow silica spheres SEM image showed that hollow spheres had a no fracture and spherical shape of them was maintained.

5. References

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