Preparation of Polysulfone-Coated Chitosan Beads by Emulsion Phase-Inversion Method

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ABSTRACT: A new coating method of emulsion phase-inversion method was suggested, and crosslinked chitosan beads coated with a thin polysulfone (PSF) layer were prepared with the new coating method. The emulsion was composed of PSF, dimethylformamide (DMF), paraffin, and Span 80 as the emulsifier. The effects of the swelling ratio (water content), PSF concentration, phase ratio between PSF in DMF solution and the paraffin phase, as well as coating time on the microstructures and thickness of the coating layer were investigated. The microstructures of the coating layer were determined by SEM microphotographs. Experimental results show that the thickness and the microstructures of the coating layer can be easily controlled with the new coating method. By changing the swelling ratio, PSF concentration, phase ratio in the emulsion, and the coating time, the desired coating layer can be achieved. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3542–3548, 2004

Key words: coatings; gelation; polyelectrolytes; phase separation; swelling

INTRODUCTION

Chitosan, one of the most abundant natural polymers, is readily processible into membrane, beads, and sponges from its aqueous solution. Chitosan beads are highly versatile in controlled drug release, removal of heavy metal ions from waste water, removal and/or recovery of acids from industrial aqueous streams, and enzyme immobilization.[1–8] These beads possess some excellent features such as hydrophilicity, biocompatibility, biodegradability, antibacterial property, affordability, as well as the potential to be chemically modified. However, there also remain some obstacles that keep them from wider applications. The most serious one is its lower mechanical robustness. Crosslink processing has been used as an effective way to improve the stability of the beads.[1,3,4,7] Even with this method, however, the life cycles of the beads are still limited. Thus, new effective ways to treat the beads are profoundly required.

Surface coating has been thought as one of the most effective ways to modify the surface performance. If suitable material can be coated on the surface of the chitosan beads, the stability of the beads will be effectively improved. Polysulfone is in the class of macromolecules that have both sulfone and aryl groups. Polysulfone is very stable chemically and mechanically and has excellent thermal, electrical, and creep resistant properties over a wide temperature range.[9,10] Especially as a medical polymer, because of its durability to hot water, steam, and alcohol, and because it is not noxious, polysulfone is widely used in the manufacture of medical devices. Because of the lack of biocompatibility as well as the porous microstructure of the polysulfone, it can prevent microbes from crossing to chitosan beads, thus making the chitosan beads more stable in microbial environments. In addition, chitosan is a hydrophilic biopolymer, whereas polysulfone is a hydrophobic polymer, which has stronger affinity to nonpolar molecules than polar ones and to organic than to inorganic materials. The polysulfone layer can therefore change the hydrophilicity of chitosan beads and improve their selectivity to organics such as low molecular weight drugs.

In this work a new method to coat a thin layer of inert polymer on chitosan beads is suggested, and polysulfone was selected as the coating material. The polysulfone-coated chitosan beads were prepared and the preparation process was described and discussed in detail. The factors influencing the new coating method were also investigated. As a new technique of microencapsulation, the polysulfone-coated chitosan beads may find applications in controlled release[11] applications and in the removal of heavy metal ions in water extraction solution of Chinese herbal medicines.[12]

EXPERIMENTAL

Materials

Chitosan (deacetylation degree: 0.952; average molecular weight: 1500 kD) was purchased from Yuhuan
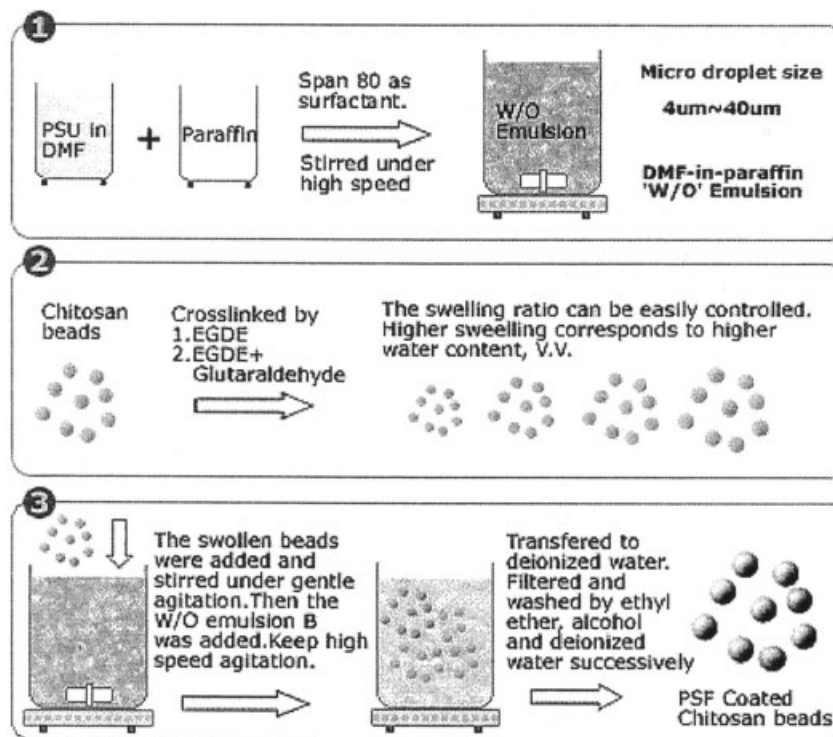
Figure 1   Procedure of the new coating method.

Ocean Biochemical Co. (China). Polysulfone (intrinsic viscosity: 0.56) was purchased from BoXiong Chemical Industry (China). Ethylene glycol diglycidyl ether (EGDE) was obtained from TCI (Tokyo Kasei Kogyo Co., Japan). SPAN 80, glutaraldehyde, N,N-dimethylformamide (DMF), and paraffin were purchased from VAS Chemical Co. (China). All materials were used directly without any further purification.

Methodology

The coating approaches used in the present work were derived from the concept of the internal gelation method, which is mainly used to prepare alginate microspheres.[13–17] First, water was impregnated in the chitosan beads as the nonsolvent of polysulfone. Then, the swollen chitosan beads contacted with the solution of polysulfone in DMF. After that, polysulfone was solidified on the surface of chitosan beads, forming a thin layer. Based on this principle, two methods of coating polysulfone on chitosan beads were applied in this work.

The first one is similar to the wet phase-inversion method.[15] With this method, the swollen beads were directly added to the polymer solution. An asymmetric polysulfone layer was then formed and tightly covered on the chitosan beads.

The second is a novel coating method in which the PSF solution was replaced by an emulsion. A certain amount of paraffin and emulsifier (SPAN 80) were added to the PSF solution, and the mixture was stirred at high speed to form a uniform emulsion A. The swollen chitosan beads were then added to the emulsion. After a while, another water/oil emulsion B composed of water and paraffin was added to the mixture under magnetic stirring, thus allowing all the PSF microdroplets in emulsion A to be gelated. The coated beads were separated, filtered, and successively rinsed with ethyl ether, alcohol, and deionized water. The coating procedure is illustrated in Figure 1.

Preparation of crosslinked chitosan beads

Chitosan solution was prepared by dissolving 5 g of chitosan in 100 mL, 2 wt % acetic acid. This solution was dropped through a nozzle into a gelation medium, which was composed of 20% sodium hydroxide, 30% methanol, and 50% deionized water. The formed chitosan beads remained in this solution for 1 h after which they were rinsed with deionized water. The uncrosslinked chitosan was designated as beads **1**. Considering that different crosslinking reagents may result in different hydrophilicity and swelling/dewatering characteristics of chitosan beads, two crosslink methods were adopted. Beads **1** were crosslinked chemically by 5% EGDE in a water–ethanol mixing solution for 12 h at room temperature, then successively rinsed with ethanol and deionized water. The EGDE crosslinked chitosan beads were designated as beads **2**. Beads **3** was obtained by further crosslinking
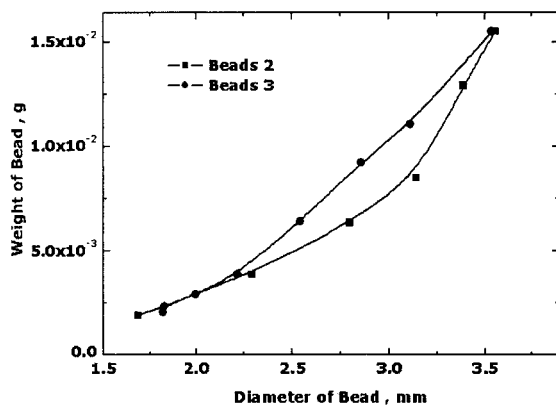
Figure 2 Dewatering curve of crosslinked beads.

Figure 4 SEM microphotograph of coating surface with method 1.

beads **2** by 20% glutaraldehyde in deionized water for 2 h.

The dewatering ratio, swelling ratio, and the change of the average diameter with time at room temperature were measured by weighting and photographing methods. These parameters were used to evaluate the stability of the beads.

Coating of PSF on swollen chitosan beads

Emulsions with different ratios between the polymer solution of 10 wt % PSF in DMF solution and the organic phase of 5 wt % SPAN 80 in paraffin phase were prepared, and the average droplet size was in the range from 3.6 to 6.5 μm. A 1-g sample of the swollen chitosan beads was added to 20 mL of the emulsion under gentle agitation. After 30 s, 5 mL of the water-in-paraffin emulsion (composition: water : paraffin : SPAN 80 = 70 : 28 : 2) was added to the mixture and stirred at high speed for 1 min. The mixture was filtered and the coated chitosan beads were washed with water. The coated and uncoated chitosan beads were photographed, and the diameter and the thickness of the coating layer were calculated.
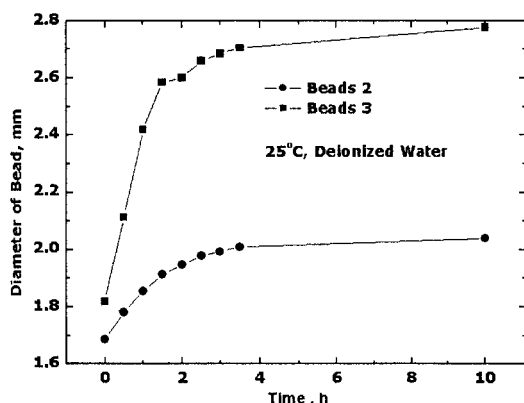
RESULTS AND DISCUSSION

Hydrophilicity of crosslinked chitosan beads

The hydrophilicity of the crosslinked chitosan beads was evaluated by measuring the dewatering curve (D-curve) and swelling curve (S-curve). Figures 2 and 3 show the D-curve and S-curve, respectively. The D-curve in Figure 2 shows that the volume change of beads **3** is much greater than that of beads **2** at a given dewatering ratio. It means that the volume of beads **3** is more sensitive to water loss than that of beads **2**. From the S-curve in Figure 3, it can be seen that beads **3** are swollen more rapidly than beads **2** and have a greater volume increment in a short time, which means that beads **3** have greater hydrophilicity than that of beads **2**. Therefore it can be concluded that the swelling ratio and water content in beads **3** can be controlled in a relatively easier way. The following coating experiments were carried out with beads **3** only.

Surface structure of coating layer with two methods

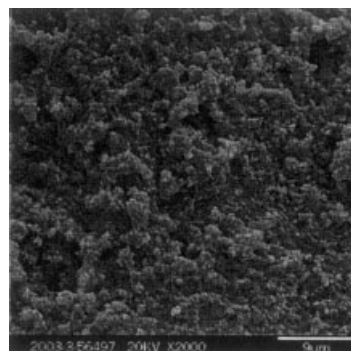Figures 4 and 5 show the SEM microphotographs of the surface of the coating layer with method 1 and

Figure 3 Swelling curve of crosslinked beads.

Figure 5 SEM microphotograph of coating surface with method 2.

TABLE I
Effect of Swelling Ratio on Thickness of Coating Layer

Swelling ratio	Average diameter (mm)		Thickness of coating layer (mm)
	Before coating	After coating	
1.445	1.867	2.378	0.255
2.194	2.166	2.763	0.299
3.592	2.495	3.515	0.510
4.793	2.735	3.878	0.571
7.726	3.305	4.494	0.594
9.688	3.627	4.887	0.630

method 2, respectively. The swelling ratio of the beads was 9.688%, and 10 wt % PSF in DMF was polymer solution. With method 2, the phase ratio of 10 wt % PSF solution over the paraffin phase was 7 : 3, and coating time was 30 s. The surface of the coating layer with method 1 is a uniform porous structure, and the pore size and the thickness of the coating layer are substantial. It was determined that the gelation process with method 1 is too fast to be controlled, which results in a significant degree of clumping and conglutination of beads; thus, the application of method 1 is highly limited. With method 2, the surface of the

coating layer shown in Figure 5 is much denser. When the PSF microdroplets in the emulsion met the swollen bead, they were immediately gelated to form PSF microspheres that adhered to the bead. During the gelation process, millions of PSF microspheres collide with each other and congregate together, finally forming a thin layer on the surface of chitosan beads. The surface structure and thickness of the coating layer are thus more convenient to control with method 2.

Effect of swelling ratio

The solidification of PSF/DMF microdroplets requires adequate water content in the beads. Different swelling ratios (i.e., different water contents) may result in different properties of the coating layer. The effect of the swelling ratio on the coating layer was studied while the phase ratio between 10 wt % PSF solution and paraffin phase was kept at 7 : 3, and the coating time 40 s. The results are summarized in Table I.

The coating layer thickness ranged from 250 to 650 μm. As the swelling ratio increased, the beads contained more water and therefore the coating layer thickness increased. The representative microphotographs of the coating layer at different swelling ratios
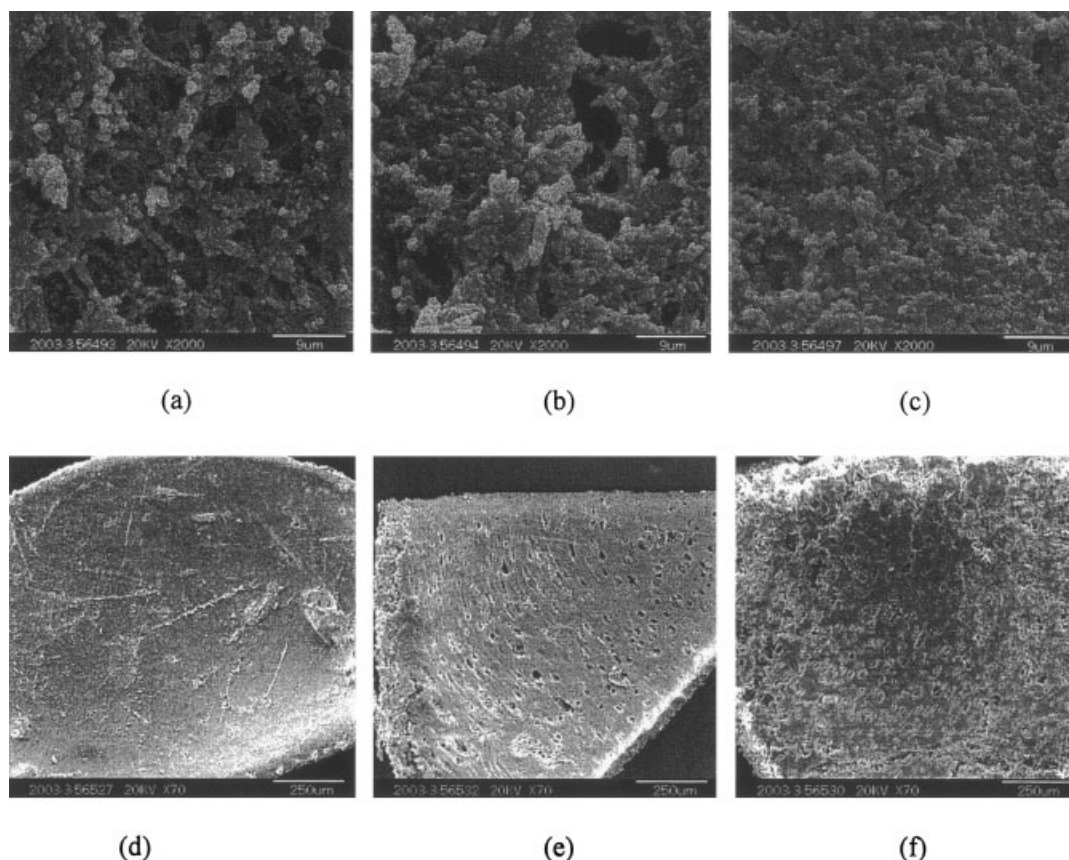

Figure 6 Effect of swelling ratio on the coating layer. Swelling ratio: (a), (d) 3.592; (b), (e) 7.726; (c), (f) 9.688. (a)–(c) outer surface of the coating layer; (d)–(f) inner surface of the coating layer.
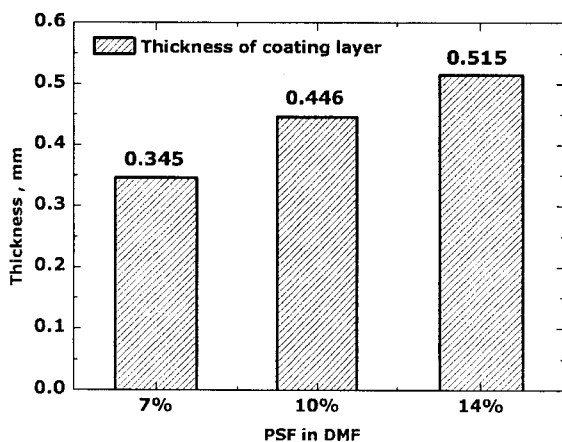
Figure 7 Effect of PSF concentration on coating layer thickness.

are shown in Figure 6. Figure 6(a)–(c) show the variation of the surface structure of the coating layer. It can be seen that the surface of the coating layer becomes much denser with an increase of the swelling ratio. Figure 6(d) and (e) depict the inner surface of the coating layer, which tells us that the porosity of the coating layer also increases with an increase of the

swelling ratio. The reason is that the increase of the water content will result in a fast solidification of PSF in the emulsion phase-inversion process.

Effect of PSF concentration in DMF

The PSF concentration solution also influenced the coating layer: 7, 10, and 14 wt % PSF solutions were tested, respectively. The swelling ratio of the beads was 9.688 and the coating time was 30 s. The other conditions were the same as in the previous section. The thickness of the coating layer in different initial PSF concentrations was measured and the results are illustrated in Figure 7. With the PSF concentration increasing, the coating layer thickness also increased. The microstructures of the coating layer with different PSF concentrations are shown in Figure 8. It is obvious that with the increase of the PSF concentration, the outer surface becomes denser and rougher, although the internal surface (although smooth all the time) contains fewer pores in low PSF concentration and more pores in high PSF concentration.

When the PSF concentration is lower, the microdroplet contains more DMF. This induces a prolonged time of solidification. In the solidification process, the
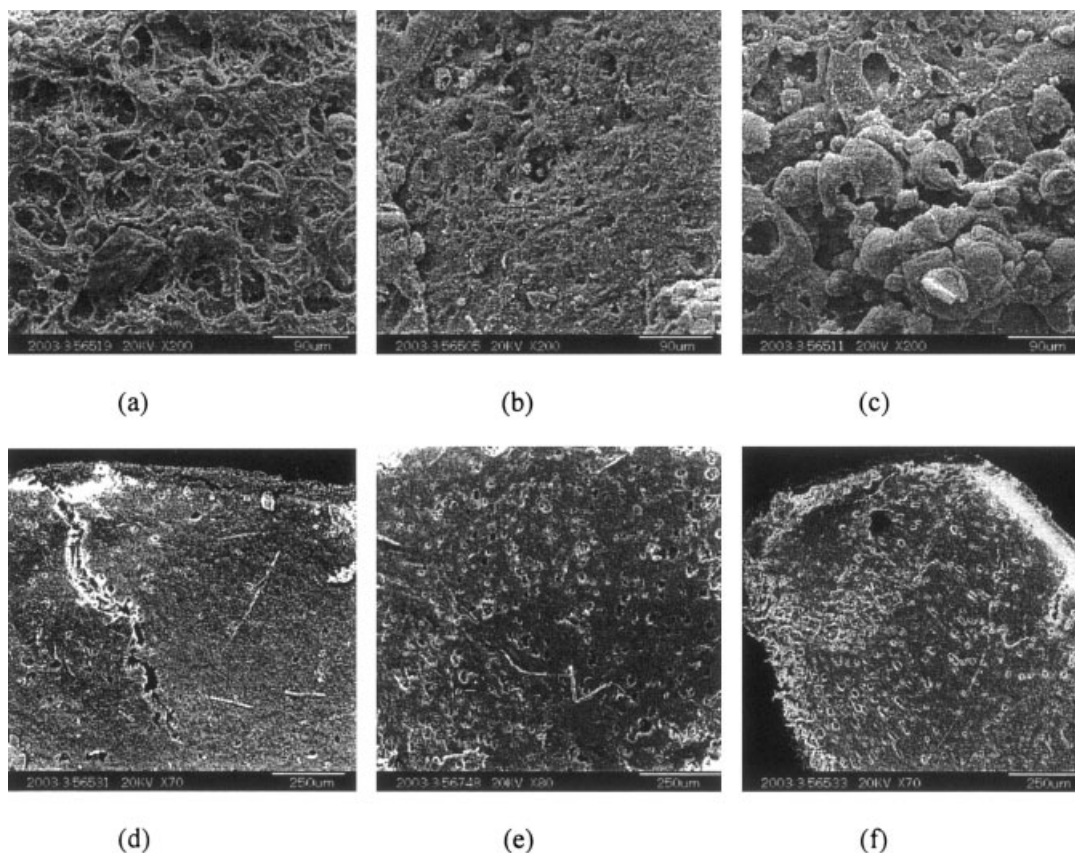

Figure 8 Effect of PSF concentration on coating layer. PSF concentration: (a), (d) 7%; (b), (e) 10%; (c), (f) 14%. (a)–(c) outer surface of the coating layer; (d)–(f) inner surface of the coating layer.
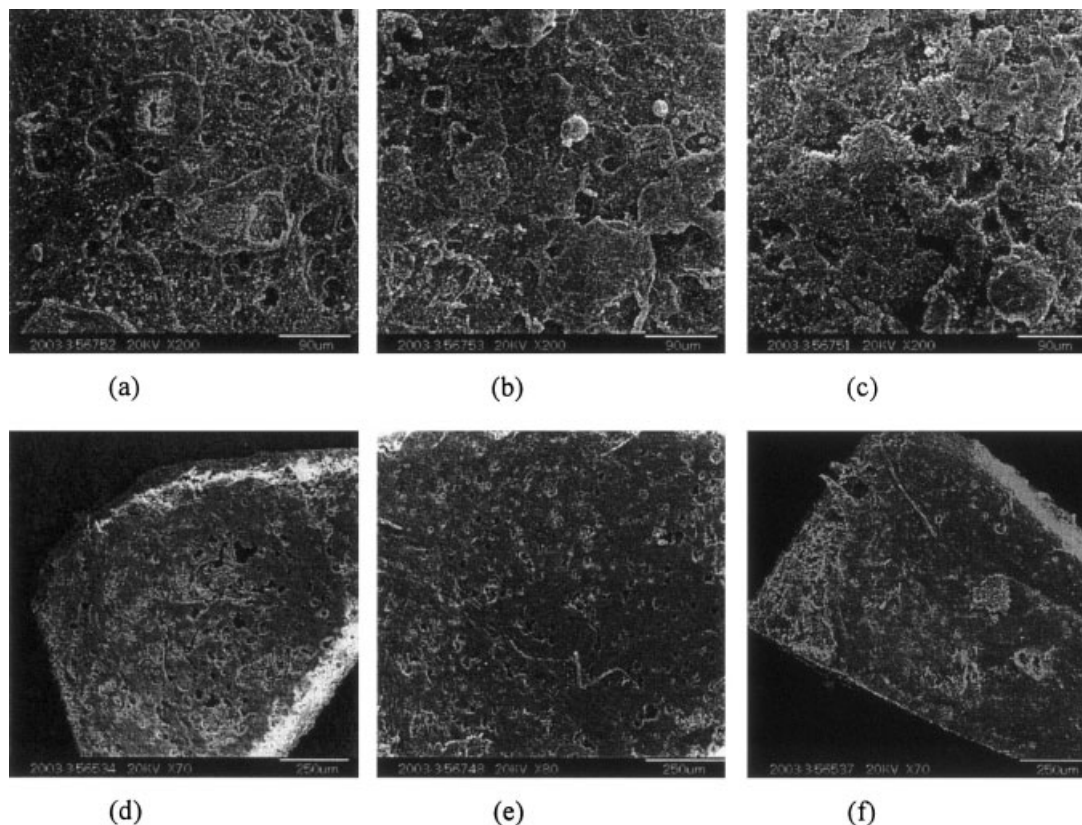
Figure 9 Effect of emulsion phase ratio on the coating layer. Phase ratio: (a), (d) 60 : 40; (b), (e) 70 : 30; (c), (f) 80 : 20. (a)–(c) outer surface of the coating layer; (d)–(f) inner surface of the coating layer.

unsolidified PSF microdroplets deform and even rupture as a result of collision and adhesion with other unsolidified microdroplets, finally resulting in a relatively dense structure. When the PSF concentration was higher, PSF microdroplets solidify more rapidly, and therefore the PSF microdroplets were able to maintain their initial shape. Actually the pores on the outer surface were the void spaces formed by the accumulation of quickly solidified PSF microdroplets.

Effect of phase ratio in emulsion

The emulsion phase ratio was varied from 60 : 40 to 80 : 20 and the other experimental conditions were the same as those presented earlier. The results are shown in Figures 9 and 10. As can be seen, only a slight change of microstructure is observed in the coating layer, whereas significantly increased thickness was obtained as the phase ratio increased. It is well known that an increase in phase ratio can induce an increase
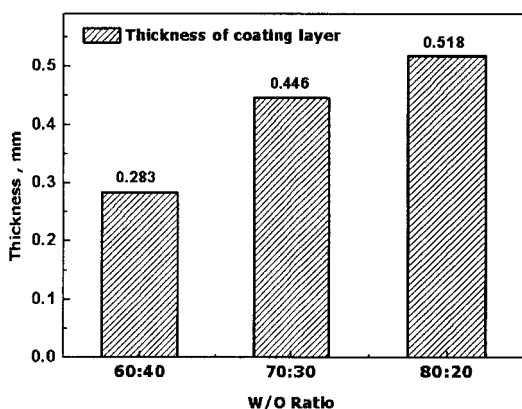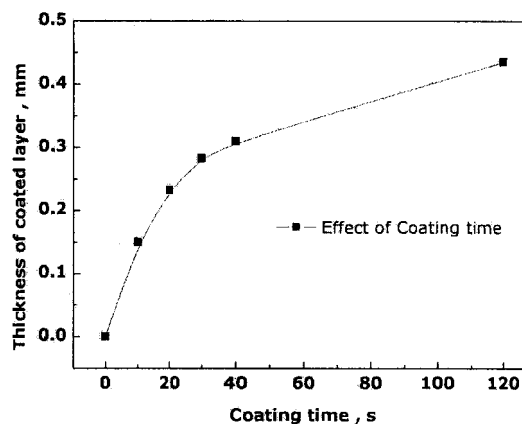

Figure 10 Effect of phase ratio on layer thickness.

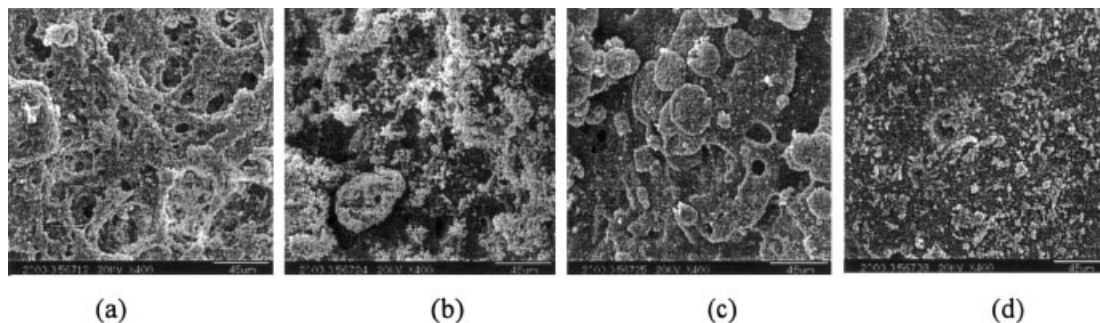**Figure 11** Effect of coating time on layer thickness.

Figure 12   Effect of coating time on external morphology of coated layer coating time: (a) 10 s; (b) 20 s; (c) 40 s; (d) 120 s.

of the number of PSF microdroplets per unit volume, which can influence the frequency of the microdroplets colliding with the beads, resulting in an increase in the thickness.

Effect of coating time

Different coating times were tested, and the results are shown in Figures 11 and 12. Based on the coating theory, an increase of thickness of coating layer is expected over a prolonged coating time. With the increase of coating time, the surface changed from a porous and uneven structure to a compact and even surface.

CONCLUSIONS

Polysulfone can effectively be coated onto swollen chitosan beads with the new coating method of emulsion phase-inversion method. Two kinds of highly swollen crosslinked chitosan beads were prepared: one crosslinked by EDGE only and another successively crosslinked by EGDE and glutaraldehyde. The dewatering curve and the swelling curve of the crosslinked beads show that beads **3** are more suitable for control of swelling ratio and were selected for the coating experiments. Effects of swelling ratio, PSF concentration, phase ratio, and coating time on the coating layer ware investigated. The increased swelling ratio, initial PSF concentration, emulsion phase ratio, and coating time all result in an increase of the thickness of the coating layer. The morphology of the coated PSF layer is mainly determined by the rate of

the PSF microdroplet solidification. It can be concluded that the thickness and the porosity of the coating layer can be easily controlled with the new coating method.

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