

Preparation of Core–Shell Glass Bead/Polysulfone Microspheres With Two-Step Sol–Gel Process

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ABSTRACT: Core–shell microspheres made from glass beads as the core phase and polysulfone (PSf) as the shell phase can act as an absorbent in the separation process or a supporter for chemical reactions. Based on phase-inversion principles, a two-step sol–gel method was developed in this work in which ether was added first and H₂O was added second to a PSf-containing dimethylformamide (DMF) solution to help PSf solidify on the surface of glass beads. The results from scanning electron microscopy, Fourier transform IR, and X-ray photoelectron spectroscopy showed that a dense layer of PSf (thin to several microns) was coated on the glass beads and the core–shell microspheres were almost

monodispersed. The utilization percentages of the glass beads and PSf were high as 100 and 80%, respectively. The thickness of the PSf membrane was calculated to be about 4.3 μm . To obtain well-monodispersed microspheres, the practical volume ratio of ether to DMF was recommended to be larger than 4.5. The results suggested that the two-step sol–gel method is a highly efficient process for preparation of glass bead/PSf core–shell microspheres. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3365–3369, 2006

Key words: core–shell polymer; coatings; polysulfone; glass beads; sol–gel process

INTRODUCTION

Core–shell inorganic/polymer and polymer/polymer microspheres have recently gained more importance as media for chemical separation, reaction, and additives in polymers because their structure possesses enough mechanical strength and can be easily modified to improve the separation efficiency and selectivity.^{1–3} Many kinds of materials such as polystyrene,⁴ chitosan, and polypyrrole were employed as shells. Bai and Zhang prepared polypyrrole-coated granules for humic acid removal.⁵ Liu et al. immobilized chitosan onto nonporous glass beads through a 1,3-thiazolidine linker.⁶ In this work polysulfone (PSf) was used as the shell phase, because PSf is a stable, cheap, strong, and nonbiodegradable functional material, which is widely used for making ultrafiltration membranes and supporters for composite membranes, and it can be functionalized with dipyrityl.^{7–9} Glass beads are well known as being preferable as a supporting material. Core–shell microspheres made from glass beads as the core phase and PSf as the shell phase can act as absorbents in separation processes or supporters for chemical reactions.

Normally, emulsion polymerization,^{10–14} surface modification and polymerization,⁶ and rapid expansion of a supercritical fluid solution¹⁵ are used to fabricate core–shell microspheres. In this study, the PSf film coating on the glass beads is formed by the phase-inversion principle. First, PSf is dissolved in dimethylformamide (DMF); second, the PSf-containing DMF solution contacts with water or alcohol, whereby DMF is quickly dissolved in the added water or alcohol while PSf solidifies as a membrane by the phase-inversion process.¹⁶ In the whole process the most critical step is the formation of the shell phase to achieve the monodispersion of core–shell microspheres. The phase inversion of PSf is a complicated sol–gel process; only good control of the process of dynamics and thermodynamics can generate core–shell microspheres with glass beads. At the same time, the microsphere monodispersion and the high utilization to core and shell materials are of importance to the evaluation of the whole preparation process. A new two-step sol–gel method is used to prepare core–shell glass bead/PSf microspheres. The dispersion of the microspheres and utilization efficiency as raw materials are further evaluated.

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EXPERIMENTAL

Preparation of core–shell microspheres

PSf was dissolved in DMF to a final concentration of 5% (w/w). A certain DMF solution was placed in a

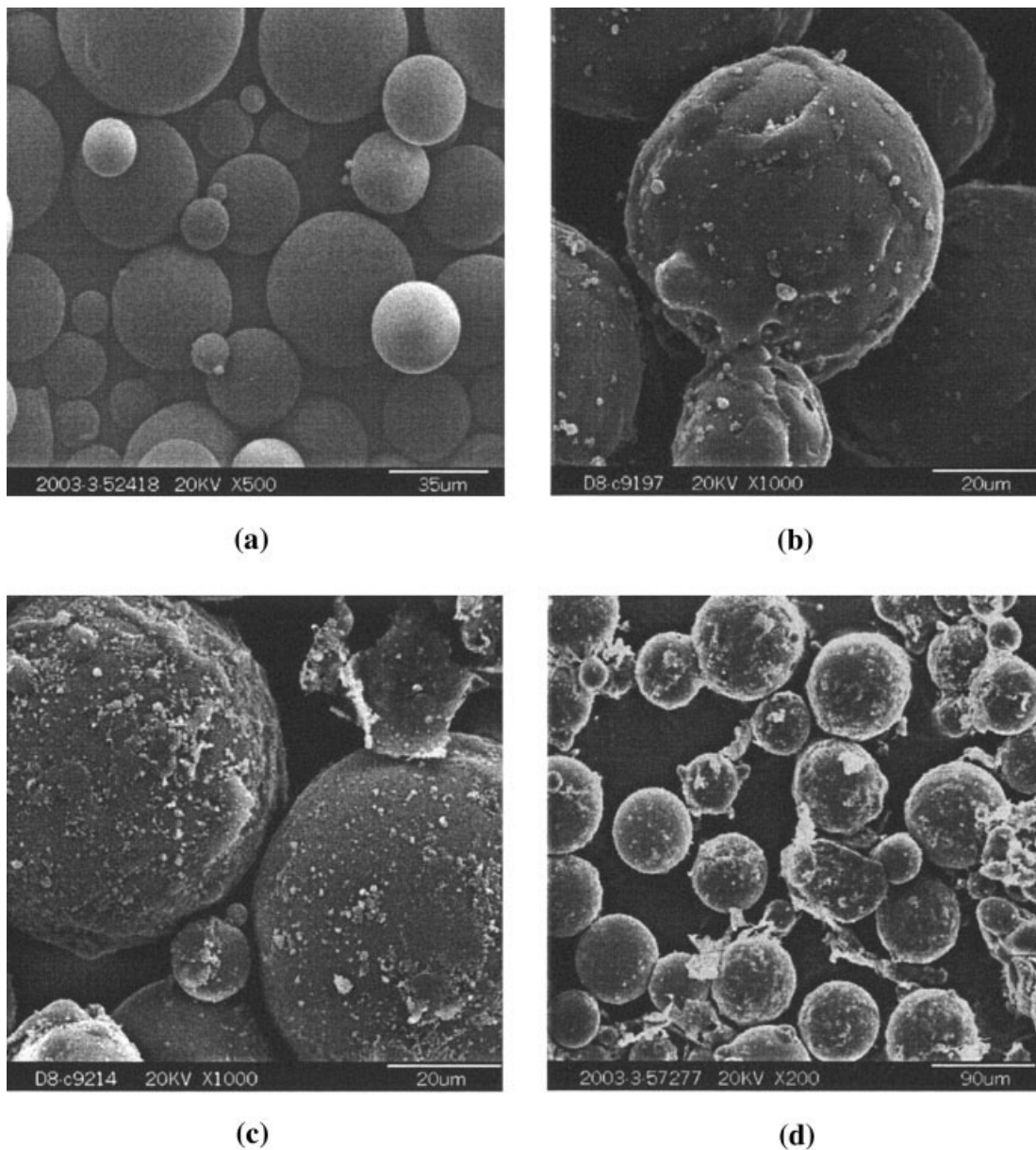


Figure 1 SEM photos for (a) bare glass beads and (b–d) core-shell microspheres.

flask, and then the micron-size glass beads were added and immersed in the solution. Ether was dropped into the mixture while stirring with a glass rod, and distilled water was added. After being separated from the liquid by centrifugation, the formed microspheres were washed with acetone and water 4 times and then dried at 55°C. Because the solvents used as precipitators (ether and water) were added in two consecutive steps, the procedure is named the two-step sol-gel method. Ether is miscible with DMF; as a result, it can be used as a precipitator whereas its small polarity produces a different solubility for DMF in the dynamics and thermodynamics compared to the solubility of DMF in water. For comparison, a one-step sol-gel process for microsphere preparation was in-

cluded, in which the distilled water was directly dropped into the mixture of glass beads and DMF solution to solidify PSf. The microspheres formed in the two processes were further evaluated with different methods.

Scanning electron microscopy (SEM)

SEM (Hitachi S-450) was employed to observe the surface morphology of bare glass beads and the obtained core-shell microspheres.

Fourier transform ir (FTIR) spectroscopy

FTIR (Shimadzu FTIR-8201 PC) was used to characterize the absorption peaks for different materials.

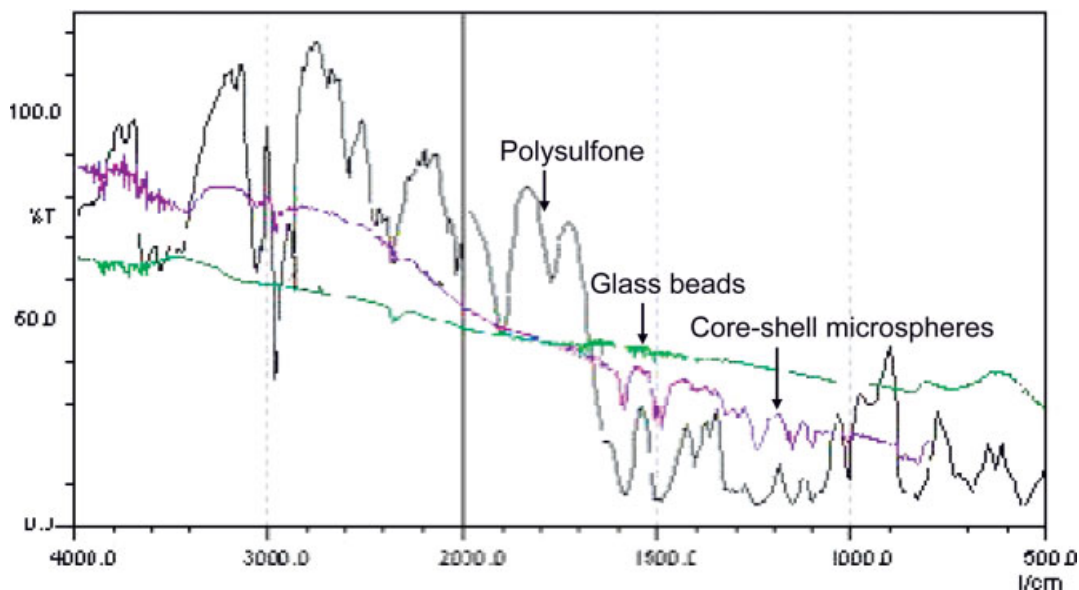


Figure 2 FTIR spectra for PSf, bare glass beads, and core-shell microspheres obtained in the two-step sol-gel process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

X-ray photoelectron spectroscopy (XPS)

XPS (PHI-5300 ESCA) was used to analyze the element composition on the surfaces of the glass beads and core-shell microspheres.

Off weight method

The weights of coated microspheres before (M_1) and after (M_2) being dissolved with DMF and the weight of PSf in the initial DMF solution (M_3) are used to calculate the utilization efficiency of PSf (E):

$$E = (M_1 - M_2) / M_3 \times 100\% \quad (1)$$

The PSf content in the core-shell microspheres (ω) can be obtained by

$$\omega = (M_1 - M_2) / M_1 \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

PSf solidification in one-step and two-step sol-gel processes

In the one-step sol-gel process, many millimeter-size PSf spheres containing several glass beads were formed and many glass beads were not coated, which means that the desired micron-size monodispersed core-shell microspheres were not obtained. This was because DMF rapidly dissolved in water and at the same time PSf solidified, surrounding the water droplets before water was dispersed into micron-size droplets. Consequently, many glass beads were not coated by PSf.

In the two-step sol-gel process, upon the ether addition in the first step, two phases were formed: the upper milky phase was a mixture of DMF, ether, and some PSf microspheres whereas the bottom phase was a mixture of PSf gel, glass beads, and some solvents of DMF and ether. We found that the PSf gel was not completely solidified and the viscosity was very high. Although ether and DMF are miscible, the presence of PSf in the system had an impact on their solubility in each other. Ether is organic and has a strong interaction with PSf; the added ether would extract most of the DMF from the PSf-DMF solution. As a result, PSf was partly solidified by a sol-gel process. Moreover, because of the weak polarity of ether, the solubility between ether and DMF differs from that between H_2O and DMF, which is not enough to completely solidify the PSf in the system. Then, in the second step, H_2O with a strong polarity was added, a relatively slowly solidification rate of PSf was observed because H_2O and ether are immiscible. Complete solidification could only be achieved when the existing ether in the micropores of PSf was replaced by H_2O . Ether dispersed among the glass beads in the bottom phase probably helped to avoid the congregation of glass beads during the complete solidification of PSf, which led to the monodispersion of core-shell microspheres.

Observation of microspheres obtained in two-step process by SEM

The SEM photos of pure glass beads and core-shell microspheres are shown in Figure 1. The preparation system contained 1.320 g of DMF containing 5 wt % PSf, 2.0 g of glass beads, 6 mL of ether, and 10 mL of

TABLE I
Element Composition for Different Samples with XPS

Sample	Atom %			
	C1s	O1s	Si2p	S2p
Pure glass beads	60.18	35.30	4.51	0
Polysulfone	86.86	11.48	0.92	0.74
Core-shell microspheres	71.07	25.48	3.08	0.37

H₂O. The pure glass beads showed a very smooth surface [Fig. 1(a)], but there was a layer of irregular material covering the beads after being subjected to the two-step sol-gel process [Fig. 1(b)]. The wrapping layer was very dense [Fig. 1(c)] and the core-shell microspheres were well monodispersed [Fig. 1(d)]. Furthermore, almost all of the glass beads were coated with a thin PSf film, so the utilization percentage of glass beads was nearly 100%.

Characterizing sulfone by FTIR

The FTIR spectra of pure glass beads, PSf, and core-shell microspheres are provided in Figure 2. There are two characteristic absorption peaks for O=S=O bonds in PSf at 1100 and 1250 cm⁻¹. The obtained core-shell microspheres also showed two peaks but there is no peak for pure glass beads, suggesting that PSf exists in the core-shell microspheres.

Elemental component analysis by XPS

The element composition on the surface of the pure glass beads and core-shell microspheres is detailed in Table I. No sulfur was detected on the surface of the pure glass beads, whereas the coated PSf on the surface of the core-shell microspheres led to a positive result for the existence of sulfur. The measured constitution of elements was not consistent with the actual molecular composition because the XPS equipment was too sensitive to C and O elements.

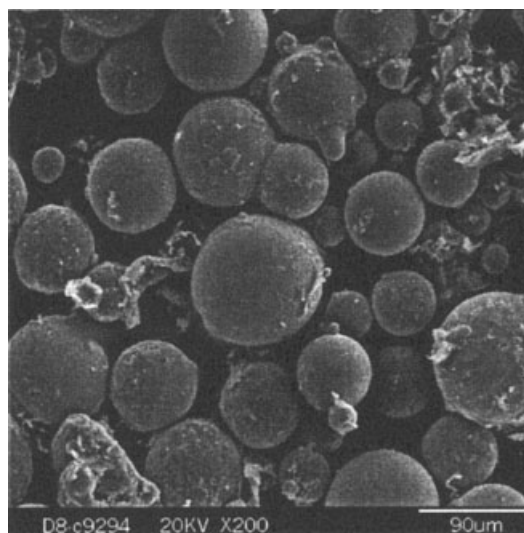
TABLE II
Impact from Addition Amount of Glass Beads and Ether on Utilization Efficiency

Weight of pure glass beads (g)	Volume of aether, (mL)	E (%)	ω (%)
1.8	4.5	98.2	0.036
2.0	6.0	95.0	0.031
2.2	7.5	80.0	0.024
2.4	9.0	87.3	0.024
2.6	6.0	98.5	0.025

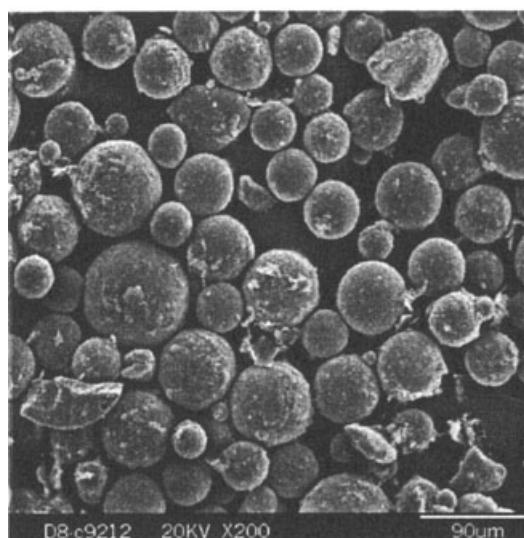
PSf concentration = 5%, DMF solution = 1.320 g.

Impact from amounts of glass beads and ether on utilization efficiency and calculation of thickness of PSf membrane

The utilization efficiency and weight content of PSf in the microspheres are shown in Table II. More than 80% of the PSf was utilized under various conditions. The weight content of PSf in the microspheres was below 5%. The thickness of the PSf film can be estimated by calculation. It was assumed that the densities of the glass beads and PSf membrane were 4.0 and 0.2 g/cm³, respectively. The radius of the pure glass beads was 25 μ m as determined through SEM photos, so the quantity of glass beads was 7.66×10^6 and the weight of coated PSf was 0.062 g (line 2, Table II) with



(a)



(b)

Figure 3 The effect on the monodispersion of microspheres from the addition of (a) 4.5 or (b) 9.0 mL of ether.

a corresponding volume of 0.31 cm^3 . Therefore, the thickness of the coated PSf membrane was $4.3 \mu\text{m}$.

Effect of amounts of ether on monodispersion of microspheres

In a preparation system with 1 mL of DMF containing 5 wt % PSf, 2.0 g of glass beads, and 10 mL of H_2O , a similar monodispersion of the microspheres was obtained with different amounts of ether (Fig. 3). The amount of ether should be enough to extract DMF and separate the glass beads. The practical ratio of ether to DMF should be larger than 4.5.

CONCLUSIONS

A two-step sol-gel method was developed in this work in which ether was added first to a PSf-containing DMF solution and H_2O was added second to help PSf solidify on the surface of glass beads. Results by SEM, FTIR, and XPS showed that well-monodispersed core-shell microspheres were obtained in which the shell was thin to several microns. The utilization percentage of PSf was more than 80% and almost all of the glass beads were coated. The thickness of the PSf membrane was calculated to be about $4.3 \mu\text{m}$. To obtain well-monodispersed microspheres, the practical ratio of ether to DMF was recommended to be larger than 4.5.

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