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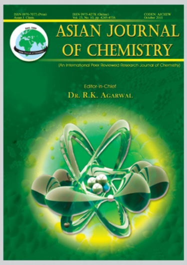

Preparation of Poly(urea-formaldehyde) Microcapsules Containing Sulfur by *in situ* Polymerization

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Poly(urea-formaldehyde) microcapsules containing sulfur were prepared by *in situ* polymerization in a sulfur-in-water suspension. The two preparation steps of sulfur-water dispersion and coating process were investigated. Sedimentation experiments showed that the stability of the suspension decreased with an increase in the weight ratio of water and sulfur and the optimal adding amounts of sodium dodecyl sulfonate and gelatin were 0.7 and 7 wt % for maintaining the stability of the suspension. Scanning electron microscopy analysis showed that the mean diameter and size distribution of microcapsules were narrowed down with increasing the concentration of sodium dodecyl sulfonate and the emulsifying speed. The encapsulation test and morphology observation showed that poly(urea-formaldehyde) microcapsules with spherical shape and high encapsulation efficiency were achieved at pH 3, shell-core weight ratio of 2.0-2.5 and sodium dodecyl sulfonate concentration of 0.7 wt %.

Key Words: Microencapsulation, Sulfur, Poly(urea-formaldehyde), Suspension, Shell formation.

INTRODUCTION

Microencapsulation is the technique of packing the specific functional materials within a coating or wall material (usually polymers) to protect them from physico-chemical effects of the surrounding medium[1-4]. Currently, much attention has been devoted to developing microcapsules filled with sulfur as new vulcanizing agent and self-healing material[5-7]. It is already known[8] that sulfur as a cheap vulcanizing agent used in rubber industry usually blooms out of a rubber compound and crystallizes when large amounts of sulfur are used. Sulfur bloom reduces the "tack" of a rubber compound, a necessary property if layers of rubber are to be plied up to make a composite structure, such as a tire. This shortcoming limits its wide application in rubber industry. Therefore, a new strategy toward "economic and safe" synthesis a new form of sulfur vulcanizing agent has driven the generation of sulfur coated by polymer materials. Sulfur can not be released out from microcapsules for the hinder of the polymer coating in the processing step of a rubber compound. However, the polymer wall commonly has a permeable part with high porosity. Therefore the release of sulfur can occur through pores and microcracks of the shell trigged by heat in vulcanizing step of a rubber compound.

The preparation of urea-formaldehyde capsules by *in situ* polymerization has been described by many researchers[9,10]. The preparation process usually has three steps: preparation of urea-formaldehyde prepolymer, emulsion step and coating. In present study, the two steps of sulfur-water dispersion and microencapsulation process were investigated. The dispersion of sulfur in the continuous phase is a significant step in the preparation of microcapsules filled with sulfur because sulfur particles with high density are easy to settle. Thus they must be suspended before the formation of the capsules' polymer wall. The dispersion of solid phase in aqueous phase was affected by surfactant and stabilizer as well as by the characteristics of the agitation system[11,12]. In addition to obtaining a stable solid suspension, it is necessary to know the coating mechanism of polymer shell to control the morphology and particle size of microcapsules and obtain microcapsules with high encapsulation efficiency. Fan and Zhou[13] reported that the process of poly(urea-formaldehyde) (PUF) shell formation during microencapsulation had four distinct regions. Salaün *et al.*[14] successfully investigated the shell formation mechanism of melamine-formaldehyde microcapsules containing *n*-hexadecane by measuring surface tension and variation of pH. The aims of this study are initially first to study the influence of parameters governing the dispersing step and then to investigate the parameters affecting the membrane formation.

EXPERIMENTAL

Sublimed sulfur was purchased from Tianjin Fuchen Chemical Reagent Co., China. Gelatin, biochemical reagent, polyvinyl alcohol (PVA), sodium dodecylbenzene sulfonate (SDBS) and sodium dodecyl sulfonate (SDS) were provided by Tianjin Yingdaxigui Chemical Reagent Co., China. Urea (U), analytically pure agent, OP-10, Span-80 and formaldehyde (F), analytically pure agent, 37 wt %, were supplied by Tianjin Fuchen Chemical Reagent Co., China. Triethanolamine and formic acid used for controlling pH value of solution were provided by Beijing Chemical Works, China. Dichloromethane was supplied by Tianjin Fuchen Chemical Reagent Co., China.

Microcapsules preparation: Poly(urea-formaldehyde) (PUF) microcapsules were prepared by the following three-step process: (1) 37 wt % formaldehyde solution and urea were mixed in a 250 mL three-neck round-bottomed flask equipped with a mechanical stirrer at room temperature and connected to a reflux condenser. The pH of the solution was adjusted to 8-9 with triethanolamine. After that, the solution was gradually heated to 70 ºC and maintained at that temperature for 1 h to prepare the prepolymer solution of urea-formaldehyde. (2) Then SDS, gelatin aqueous solution, sulfur and the prepolymer solution of urea-formaldehyde prepared in the first step were placed into a 200 mL glass beaker. Then the mixture was dispersed vigorously by a stirrer (FM200 Fluko) at 10000-15000 rpm for 5 min to obtain a relatively stable suspension. (3) Under agitation, the sulfur-water suspension obtained in the second step was placed into a 250 mL three-neck round-bottomed flask connected to a reflux condenser. The pH of the suspension was slowly adjusted to 2-4 with formic acid solution. Then the suspension was gradually heated to 35 ºC and maintained at that temperature for 1h to allow the polycondensation of prepolymer at a stirring rate of 350 rpm. Then the temperature was elevated to 70 ºC to cure PUF. After maintained at that temperature for 2 h, a suspension of microcapsules was obtained. Cooled down to room temperature, the suspension was rinsed with deionized water, subsequently filtered in vacuum (SHZ-DIII vacuum pump with circulated water system, China). After the filter residue was air-dried for 24 h, the microcapsules were obtained.

Test of the stability of sulfur-water suspension: Sulfur particles in suspension are easy to agglomerate with bigger ones and settle in a gravitational field, related to the difference in density between sulfur and water[15]. Hence, in order to prepare a stable suspension, it is significant to investigate the factors influencing the stability of the suspension. The stability of a suspension is often evaluated by stability ratio (r). This ratio is defined as:

$$r = \frac{k(f)}{k} \qquad (1)$$

where k is the number of collisions resulting in coagulation and the rapid coagulation rate, k(f) can be a theoretical value or the number of collision between particles[16]. Since it is hard to find a reliable way to measure stability ratio, it can be inferred from settling time (t_s)[17-19]. The test of settling time is as following: firstly, the sulfur-water suspensions with different concentrations of surfactant and stabilizer, which are prepared as step 2 of the microcapsules preparation, were added into several 10 mL measuring tubes. Then the tubs were placed in a rack slightly. The suspensions began to separate in three phases because of the sedimentation behavior of sulfur particles where the lowest phase was the settled sulfur particles and the intermediate phase was water whereas the highest phase was mainly made up of sulfur-water suspension. Settling time was immediately recorded until 1 mL water layer appeared. The settlement process is shown in Fig. 1. Settling time describes the destabilization of the suspension as a function of settling velocity, which shows that the longer the settling time is, more stable the suspension is.

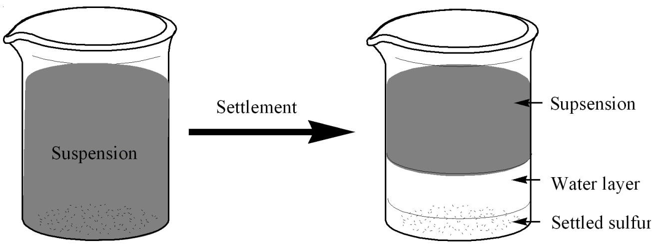


Fig. 1. Scheme illustration of settlement

Test of encapsulation efficiency of microcapsules: Microencapsulation efficiency is measured by the ratio of microcapsules that fully encapsulate sulfur particles to the total weight of dry coarse product[20]. Three grams of dried capsules were washed with 50 mL dichloromethane at 25 ºC. Free sulfur or partially encapsulated sulfur was leached by dichloromethane. The encapsulation efficiency (E) is calculated by the following equation:

$$E = \frac{W_S}{W_W} \times 100\ \% \qquad (2)$$

where W_S refers the weight of the original microcapsules, W_W refers the weight of microcapsules that were washed and dried.

FT-IR of microcapsules: The structure of the shell wall was analyzed by FT-IR spectra. Samples were ground and mixed with KBr to make pellets. FT-IR spectra in the transmittance mode were recorded using a FT-IR (MAGNA-IR 560).

Morphology and particle size of microcapsules: Surface morphology was monitored by scanning electron microscopy (Quanta 200F FEI, America). Samples were sputtered with a thin layer of gold-palladium to prevent charging under the electron beam. The microcapsule size and its distribution were determined by using SEM equipped with image analysis software. The mean diameter of microcapsules was obtained by calculating at least 250 microcapsules[21].

RESULTS AND DISCUSSION

Formulation of the suspension

Surfactants and stablizer selection: The stability of a suspension depends on the forces that control the movement of the particles. It can be the result of the relative movement of the particles by diffusion or be induced by an external force (shearing by agitation) or be controlled by the gravitational and/or repulsive interparticle interactions. The repulsive interparticle interactions may be provided by electrostatic interactions arising from the repellent of like-charged particles and steric interactions between particle surfaces coated with adsorbed surfactant[22].

Surfactants and stabilizer can be adsorbed on the surface of sulfur particles and form the repulsive barrier. In order to find out optimum surfactant and stabilizer for the dispersion step, several kinds of surfactants and stabilizers were used to prepare the suspension and their effects on the stability of the suspension were investigated by sedimentation test. The results are shown in Table-1. It can be found that the suspension follows a SDS > SDBS > OP-10 > Span-80 order in a decreasing suspension stability when gelatin was used as the stabilizer. The result indicates that the suspension prepared using anionic surfactant was more stable than that prepared using nonionic surfactant. This can be attributed to the fact that sulfur particle surface adsorbed SDS or SDBS through van der Waals force, forming a steric barrier to prevent the coagulation. A longer settling time of gelatin/SDS system compared with gelatin/SDBS system is attributed to the adsorption behavior of the surfactant molecules to the particle surface and the adsorption affinity. Sodium dodecyl sulfonate adsorbed on the particles surface has orientating action. The tail end of the surfactant molecules is compatible with water, forming a stretching long tail into the liquids for preventing the direct contact of particles in the proximity. Both gelatin and PVA can act as electrosteric stabilizing agent and continuous phase viscosifier for a suspension[23,24]. However, gelatin interacted strongly with hydrophobic and charged surfaces and formed hydrated films, which provided excellent steric and electrostatic stabilization of sulfur suspension. In addition, PVA with relatively small solubility was easy to gel with surfactant which increased the viscosity of the system too much, resulting in aggregation of microcapsules. From above results, it can be established that the optimal surfactant and stabilizer were SDS and gelatin for maintaining the stability of the suspension.

Effect of the concentration of surfactant: To identify the influence of the concentration of SDS on the stability of the suspension, the amount of gelatin, the weight ratio of water and sulfur and the stirring conditions were fixed, while the concentration of SDS was varied between 0 and 0.9 wt %. The effect of increasing the concentration of SDS on the settling time is shown in Fig. 2. It shows that the settling time increased from 1.5-8.7 min with increasing the concentration of SDS, suggesting that the suspension became more stable. This is ascribed to the fact that with increasing the concentration of SDS, sulfur particle surface adsorbed more SDS forming a thicker uniform coverage as a protective barrier layer, leading to a reduced settling velocity. The settling time reached a plateau after the concentration of SDS was over 0.7 wt % because the adsorption reaction almost reached the equilibrium.

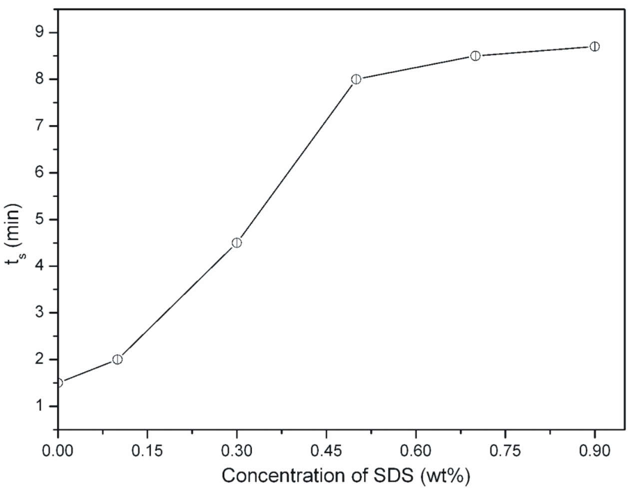


Fig. 2. Influence of the concentration of sodium dodecyl sulfonate on settling time

Effect of the concentration of stabilizer: The relationship between the concentration of gelatin and the settling time is shown in Fig. 3. The concentration of gelatin was varied between 0-11 wt %, while the amounts of SDS, the weight ratio of water and sulfur and the stirring conditions were fixed. It shows that settling time was increased from 0.5-13.8 min as the concentration of gelatin increased from 0-7 wt %, then began to decrease slightly when the concentration of gelatin was over 7 wt %. This can be explained by the following reason. Firstly, at lower concentrations, increased the concentration of gelatin resulted more adsorption of gelatin on the surface of sulfur particles and thus the dispersion stability was enhanced because of an increase in the steric hindrance between the adsorbed gelatin layers. At higher gelatin concentrations, the adsorption reaction reached an equilibrium and the bridge effect of the gelatin occurred, resulting in a reduction of settling time.

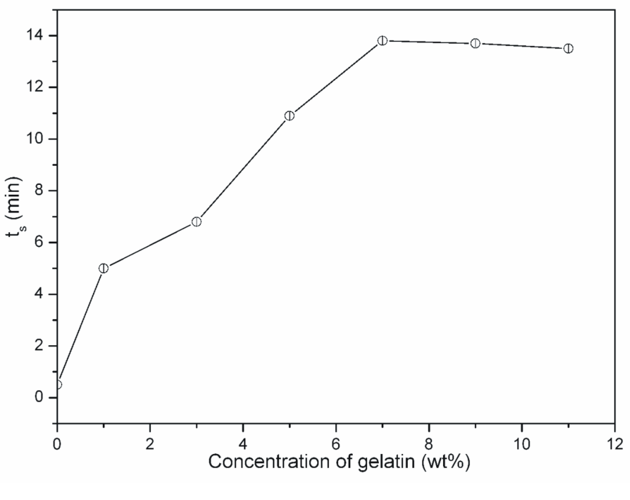


Fig. 3. Influence of the concentration of gelatin on settling time

TABLE-1

INFLUENCE ON SUSPENSION STABILITY OF DIFFERENT DISPERSANTS

Dispersant	Gelatin (SDS)	Gelatin (Span-80)	Gelatin (SDSB)	Gelatin (OP-10)	PVA (SDS)	PVA (OP-10)
t_S (min)	11	1	6	4	Flocculation	Ropiness

Effect of weight ratio of water and sulfur: As is known from published work[25], sedimentation of droplets can occur depending on the density difference between the dispersed and continuous phase and can be enhanced or restricted by the concentration of solid. The effect of the weight ratio between the continuous phase and the dispersed phase is shown in Fig. 4. Suspensions of six ratios were prepared by homogenization at 10000 rpm using a rotor/stator apparatus while the adding amounts of surfactant and stabilizer were fixed. It is found that settling time decreased from 5.2 min at ratio of 10 to 2 min at ratio of 20, which showed that the stability become weaker with increasing the weight ratio of water and sulfur. This is explained by the fact that with an increase in the weight ratio of water and sulfur, repulsive interparticle interactions reduced and the isolated particles became easier to subside under gravity force.

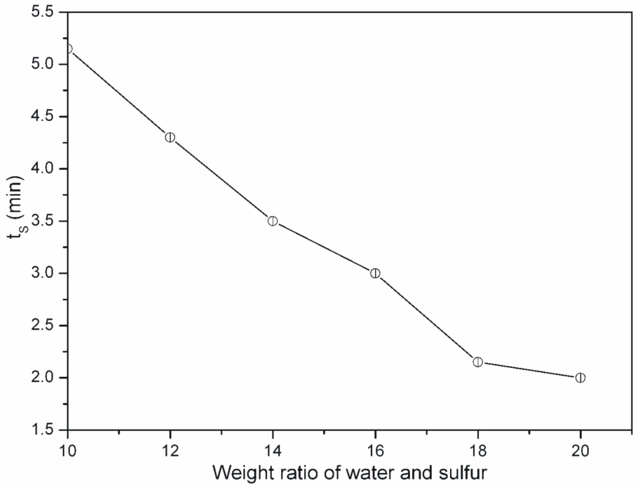
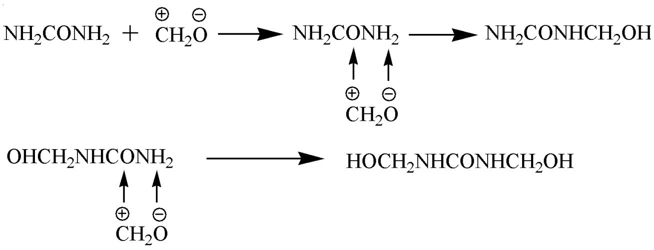


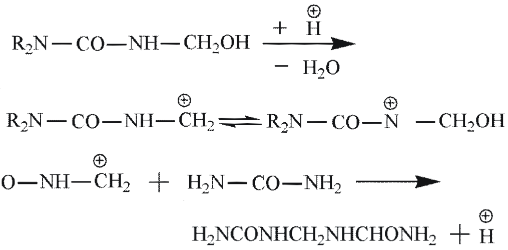
Fig. 4. Influence of the weight ratio of water and sulfur on settling time



$$NH_2CONH_2 + \overset{\oplus\ \ominus}{CH_2O} \longrightarrow \underset{\overset{\uparrow\ \uparrow}{\overset{\oplus\ \ominus}{CH_2O}}}{NH_2CONH_2} \longrightarrow NH_2CONHCH_2OH$$

$$\underset{\overset{\uparrow\ \uparrow}{\overset{\oplus\ \ominus}{CH_2O}}}{OHCH_2NHCONH_2} \longrightarrow HOCH_2NHCONHCH_2OH$$

(a) Reaction scheme of U-F prepolymer

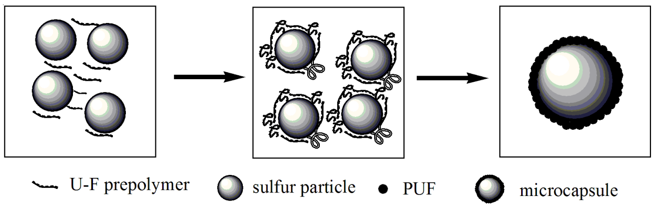


$$R_2N—CO—NH—CH_2OH \xrightarrow[-\ H_2O]{+\ \overset{\oplus}{H}}$$

$$R_2N—CO—NH—\overset{\oplus}{CH_2} \rightleftharpoons R_2N—CO—\overset{\oplus}{N}—CH_2OH$$

$$R_2N—CO—NH—\overset{\oplus}{CH_2} + H_2N—CO—NH_2 \longrightarrow H_2NCONHCH_2NHCHONH_2 + \overset{\oplus}{H}$$

(b) Reaction scheme of PUF resin



(c) Formation scheme of shell

Fig. 5. Scheme of the formation of poly(urea-formaldehyde) microcapsule

Microencapsulation process

Shell formation: In the microencapsulation process, core material is emulsified for the formation of core suspension in the previous stage and the particles suspended are covered by wall material in the succeeding stage to complete the microcapsules. The formation of the microcapsule shell occurs in following three stages is shown in Fig. 5(c). During the first 20 min, the temperature was kept at 35 ºC and the pH of the suspension was adjusted to 2-4 with formic acid solution. Hydroxyurea (Fig. 5(a)) including monomethylol urea, dimethylol urea and oligomer prepared from pre-polymerization of urea and formaldehyde obtains H^+ changing into active prepolymers to allow polycondensation (Fig. 5(b)). The reaction occurs exclusively in the continuous phase and on the continuous phase side of the interface formed by the dispersed sulfur and aqueous phase. In the second stage, from 20-60 min, low molecular weight PUF resin is formed. The low molecular weight resins which are water compatible wet the core material and created primary shell around the dispersed sulfur particles[14]. As the reaction goes on, the concentration of resins in the boundary layer is enhanced. In the last stage, from 60-240 min, the temperature was elevated to 70 ºC. The urea-formaldehyde molecule enriched on the surface of core is rich with polar groups. The number of polar groups will gradually reduce as molecular weight of polymer increases. After attaining certain molecular weight, hydrophilicity of urea-formaldehyde polymer molecule will reduce leading to separation from aqueous phase and get deposited on the already dispersed sulfur particle with the result of microcapsule shell formation. However, the deposition of PUF resins takes place simultaneously in the solution and at the microcapsule surface. The deposition in the solution produces PUF microparticles, while the deposition at the microcapsule surface forms capsule shell. The capsule shell can only be formed when the deposition rate at the phase boundary is much higher than that in aqueous phase[26]. Therefore, the resin condensation should proceed much faster in the boundary layer than in the volume phase. Further reaction of pre-polymer and the deposition of PUF nanoparticles generate thicker shell of the microcapsules.

Chemical structure of shell: In order to indicate the structure of coating, microcapsules irradiated with UV were characterized. The FT-IR spectra of microcapsules and pure PUF resin are shown in Fig. 6. It can be seen that the two spectra are closely matching at characteristic peaks of a O-H stretching vibration at 3357 cm^{-1}, N-H stretching vibration at1542 cm^{-1}, a C=O stretching vibration at 1642 cm^{-1}, C-H stretching vibration at 1388 cm^{-1}, C-N stretching vibration at 1242 and 1134 cm^{-1}. In view of above it can be established that the shell of the microcapsules obtained is made of PUF.

Particle size of microcapsules: The relationship between the particle size of the microcapsules and the concentration

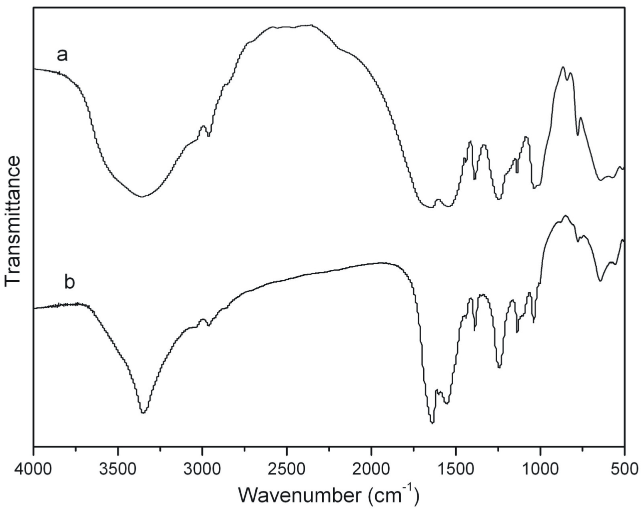


Fig. 6. FTIR of pure PUF (a) and PUF microcapsule (b)

of SDS are shown in Fig. 7. The concentration of SDS was varied between 0.3 and 0.7 wt %, while other reaction conditions were kept constant. It shows that the mean diameters of the prepared microcapsules were 37.7, 35.6 and 28.9 μm at SDS concentration of 0.3, 0.5 and 0.7 wt %, respectively. The results show that with increasing the concentration of SDS, the mean diameter of the microcapsules decreased and the size distribution became narrower. The results are in agreement of previous work that increased surfactant concentration can form fine core particles and reduce the collisions of smaller particles and accordingly prepare microcapsules with smaller size[27].

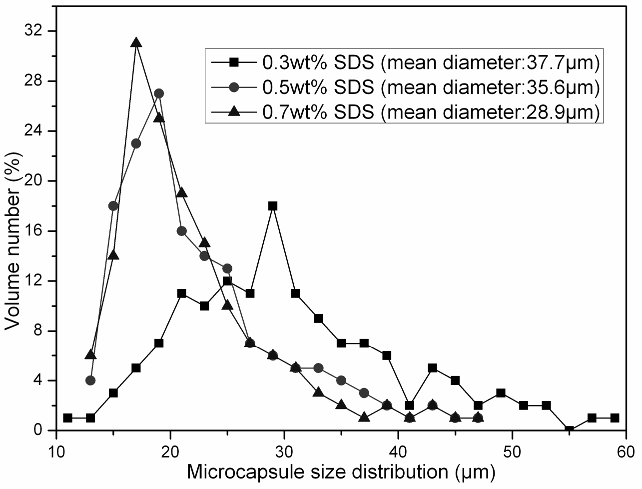


Fig. 7. Effect of SDS concentration on the microcapsule size distribution

To indentify the influence of the emulsifying speed, the stirring rate, the concentration of SDS and core content were fixed, while the emulsifying speed was varied between 10000 and 15000 rpm. The effect of the emulsifying speed on the mean diameter and particle size distribution of the microcapsules is shown in Fig. 8. The mean diameters of the microcapsules prepared at 10000, 12500 and 15000 rpm, were 33.9, 30.0 and 29.1 μm, respectively. The particle size distribution was narrowed down for the emulsifying speed up to 15000 rpm. Increased the emulsifying speed resulted in decreased microcapsule mean size, as it produced smaller suspension particles through stronger shear forces and increased turbulence.

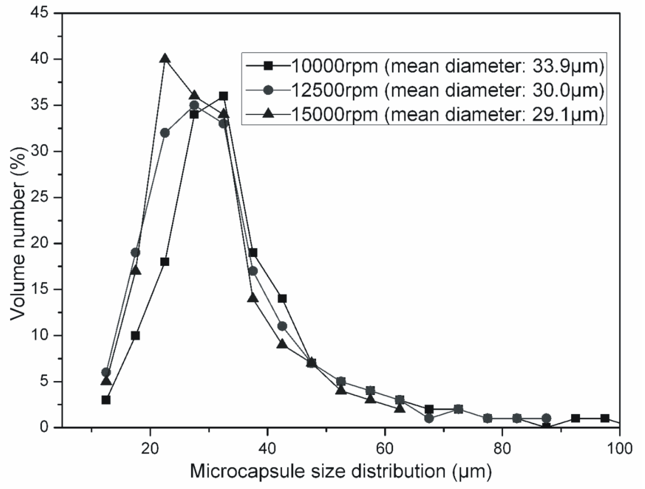


Fig. 8. Effect of the first emulsifying speed on the microcapsule size distribution

Encapsulation efficiency and morphology of microcapsules: It is well known that the polycondensation of the amino resin occurs in the continuous phase and the phase separation is linked to pH value[14]. The pH value determines the rate of reaction between urea and formaldehyde. Therefore the effect of the pH value on the preparation of microcapsules was studied at different pH values of 2, 3, 4 and 5 while other reaction conditions were held constant. Fig. 9 shows that the encapsulation efficiency at pH 3 was the highest. This can be attributed to the following reasons. A low pH led to fast polymerization of urea and formaldehyde and resulted in the deposition rate of PUF microparticles in aqueous solution. However, the molecular weight of urea-formaldehyde polymer formed at high pH was too low to deposit onto the microcapsule surface. In terms of microcapsules' shape, Fig. 10 shows that the prepared microcapsules are not spherical and the surfaces are not smooth. The rough surfaces are believed to be the result of deposition of insoluble high molecular weight pre-polymer at the sulfur-water interface. The capsules with irregular shape at pH values of 2 and 3 are ascribed to the following reasons. Firstly, the initial shape of the core solid plays a crucial role in the final shape of microcapsules. Fig. 10(a) shows that sulfur particle exhibits irregularity in sphericity. Secondly, the deposition of PUF nanoparticles is inhomogeneous in low or high pH value. At pH 2 the polycondensation proceeded so fast and at pH 4 the reaction was too slow.

The effect of the concentration of prepolymer on the preparation of microcapsules was investigated while other reaction conditions were kept constant. Fig. 11 shows that encapsulation efficiency increased from 78.3-83.5 % as the weight ratio of prepolymer solution of urea-formaldehyde and sulfur increased from 0.5-2.5 and then began to decrease when the weight ratio was over 2.5. This can be explained by the following reasons. At low concentration of wall material, they were dispersed well around sulfur particles, which facilitated encapsulation of sulfur. When the weight ratio was above 2.5,

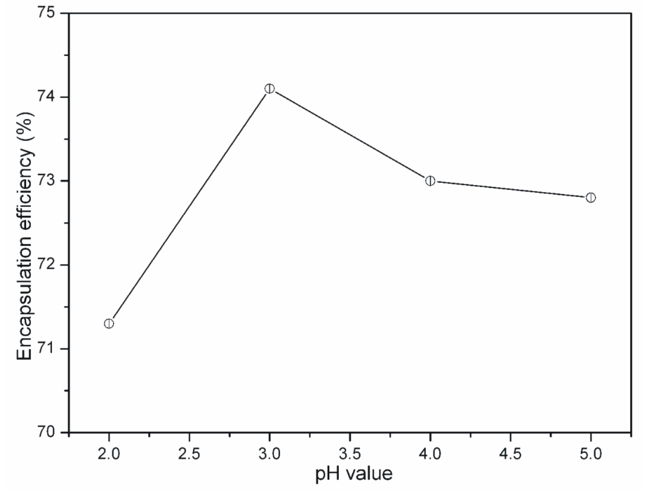
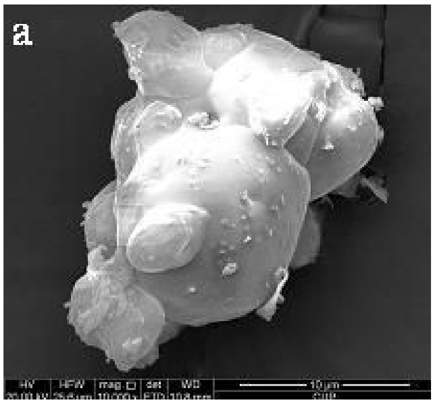
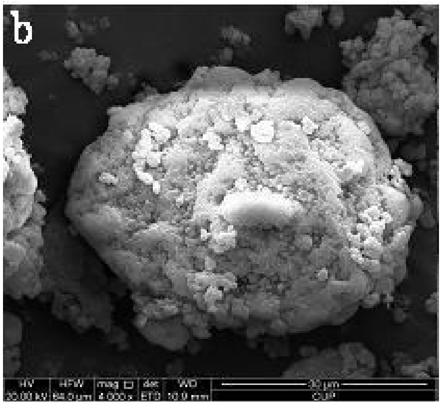
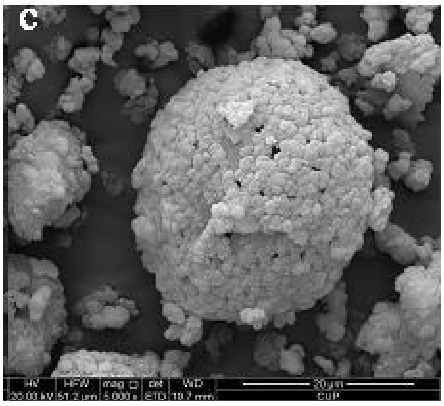


Fig. 9. Effect of pH on the encapsulation efficiency







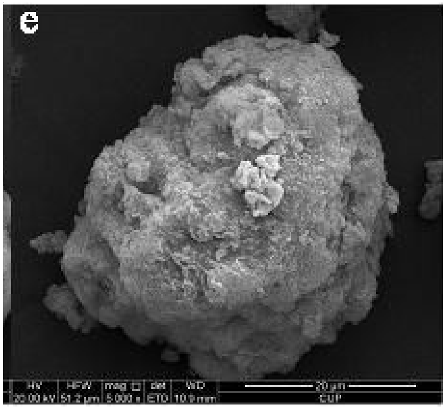


Fig. 10. SEM images of sulfur (a) microcapsules prepared at pH of 2 (b), 3 (c), 4 (d), 5 (e)

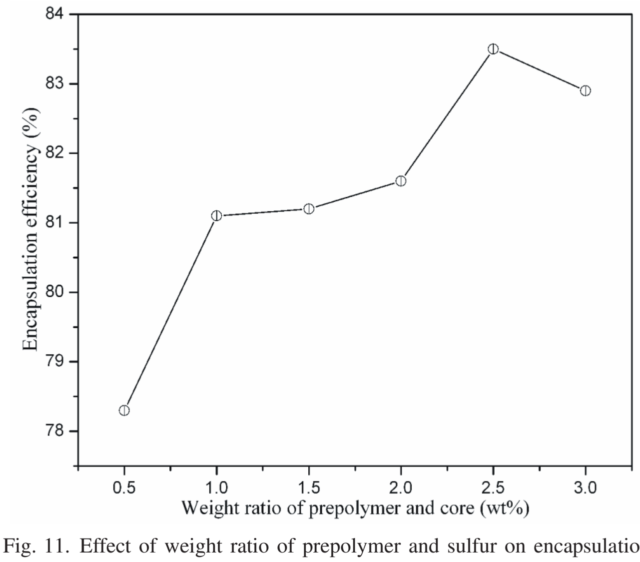


Fig. 11. Effect of weight ratio of prepolymer and sulfur on encapsulation efficiency

it led to a sharp rise in the viscosity of the system and created a gel-network consisting of the colloidal particles and sulfur, resulting incomplete encapsulation of sulfur. SEM images of the microcapsules prepared with different concentrations of wall material are shown in Fig. 12. The morphological observation implies that the microcapsules prepared at weight ratios of 2.0 and 2.5 exhibit higher degree of sphericity than that prepared at lower weight ratio. This may be attributed to the fact that at weight ratios of 2.0 and 2.5, the synthesis rate of PUF is close to the deposition rate of PUF nanoparticles on

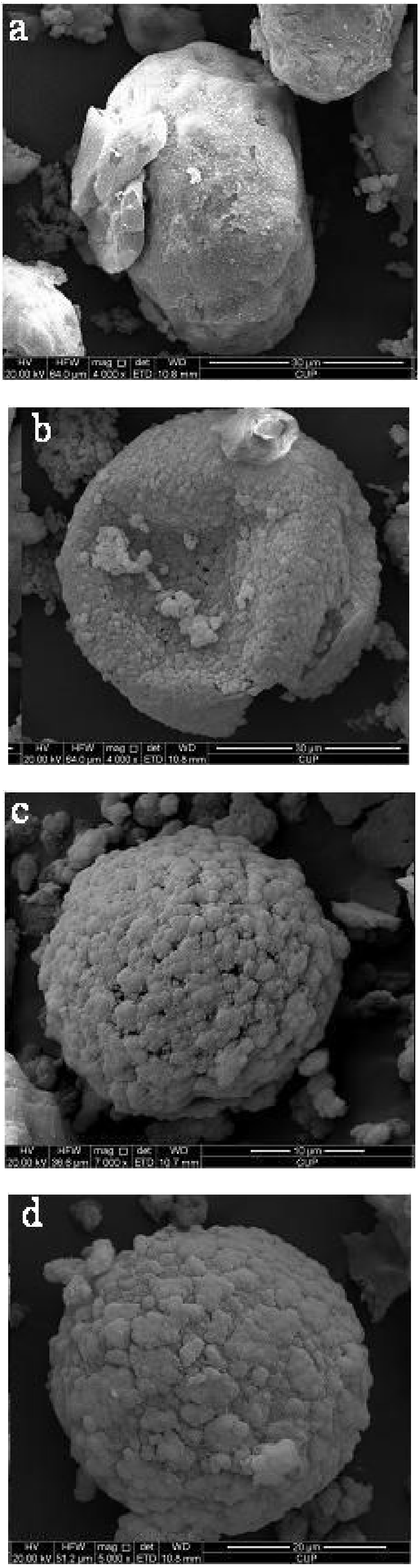


Fig. 12. SEM images of microcapsules prepared at core-shell ratio of 0.5 (a), 1.0 (b), 2.0 (c), 2.5 (d)

the surface of sulfur particles. Thus, under the given process conditions, it is benefit in using weight ratio of 2.0-2.5 for the microencapsulation process.

The effect of concentration of SDS on encapsulation efficiency is shown in Fig. 13. The concentration of SDS was varied between 0.1 and 0.9 wt % while other reaction conditions were held constant. It can be seen that with increasing the concentration of SDS, the amounts of sulfur entrapped in PUF shell increased from 79.2 to 84.3 % and then decreased when the concentration of SDS was 0.9 wt %. This is attributed to the following reason. With increasing the SDS concentration, in addition to adsorption on the surface of sulfur particles, part of the emulsifier dissolved in the aqueous phase. The formed PUF nanoparticles adsorbed the SDS molecules and were stabilized by both steric and electrostatic stabilization. Therefore PUF nanoparticles could not deposit onto the surface of sulfur particles to encapsulate it. Fig. 14 shows that microcapsules were no-spherical in shape, which is similar to others reported in literature for the microencapsulation of solids[28]. But it seems that the sphericity of microcapsules tended to increase with increasing SDS concentration. This phenomenon can be explained by the fact that increased the concentration of SDS formed a thicker steric and electrostatic layer on the surface of sulfur particls, which prevented the aggregation of sulfur particles and helped form fine core particles with regular shape and thus relatively spherical microcapsules were obtained finally.

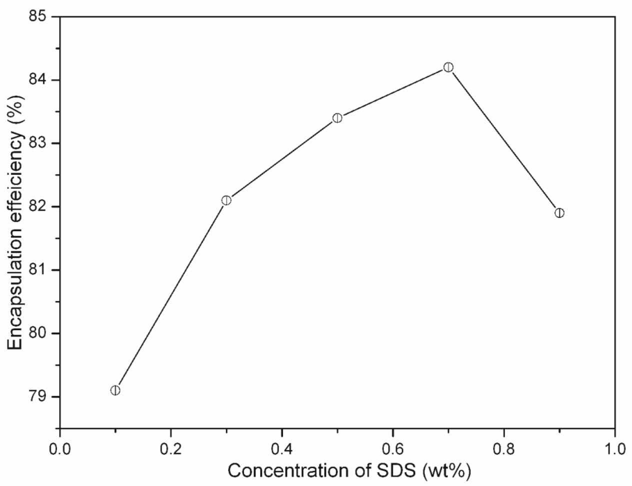
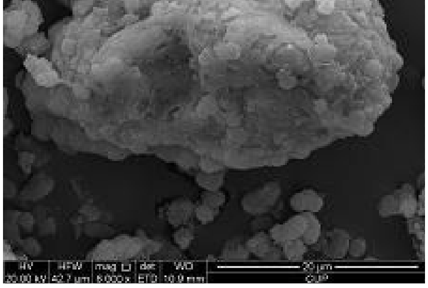


Fig. 13. Effect of concentration of SDS on encapsulation efficiency



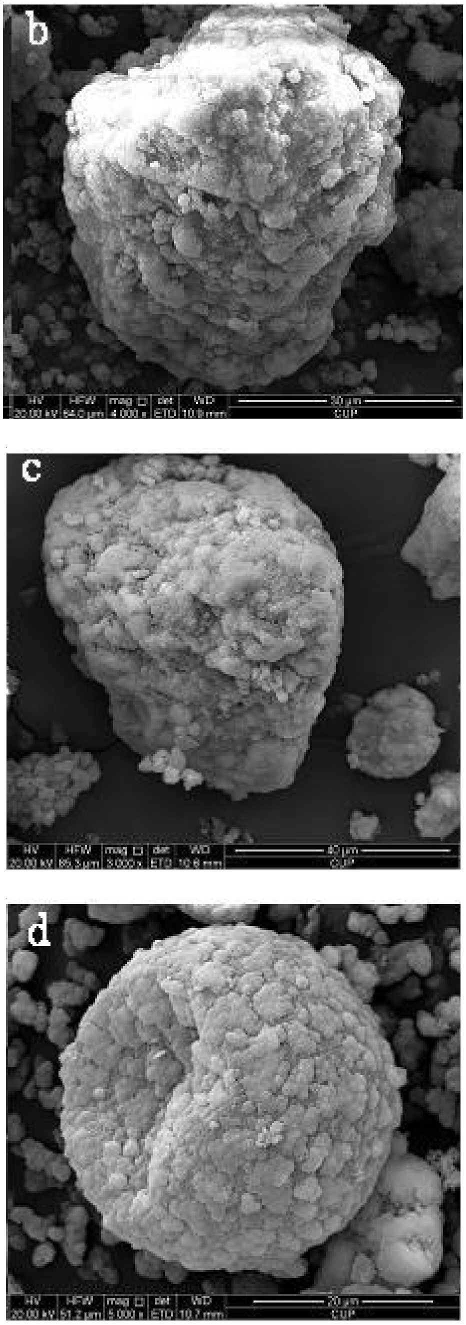


Fig. 14. SEM images of microcapsules prepared at SDS concentration of 0.1 (a), 0.3 (b), 0.5 (c), 0.7 (d) wt %

Conclusion

The poly(urea-formaldehyde) microcapsules filled with sulfur were successfully prepared in solid-in-water suspension by *in situ* polymerization. The preparation steps of the sulfur-water dispersion and coating process were investigated. Sedimentation experiments showed the optimum dispersion conditions were obtained with 7 wt % gelatin and 0.7 wt % sodium dodecyl sulfonate (SDS). The micro-encapsulation factors influencing the particle size, encapsulation efficiency and surface morphology such as the concentration of SDS, the emulsifying speed, pH value and the concentration of prepolymer were studied. The results showed that the mean diameter and size distribution of microcapsules were narrowed down with increasing the concentration of SDS and the first emulsifying speed. The encapsulation efficiency test showed it was affected by pH value, the concentration of prepolymer and the concentration of SDS. The microcapsules with spherical shape and high encapsulation efficiency were obtained at pH 3 and a shell-core ratio of 2.0-2.5.

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