

Role of Ammonium Chloride in Preparing Poly(urea-formaldehyde) Microcapsules Using One-Step Method

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ABSTRACT: This study investigates the role of ammonium chloride in the process of preparing poly (urea-formaldehyde) (PUF) microcapsules using the one-step method. Scanning electron microscopy (SEM) and optical microscopy (OM) were used to observe the morphology of the microcapsule. The results showed that the addition of ammonium chloride in the one-step process of preparing PUF resin microcapsule decreases the pH of the system. The decrease in pH of the system is due to the reaction between ammonium chloride and formaldehyde, and more so due to the reaction between ammonium chloride and hydroxymethyl urea. In addition to reducing the pH of the system, the reaction between ammonium chloride and urea-formaldehyde resin can generate surface active substances, which drives the formed UF nanoparticles to enrich the surface of the dispersed phase. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2848–2856, 2013

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INTRODUCTION

Microcapsules have been widely used in various fields, such as pharmaceuticals,^{1,2} textiles,^{3,4} food additives,^{5,6} electronic inks,^{7,8} pesticides,⁹ and self-healing materials^{10,11} among others. There are many techniques for fabricating microcapsules, including interfacial polymerization, *in situ* polymerization, and coacervation.¹² Among them, the *in situ* polymerization process with urea-formaldehyde resins as the capsule wall, has attracted the attention of researchers^{13–16} due to its simplicity and excellent mechanical strength of the resulting capsules.

The polymerization of urea and formaldehyde can be both acid- and base-catalyzed.¹⁷ Conventionally, the preparation of poly (urea-formaldehyde) (PUF) microcapsule is carried out in two steps. The first step is the addition reactions of urea and formaldehyde under basic conditions to form prepolymers, and the second one is to form a precondensate of mono-, di-, and trimethylolureas that becomes crosslinked under acidic conditions, yielding a three-dimensional water-insoluble structure that precipitates and envelops the core material droplets. The preparation process for PUF microcapsules has been reported in detail in many publications.^{13,18}

Several researchers^{14,16,19,20} use the one-step *in situ* polymerization and allow urea and formaldehyde to react under acidic conditions without preparing a precondensate. Compared to the above-mentioned two-step process, this is a time-saving process

and easily operated as a result of the omission of precondensating. In the one-step process of preparing PUF microcapsules, the addition of ammonium chloride was found to be very important. According to a US patent,²¹ adding ammonium salt in preparing PUF microcapsule can improve the strength, heating resistance, and sealing performance of the microcapsules. Addition of sodium chloride had a similar effect, however, the microcapsules obtained by adding ammonium chloride were found superior with respect to their shelf life and robustness during handling.²² In a previous study,²³ we also found that the addition of ammonium can cause a substantial drop in the pH value during the reaction and affects the surface morphology of the microcapsules. But the exact mechanism of this action is not known. To study the wall-forming mechanism and propose the guidelines to prepare microcapsules with desired morphology and physical properties, it is necessary to know the role of ammonium chloride in the process of preparing poly (urea-formaldehyde) microcapsules using the one-step method. This study primarily clarifies the mechanism of the addition of ammonium chloride on the formation of PUF microcapsules.

EXPERIMENTAL PART

Materials

Urea, formaldehyde (37% aqueous solution), ammonium chloride (NH₄Cl), sodium chloride, and resorcinol were analytical

grade reagents, purchased from Shanghai Lingfeng Chemical reagents Factory, China. Tetrachloroethylene (TCE) used as core material was analytical grade reagents, purchased from Shanghai Resin Plant, China. Oil red was used as oil-soluble dyes to differentiate the microcapsules and UF resins that did not deposit on the surface of the microcapsule. It was purchased from Kunshan Zhongxing Chemicals, Jiangsu, China. The polymer surfactant, poly (ethylene-alt-maleic anhydride) (poly (E-MA), average M_w , 100, 000–500,000), was purchased from Sigma–Aldrich (China). Hydrochloric acids (HCl, 1 mol L⁻¹) and sodium hydroxide solutions (NaOH, 2 mol L⁻¹) were prepared separately to control the pH value of the emulsion. All the materials are commercial products and used without further purification.

Microcapsule Preparations and Characterization

Formation of urea–formaldehyde microcapsules was achieved by *in situ* polymerization in an oil-in-water emulsion. The detailed descriptions of the experimental procedures can be found in literature¹⁶ and a typical procedure was summarized as follows. Under agitation and at room temperature (20–25°C), 2.5 g urea, 0.25 g ammonium chloride, 0.25 g resorcinol and 5 mL of 10 wt % aqueous solution of EMA copolymer were dissolved in 115 mL of deionized water. The pH of the solution was adjusted accurately using pH meter (PHB-2, San-xin, accuracy: ±0.1 pH) to 3.5 by drop-wise addition of NaOH (2 mol L⁻¹) or HCl (1 mol L⁻¹) solution. Then, the obtained solution was poured into a 250 mL three-necked flask which was suspended in a temperature-controlled water bath on a programmable hotplate with external temperature probe (MPG-100H, Blue pard). After that, a slow stream of 20 mL of TCE dyed by oil red was added to the solution to form an emulsion and allowed to stabilize for 20 min under the agitation of 500 rpm. After stabilization, 6.3 g of 37 wt % aqueous solution of formaldehyde was added to the emulsion. The emulsion was heated at a rate of 1°C min⁻¹ to the target temperature of 55°C. After 3 h, the reaction was ended. The obtained suspension of microcapsules was cooled down to ambient temperature, rinsed with deionized water, filtered and air-dried for 12 h.

Surface morphology of microcapsule was observed using a scanning electronic microscope (SEM, S4800, Hitachi). Microcapsule were mounted on adhesive tape and sputtered with a thin layer of gold before observation.

The macroscopic and microscopic morphology of microcapsules was observed by digital camera (LX-3, Lumix) and optical microscopy (XSP-8C, Changfang), respectively. Microcapsule size distribution was analyzed by image analysis software (motic image plus 2.0). Mean diameter was determined from data sets of at least 250 measurements.

FTIR spectra of microcapsules that prepared without adding core materials were obtained by using a spectrophotometer (Nicolet 5700, Thermo Electron Corporation) to identify the chemical structure. The microcapsule specimens were prepared by grinding the sample with potassium bromide (KBr).

The ζ -potential of the PUF colloidal particles was determined using a particle electrophoresis instrument (Zetasizer, Nano series—ZS, Malvern). Prior to analysis emulsions were diluted

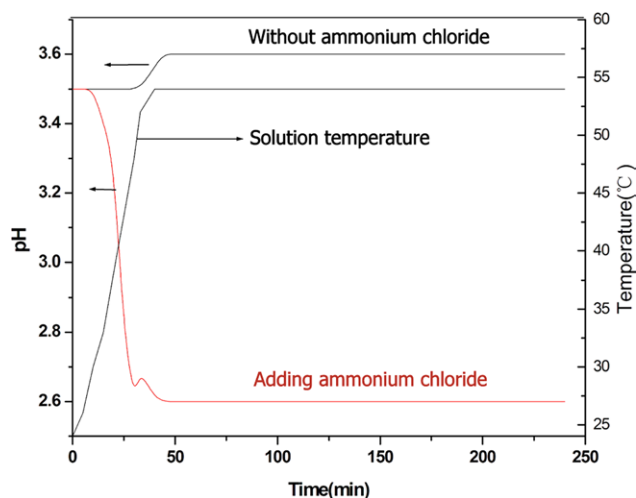


Figure 1. Temperature and pH profile during microencapsulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

500× with different concentration of NaCl solutions at the pH of 2.5, and equilibrated for 5 min at 25°C inside the instrument. Data was collected over at least five sequential readings and processed using the Smoluchowski model.

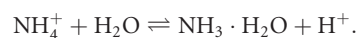
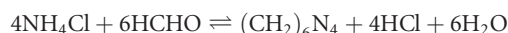
The ionic strength of the solutions was measured by a conductivity meter (DDSJ-308A, Lei-ci).

RESULTS AND DISCUSSION

Effect of Ammonium Chloride on the pH of the Microencapsulation Process

In this study, the pH value changes were measured for 4 h during the microencapsulation and after adding formaldehyde.

From Figure 1, it is observed that after adding formaldehyde, the pH value of the reaction system that involved ammonium chloride dropped precipitously from 3.5 to 2.6 during the first 30 min. After 30 min, the pH values of the reaction system increased slightly to the 2.7 and then gently decreased to a stable value of 2.6. The pH value of the reaction system that did not contain ammonium chloride did not change greatly and only increased slightly to 3.6 during the reaction. Comparing the two reaction systems, we concluded that ammonium chloride significantly influenced the pH of the reaction system. It is generally considered that reactions that reduce the pH of NH₄Cl with UF resin are²⁴:



However, Nesterova et al.²⁵ reported that the core material epoxy resin participates in a side reaction with ammonium chloride and formaldehyde decreasing the pH. When the core material epoxy resin is protected by a layer of pure PUF that isolates the epoxy core material from the ammonium chloride, the pH drop did not occur. Aiming at finding the cause of the pH drop, several experiments were performed. The results are summarized in Table I. It can be seen that just by adding ammonium chloride or by having ammonium chloride and urea in

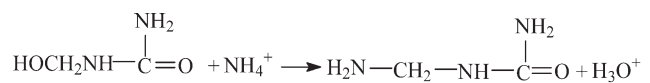
Table 1. Experimental Results for the pH Drop During the One-Step Microencapsulation Process

No.	Experiment	Initial pH ^a	Final pH ^a
1	0.25 g NH ₄ Cl + 110 mL deionized water	5.4 ± 0.063	5.4 ± 0.049
2	0.25 g NH ₄ Cl + 2.5 g urea + 110 mL deionized water	5.8 ± 0.075	5.8 ± 0.049
3	0.25 g NH ₄ Cl + 6.4 g formaldehyde + 110 mL deionized water	4.1 ± 0.069	3.5 ± 0.040
4	Continue adding 2.5 g urea into the No. 3 sample	3.5 ± 0.040	2.2 ± 0.045

^aAmmonium chloride, urea, and formaldehyde were added to deionized water of 40°C, and measure the pH changes in the solution. The initial pH is the pH of the solution just after the addition of with the reactants and the final pH is that after stirring for 20 min.

the deionized water did not cause the pH drop. However, ammonium chloride with formaldehyde caused the pH to drop from 4.1 to 3.5. What is interesting is that adding more urea to the mixture of ammonium chloride and formaldehyde (the pH of the mixtures is maintained stable at 3.5 after 20 min) reduces the pH from 3.5 to 2.2. This means there are other reactions between ammonium chloride and UF resin that cause the reduction in pH besides the hydrolysis of ammonium chloride and its reaction with formaldehyde.

Wu et al.²⁶ reported that during the initial stage of the reaction between urea and formaldehyde, NH₄⁺ could react with hydroxymethyl urea and cause the pH to drop according to the following chemical reaction:



Therefore, it is inferred that the main reason for the drop in pH during the one-step microencapsulation process is the reaction between ammonium chloride and formaldehyde, and ammonium chloride and hydroxymethyl urea.

Effect of Ammonium Chloride on the Formation of the Microcapsules

During the microencapsulation, two simultaneous processes occurred^{15,16,19}: (1) the reaction of the UF resin at the emulsion interface to form the smooth nonporous microcapsule shell and (2) the reaction of UF in the solution to produce UF colloidal particles. When the stability of the UF colloid particle in the solution is disturbed, the UF colloidal particles may precipitate in the solution or onto the capsule surface, which results in a rough outer layer on the UF shell.

Figures 2 and 3 show OM and SEM images of microcapsules prepared without and with ammonium chloride. It can be seen that after completion of the reaction that contains no ammonium chloride, a milky white emulsion was obtained [Figure 2(a-1)]. The UF nanoparticles remained in suspension and did

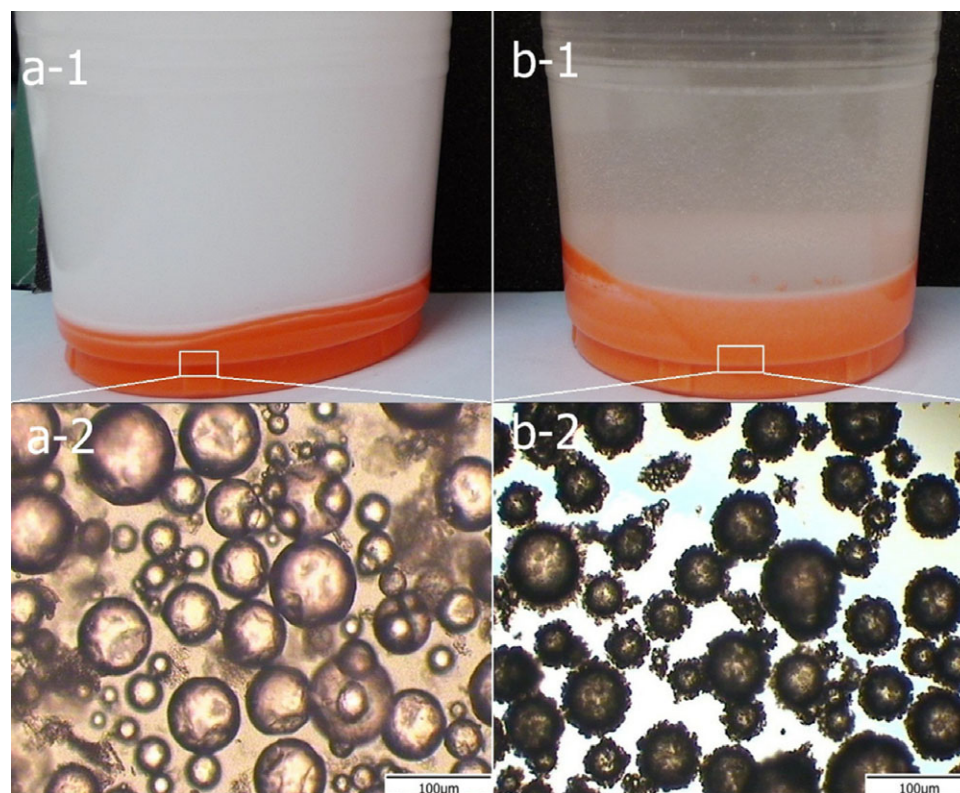


Figure 2. Digital and optical microscope (OM) photographs of PUF microcapsules prepared (a) without NH₄Cl and (b) with NH₄Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

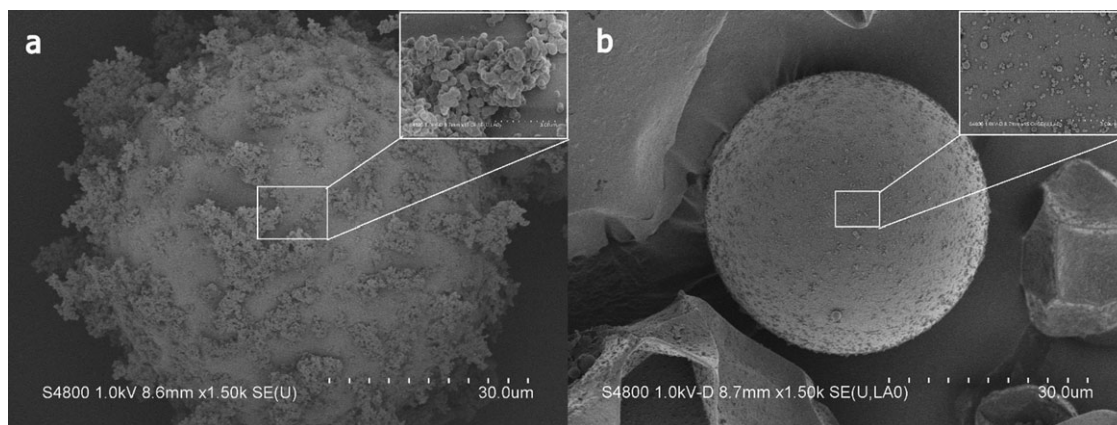


Figure 3. SEM micrographs of microcapsules prepared with (a) and without (b) NH_4Cl .

not deposit onto the microcapsule surface. Although the microcapsules produced by this method possessed a smooth surface [Figure 3(b)], the obtained microcapsules had low mechanical strength and easily collapsed after drying. In contrast, in the process with ammonium chloride, most of the UF nanoparticles deposited onto the microcapsule surface instead of remaining in suspension or precipitating in the solution [Figure 2(b-1)]. The

microcapsules produced by this method had a rough surface and high mechanical strength, and can be dried into a free-flowing powder [Figure 3(a)].

Figure 4 shows the size distributions of microcapsules prepared with different conditions. It can be found that there were no obvious differences in the size distribution of the microcapsules

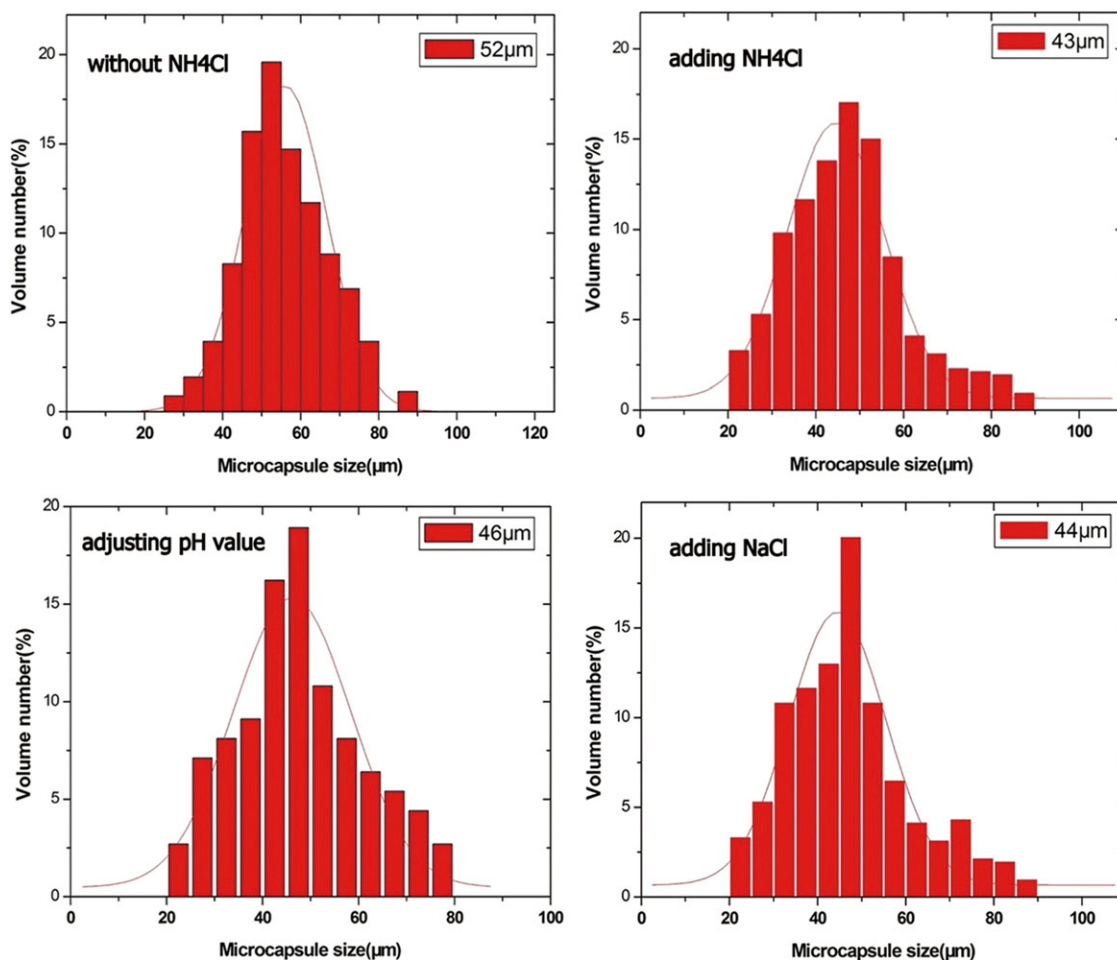


Figure 4. Size distributions of microcapsules prepared with different conditions. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

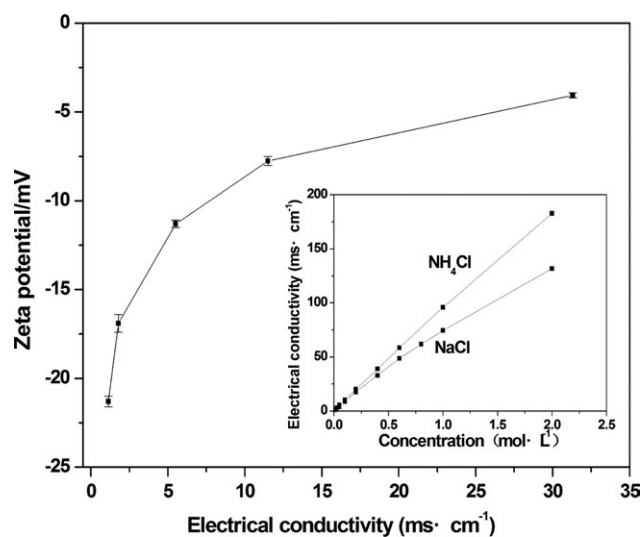


Figure 5. Zeta potential of UF colloidal particles at different ionic strength levels.

that were prepared with and without ammonium chloride. Because the amount of emulsifier and the stirring speed that affect the microcapsule size distribution were the same in both systems.

From the abovementioned results, we conclude that ammonium chloride is essential for making microcapsules by the phase separation method. Clearly, ammonium chloride is essential to form microcapsules with high thermal stability and strength. First, adding ammonium chloride can destroy the stability of the formed UF colloidal particles and make them precipitate. Second, adding ammonium chloride can drive the UF nanoparticles that precipitated from the emulsion to enrich the oil-water interface and form microcapsules with rough surface and high mechanical strength instead of precipitating in the solution.

Consequently, the following question arises. Why the introduction of ammonium chloride causes the deposition of the UF nanoparticles onto the surface of the microcapsules? Johns and Dunker²⁷ reported that the colloidal structure of the UF resin was formed by the presence of a double layer of formaldehyde. Thus, the addition of ammonium chloride could disrupt the double layer of formaldehyde, which subsequently caused the UF colloidal particles to aggregate and precipitate from the emulsion. On the other hand, as a traditional hardener, the addition of ammonium chloride would condense the linear structure of the UF resin into a three-dimensional cross-linked network, thereby decreasing the water solubility of the UF resin and causing it to precipitate. However, this does not explain why the precipitated UF nanoparticles deposit onto the surface of the microcapsules but not in the solution.

In a previous study,²³ we found that the pH of the system had a great influence on the deposition of UF nanoparticles onto the surface of the microcapsule, and high pH would prevent the deposition of UF nanoparticles. Brown et al.¹⁶ also found that microcapsules prepared at constant pH conditions have a smooth surface without UF nanoparticle deposition. Therefore, could the difference in the morphology of the PUF microcap-

sules be due to the reduction in pH by ammonium chloride during the reaction and the intensification of the deposition of UF colloidal particles onto the surface of the microcapsule? It is also possible that the addition of ammonium chloride increases the ionic strength of the medium, and compressed double electric layers destroy the stabilization of the UF colloidal particles (Figure 5), thereby causing the UF nanoparticles to precipitate on the microcapsule surface.

To ascertain whether these two assumptions are correct, two modified processes were performed without ammonium chloride. First, the microencapsulation was carried out by gradually reducing the pH conditions by drop-wise addition of HCl. The drop in pH in the microencapsulation process is consistent with that of adding ammonium chloride. Second, sodium chloride (0.715 mol L^{-1} with a conductivity of 50.10 ms cm^{-1}) was used as the electrolyte instead of ammonium chloride to investigate the effect of the electrolyte on the deposition of the UF colloidal particles on the surface of the microcapsules. The results are shown in Figure 6. It can be seen that the microcapsules prepared by the aforementioned modified processes have a smooth surface without UF colloidal particles deposition and easily collapsed after drying. The difference is that, in the first modified process, the UF colloidal particles remained in suspension after completion of the reaction [see in Figure 6(a-1)], whereas, in the second modified process, although the stability of the UF colloidal particles in solution was destroyed, the aggregated UF nanoparticles precipitated in the solution and not on the surface of the microcapsules [indicated by the arrow in Figure 6(b-1)]. These results indicate that the pH drop and the improvement in ionic strength in the solution by the addition of ammonium chloride are not the reasons of the UF nanoparticles deposition onto the surface of the microcapsules.

Driving Force for the Enrichment of the UF Nanoparticles at the Surface of Microcapsules

From the above results, it can be concluded that the addition of ammonium chloride could drive the formed UF nanoparticles to deposit onto the surface of the microcapsules; however, the mechanism remains unknown. Dietrich et al.²⁸ reported that the driving force for the enrichment at the surface of the dispersed phase is the tensile character of the amino resin. However, in their study, the researchers found the urea-formaldehyde resins are not surface active. However, in a previous work,²³ we found that the UF resins have some degree of surface activity. The difference between these two types of UF resins is that, in our work, ammonium chloride was added during synthesis. Therefore, the obvious question is whether the surface activity of the UF resins is caused by adding ammonium chloride. To illustrate this, we need to measure the surface tension of the UF resin solution. However, the problem is that in the one-step process of preparing PUF microcapsules, the urea and formaldehyde react under acidic conditions and the generated water-soluble surface active substances are intermediate products that quickly cure irreversibly forming water-insoluble substances and lose their surface activity. This makes difficult to measure the surface activity of the generated surface-active substances. To overcome this, we adopted an alternative method to compare the surface activity of the UF resin prepared with and

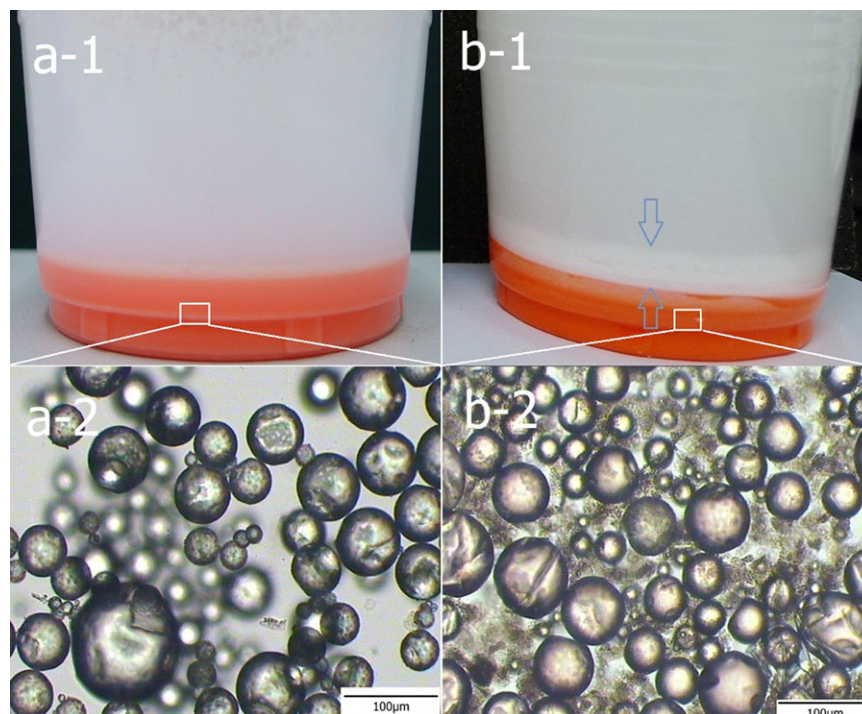


Figure 6. Digital and optical microscope (OM) photographs of PUF microcapsules prepared with (a) adjusting pH value and (b) adding sodium chloride. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

without ammonium chloride. In these two modified experiments, microcapsules were prepared without adding a surfactant while the rest of the experimental conditions remained the same. The only difference was adding ammonium chloride and not adding ammonium chloride (the pH drop during the microencapsulation process is consistent with that of adding ammonium chloride). Figure 7 shows digital and OM pictures of microcapsules prepared by the aforementioned modified processes. It is seen that the influence of ammonium chloride on the preparation of microcapsules is obvious. When no ammonium chloride is used, the prepared microcapsules have irregular shape and large diameter ($172\ \mu\text{m}$) as shown in Figure 7(a), which indicated that the surface activity of the generated UF resins is low and cannot stabilize the core droplets in solution even with the aid of mechanical agitation. In contrast, the microcapsules prepared with ammonium chloride show good sphericity and smaller diameter ($65\ \mu\text{m}$) as shown in Figure 7(b), which indicated that the generated UF resins have a certain surface activity that enriches the phase boundary between oil and water and lower its interfacial tension. Therefore, the result from the above experiments is that ammonium chloride can react with urea and formaldehyde to generate surface-active substances, and the surface activity may be the driving force of the enrichment of the UF resins at the surface-dispersed phase. Although ammonium chloride can increase the surface activity of the UF resins and help to form microcapsules with good morphology, the microcapsules prepared only with ammonium chloride but without a surfactant have low-barrier properties.

The FTIR spectras of the microcapsules (contain no core materials) that were prepared with and without ammonium chloride

are shown in Figure 8. Clearly, strong absorptions appear at $3302\ \text{cm}^{-1}$, which presents the stretching modes of $-\text{OH}$ and $-\text{NH}$ of the urea-formaldehyde resin. Besides, the characteristic peaks of urea-formaldehyde resin, like the amide bands (at 1650 and $1559\ \text{cm}^{-1}$), are seen in both spectra of the microcapsules. The presence of these characteristic peaks confirms the formation of urea-formaldehyde resin microcapsules. From the FTIR spectra of the microcapsules, we can also infer that there is little difference between these two samples. This indicates that adding ammonium chloride has little influence on the chemical structure of the urea-formaldehyde resin and we need the aid of other analytical characterization methods to further characterize its structure.

Impact of Time of the Ammonium Chloride Addition on the Formation of Microcapsules

Figure 9 shows microcapsules that were prepared with ammonium chloride at different times, from which we can see that the time of ammonium chloride addition impacts the formation of UF microcapsules. In the first case, ammonium chloride was added before the reaction. When the reaction started, the pH of the system slowly fell with time from 3.5 to 2.6 during the first 30 min (curve 1 in Figure 10). After the reaction, most of the UF nanoparticles were deposited on the surface of the microcapsules and rough-surfaced microcapsules were obtained [Figure 9(a-2)]. In the second case, ammonium chloride was added after 30 min of reaction. With the addition of ammonium chloride, the pH of the system decreased sharply from 3.6 to 2.6 within one minute (curve 2 in Figure 10). After the reaction, most of the core materials were not coated and were deposited at the bottom of the reactor, as indicated in Figure 9(b-1) by

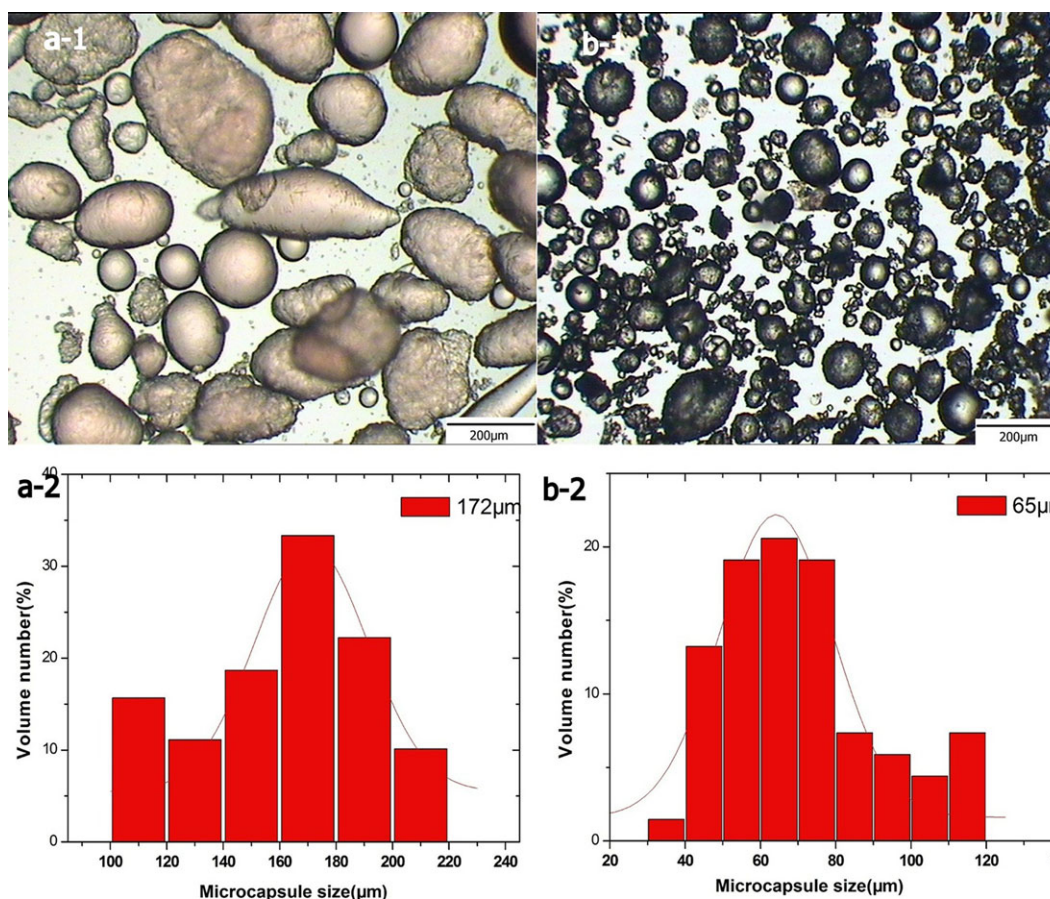


Figure 7. Digital and optical microscope (OM) photographs of PUF microcapsules prepared without adding surfactant (a) without NH_4Cl and (b) with NH_4Cl . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the red arrow. The formed microcapsules have a rough surface and irregular shape [Figure 9(b-2)]. In the third case, ammonium chloride was added after 120 min of reaction. With the

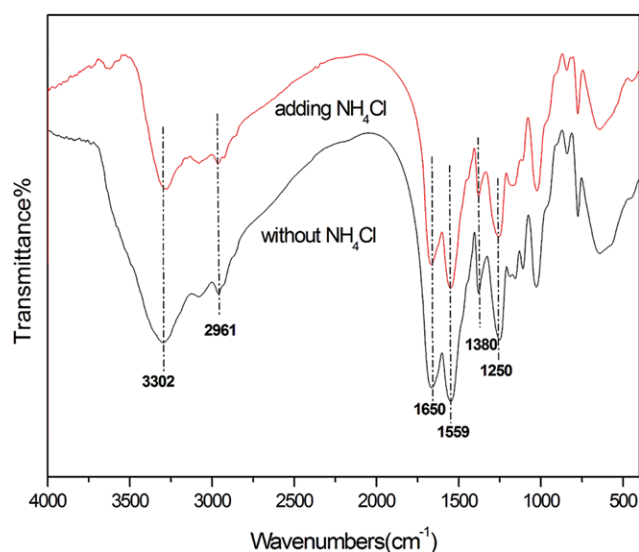


Figure 8. FTIR spectra of different microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition of ammonium chloride, the pH of the system decreased slowly from 3.6 to 3.1 in 2 h (curve 3 in Figure 10). After the reaction, the UF nanoparticles precipitated in the solution and not on the surface of the microcapsule [indicated by the arrow in Figure 9(c-1)]. Although, the microcapsules prepared by this method had a smooth surface, their mechanical strength was low and easily collapsed after drying.

The reasons for the above phenomena can be explained as follows. In the one-step method of preparing PUF resin microcapsules, the methylation reaction and polycondensation reaction are processing simultaneously.¹⁷ The rate of the reactions of the urea and formaldehyde is controlled by the pH and temperature of the solution. As the temperature increases and pH falls, the rate of the reaction increases.^{29,30} At the initial stage of the reaction, the temperature of the reaction solution is low, thereby reducing the rate of reaction between ammonium chloride and formaldehyde as well as between ammonium chloride and hydroxymethyl urea. Consequently, the formed surface-active substances have enough time to enrich the oil–water interface and form microcapsules with better morphology. When the reaction was carried out after 30 min, the temperature of the reaction solution has reached 55°C and most of the urea and formaldehyde underwent hydroxymethylation to yield hydroxymethyl urea. When ammonium chloride was added, due to the high

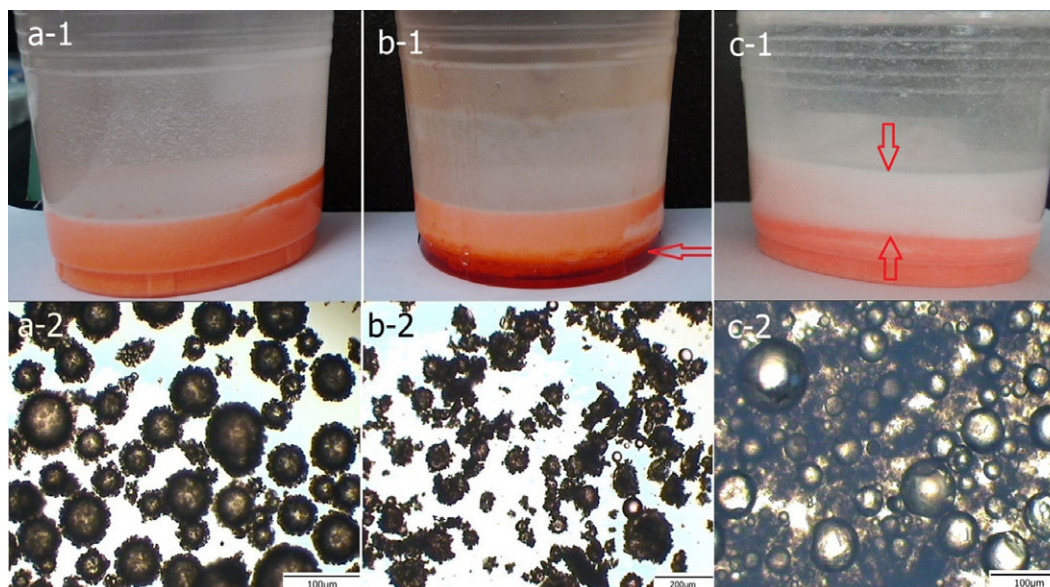


Figure 9. Digital and optical microscope photographs of microcapsules prepared with adding NH_4Cl at different times: (a) adding NH_4Cl before the reaction, (b) adding NH_4Cl after 30 min of reaction, and (c) adding NH_4Cl after 120 min of reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature, the reaction rate between ammonium chloride and formaldehyde as well as between ammonium chloride and hydroxymethyl urea rose, and the formed surface-active substances immediately converted into a water-insoluble resin that cannot wrap the oil droplets to form microcapsules. When the reaction was carried out after 120 min, most of the hydroxymethyl urea that can react with ammonium chloride to generate surface-active substances was converted into water-insoluble UF nanoparticles by the polycondensation reaction. Thus, the role of ammonium chloride in this stage is to destroy the stabilization of the UF colloidal particles, thereby causing the UF colloidal

particles to aggregate and precipitate from the emulsion. The precipitated UF colloidal particles have no surface activity. Therefore, most of the nanoparticles are not deposited on the surface of the microcapsules.

CONCLUSION

This study was undertaken to investigate the effect of ammonium chloride on the formation of PUF microcapsules and the following important conclusions were drawn based on the experimental results. The addition of ammonium chloride in the one-step process of preparing PUF resin microcapsule can cause the pH of the system to decrease. The reasons for the pH decrease are the reaction between ammonium chloride and formaldehyde and, more importantly, the reaction between ammonium chloride and hydroxymethyl urea. In addition to reducing the pH of the system, the reaction between ammonium chloride and urea-formaldehyde can generate surface-active substances, which drives the formed UF nanoparticles to enrich the surface of the dispersed phase.

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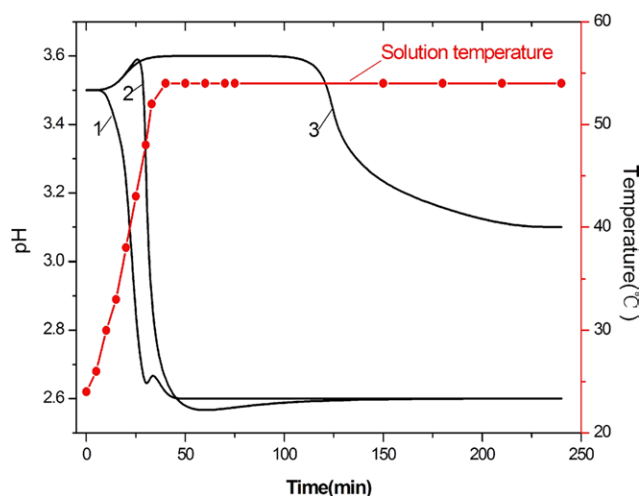


Figure 10. Temperature and pH profile during microencapsulation: (1) adding NH_4Cl before the reaction, (2) adding NH_4Cl after 30 min of reaction, and (3) adding NH_4Cl after 120 min of reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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