Synthesis of Enhanced Urea–Formaldehyde Resin Microcapsules Doped with Nanotitania

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ABSTRACT: Urea–formaldehyde (UF) resin microcapsules doped with TiO_2 nanoparticles were prepared by *in situ* polymerization, and the properties of the microcapsules, such as the surface morphologies, thermal properties, and chemical elemental composition, were measured by optical microscopy, scanning electron microscopy, thermogravimetric analysis, and energy-dispersive X-ray spectrometer analysis. The effects of the presence of ammonium chloride and its concentration and the concentrations of UF resin prepolymer and TiO_2 nanoparticles during the reaction and deposition of UF on the microcapsule surface on the properties of the microcapsules were investigated. Enhanced UF resin microcapsules with more stability and mechanical strength could be obtained under the optimal conditions. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 248–256, 2012

Key words: microencapsulation; nanoparticle; resins

INTRODUCTION

Microencapsulation is a process of enwrapping microscopic amounts of solid, liquid, or both within a thin film of polymer. This core/shell structure confers to microcapsules many properties, such as the targeting of active ingredients to specific sites, the protection of the active component in a single mixture, increased environmental stability, the mixing of immiscible and incompatible materials, and the conversion of liquids or tacky solids to free-flowing powders.[1] These advantages enlarge the wide application of microencapsulation, such as in carbonless copying paper,[2] food additives,[3] pharmaceuticals,[4] cosmetics,[5] insecticides,[6] catalysts,[7] and electrophoretic display.[8,9]

One of the microencapsulation methods often used is *in situ* polymerization with amino resins, such as urea and melamine, which form the capsule wall by condensation polymerization with formaldehyde[10,11] because of their low cost and easy operation. Nevertheless, urea–formaldehyde (UF) resin has many drawbacks, including poor water resistance, easy aging, and cracking,[12] and the microcapsules prepared in normal way lack enough elasticity and show clear collapse and breakage under drying or compression.[13,14] To solve the problem, many novel capsule wall materials have been adopted with the purpose of gaining microcapsules by other methods, such as complex coacervation.[15,16] However, these methods require quite complex processes and cost expensive raw materials.[17] Hence, improving the performance of UF resin microcapsules is still a challenge.

The preparation of UF microcapsules consists of the reaction between urea and formaldehyde to obtain methylol urea, which further condenses under acidic conditions to form the shell material.[18] The morphology and physical properties of the capsules are highly affected by the reaction conditions,[19] such as the pH value, formaldehyde/urea molar ratio, sort of emulsifier, core content, and stirring rate. A proper curing agent is also of high importance for improving the robustness of UF microcapsules.[20] Fan and Zhou[18] reported that the addition of ammonium chloride (NH_4Cl) can cause a substantial drop in the pH value during the reaction and facilitate the

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TABLE I
Experimental Parameters and Test Results

Sample	Concentration of NH_4Cl (wt %)	Concentration of UF prepolymer (wt %)	Concentration of nano-TiO_2 (wt % oil core)	Morphology of the microcapsules	Collapsed or not after drying	Empty or not after drying
N1	0	24.7	0	Regular and smooth	+	+
N2	0	32.7	0	Regular and smooth	+	+
N3[a]	0.05	24.7	0	Regular and smooth	−	+
N4	0.5	24.7	0	Regular and smooth	−	+
N5[b]	0.05	24.7	0.04	Regular and smooth	−	−
N6	0.5	24.7	0.04	Hedgehog shape and broad distribution	−	−
U1	0.05	16.5	0.04	Regular and smooth	+	+
U2	0.05	21.4	0.04	Regular and smooth	+	+
U3[b]	0.05	24.7	0.04	Regular and smooth	−	−
U4	0.05	32.7	0.04	Multilayer shell and rough	−	−
T1[a]	0.05	24.7	0	Regular and smooth	−	+
T2	0.05	24.7	0.2	Regular and smooth	−	−
T3	0.05	24.7	0.4	Hedgehog shape and broken	−	−

+/−: Samples were collapsed/empty (+) or not (−) after drying.
[a] Samples N3 and T1 had the same process parameters.
[b] Samples N5 and U3 had the same process parameters.

deposition of UF nanoparticles onto the surface of the microcapsule. However, further research on the effect of NH_4Cl content on the morphology of microcapsules was not done.

Microcapsules with nanoparticle-doped polymer walls have attracted a great deal of interest recently, as rigid nanoparticles incorporated with polymer matrices can create nanocomposite structures that exhibit superior properties in mechanics, optics, magnetism, and so on.[21–23] Xuan et al.[24] introduced iron nanoparticles into the shells of UF resins to endow the microcapsules with excellent magnetic properties. Li et al.[25] prepared phase-change material microcapsules incorporated with silver nanoparticles to increase the wall toughness and mechanical strength. It was reported that nanotitania (nano-TiO_2) can be used to enhance the bonding strength of UF resin plywood,[26] and nanoparticles can be added to polymeric materials to improve their mechanical performance.[27] Therefore, it can be expected that nano-TiO_2 can be doped to enhance the compact densification and collapse-resistant capacity of UF resin shells.

In this study, enhanced UF resin microcapsules were obtained by *in situ* polymerization and incorporated with TiO_2 nanoparticles. Meanwhile, the effects of several processing parameters, such as the presence of a curing agent and its concentration and the concentrations of the prepolymer and nanoparticles during the reaction, on the properties of the obtained microcapsules were investigated in detail.

EXPERIMENTAL

Materials

Tetrachloroethylene (TCE) and oil blue N dyes [1,4-bis(pentylamino)anthraquinone, an oil-soluble dye; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China] were used as core materials. Urea and formaldehyde from Sinopharm were used to produce microcapsules by *in situ* polymerization. Maleic anhydride and triethanolamine from Sinopharm were used as pH controllers. Gelatin, resorcinol, and sodium chloride (NaCl) from Sinopharm were used as colloidal stabilizers and system modifiers. Titanium dioxide (HTTi-04-01, rutile powder, 30 nm) was obtained from Nanjing Hai Technology Nano Co., Ltd. (China). NH_4Cl from Sinopharm was used as a curing agent.

Preparation of UF prepolymer

Urea (15 g) was dissolved in 32.5 mL of 37 wt % aqueous formaldehyde. Then, the mixture was adjusted to a pH of 8.5–8.9 with triethanolamine. After reaction for 1 h at 70°C, a double amount of deionized water was added. The mixture was cooled to room temperature rapidly and stored in the refrigerator for further use.

In situ polymerization of UF resin microcapsules

UF resin microcapsules doped with nano-TiO_2 were prepared by an *in situ* polymerization method.[20,24,28] First, a certain amount of this prepolymer was adjusted to a pH of 4.0 with 10 wt % aqueous maleic anhydride. After it was stirred for 1 h, the adjusted prepolymer was diluted by 40 mL of deionized water containing 3 g of NaCl, 0.1 g of gelatin, and 0.04 g of resorcinol. This mixture was marked as solution A. Suspension liquid B was obtained by dispersing a certain amount of nano-TiO_2 powder into 4.5 mL of TCE containing 5 mg of oil blue N dye under ultrasonification. Under rapid agitation, suspension liquid B was dropped into the solution A to

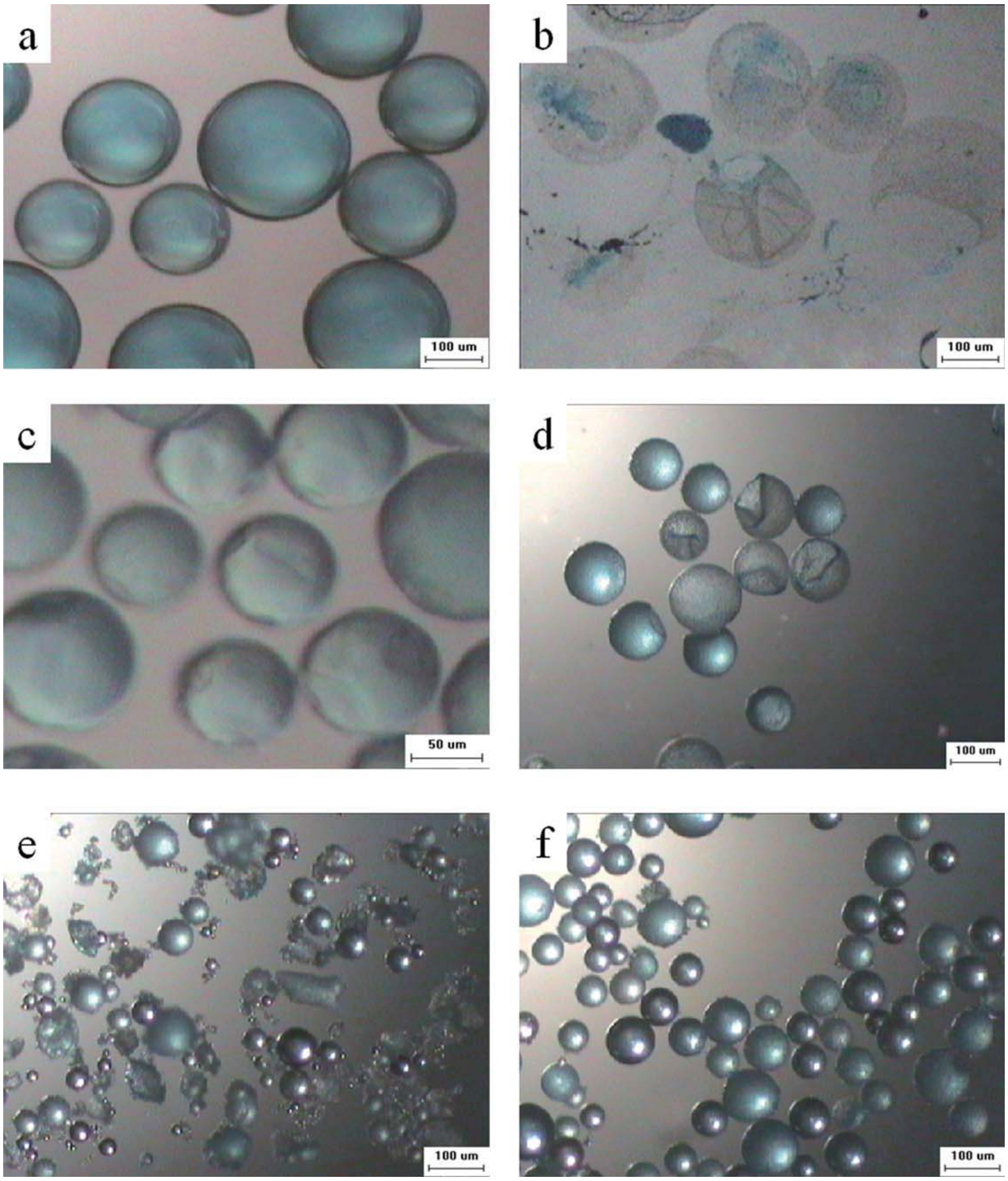


Figure 1 OM images of microcapsules (a) before curing; cured with different concentrations of NH_4Cl: (b) 0, (c,f) 0.05, and (d,e) 0.5 wt %. (a–d) microcapsules without TiO_2; and (e,f) microcapsules with 0.04 wt % TiO_2 oil core. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

form an oil-in-water (O/W) emulsion. Then, the pH of the emulsion was adjusted to 3.0. After the reaction ran for 1 h at room temperature, a certain amount of 15 wt % NH_4Cl aqueous was added, and the temperature was increased to 45°C. This temperature was retained with stirring for another 2 h, and after that, it was washed/filtered with deionized water and air-dried at room temperature. The UF resin microcapsules without TiO_2 were also prepared as a reference sample (sample T1) for contrast analysis by the same procedure, except that the core materials contained only TCE and oil blue N. The various process parameters considered in this study, their effects on the properties of the resultant microcapsules, and the sample identifications are given in Table I.

Characterization

The morphologies of the microcapsules were observed by optical microscopy (OM; CFM-300E, Shanghai Changfang Optical Instruments, Shanghai,

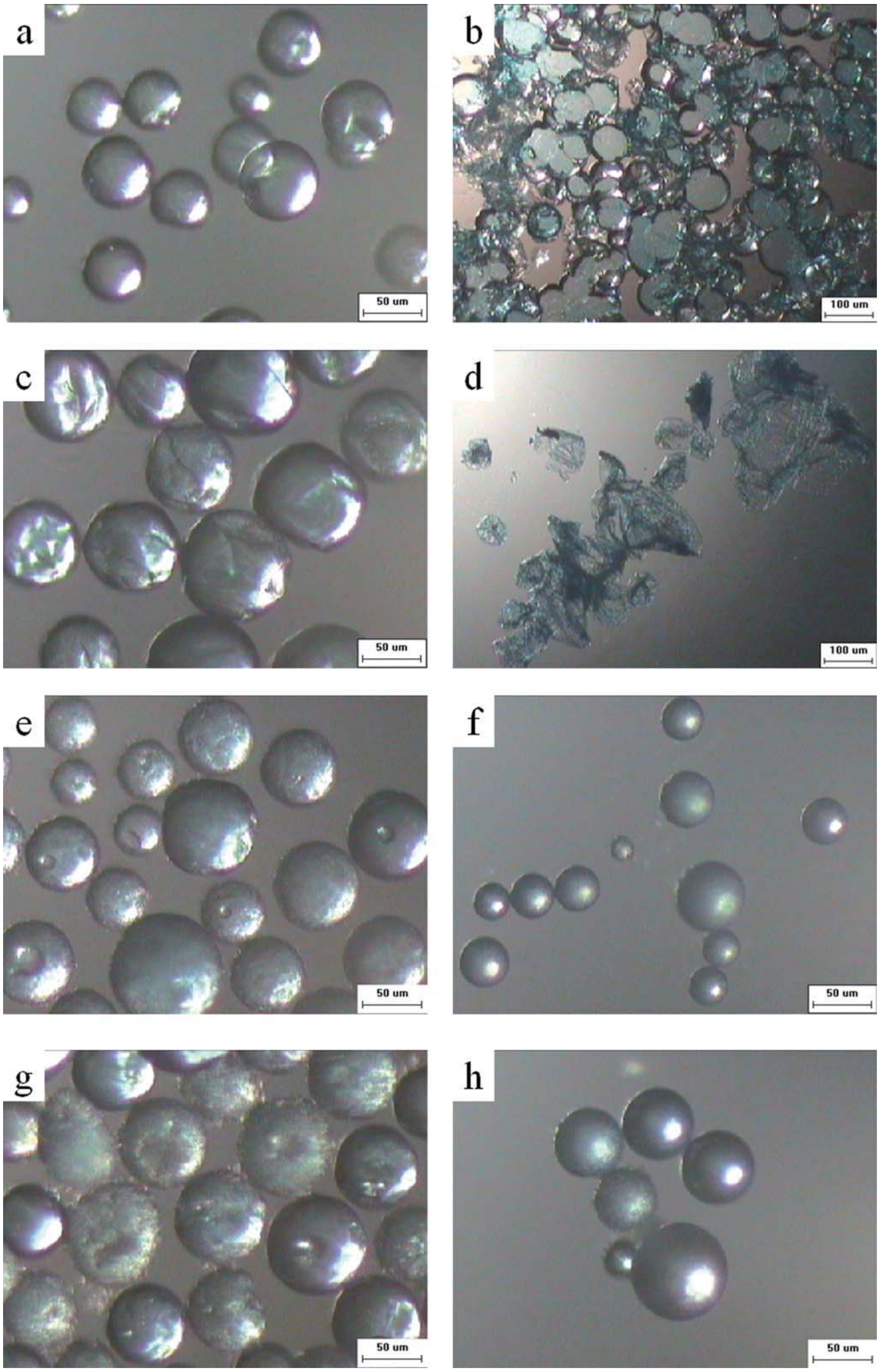


Figure 2 OM images of microcapsules (a,c,e,g) before and (b,d,f,h) after drying prepared with different concentrations of UF resin prepolymer: (a,b) 16.5, (c,d) 21.4, (e,f) 24.7, and (g,h) 32.7 wt %, where the concentration of TiO_2 nanoparticles was 0.04 wt % oil core.

China) and scanning electron microscopy (SEM; Sirion, FEI, The Netherlands).Thermal characteristics of the microcapsules were examined by thermogravimetric (TG) analysis (STA 409, Netzsch, Germany) at a heating rate of 10°C/min in an N_2 environment. The chemical elemental composition was analyzed with an energy-dispersive X-ray spectrometer (Genesis 60S, EDAX) attached to an SEM instrument.

RESULTS AND DISCUSSION

Effect of the concentration of NH_4Cl

Figure 1 shows the OM image of the microcapsules prepared with different concentrations of NH_4Cl. Although the surface of the microcapsules without NH_4Cl was smooth and transparent [Fig. 1(a)], the obtained microcapsules easily collapsed after drying [Fig. 1(b)]. Interestingly, the uncollapsed and transparent microcapsules were gained in the presence of 0.05 wt % NH_4Cl [Fig. 1(c)]. The reason for the difference was that NH_4Cl could reduce the pH value effectively during the condensation reaction and intensify the deposition of UF colloidal particles onto the surface of the microcapsule and, thus, could be used as a proper curing agent for the UF microcapsules.[18,20] Increasing the content of NH_4Cl could reinforce the shell strength as more UF colloidal particles covered the surface of the microcapsules, but many empty microcapsules also appeared [shown in Fig. 1(d)]; this indicated the short shelf life during handling. To enhance the compact densification and collapse-resistant capacity of the UF shells, titania nanoparticles were doped into the shell. With the concentration of TiO_2 nanoparticles as 0.04 wt % of the oil core, we found that lots of colloidal particle agglomerations appeared around the microcapsules, and the size distribution became broad with the higher concentration (0.5 wt %) of NH_4Cl [Fig. 1(e)]. Nevertheless, smooth and compact UF microcapsules were obtained with a lower concentration (0.05 wt %) of NH_4Cl [Fig. 1(f)]; this revealed the fact that excessive NH_4Cl reduced the pH value of the system transiently and thus accelerated the condensation of crosslinking and the deposition process of the UF resin. Meanwhile, excessive NH_4Cl caused the emergence of colloidal particle agglomerations and hampered the formation of compact microcapsules.

Effect of the amount of UF resin prepolymer

The content of UF resin prepolymer was also adjusted to improve the collapse-resistant capacity of the UF microcapsules. As shown in Figure 2, UF microcapsules prepared with low prepolymer content (16.5–21.4 wt %) were thin and transparent, as most of the prepolymer was consumed to form the inner membrane of the microcapsule; thus, few UF resin colloidal particles formed in the solution. However, they all collapsed, even when NH_4Cl and titania were added [Fig. 2(a–d)]. An amount of 24.7 wt % prepolymer was adequate to ensure optically transparent and collapse-resistant microcapsules [Fig. 2(e,f)]. However, more prepolymer induced multilayer encapsulation, which made the microcapsules rough and opaque [Fig. 2(g,h)] because of the formation of numerous UF resin colloidal particles.

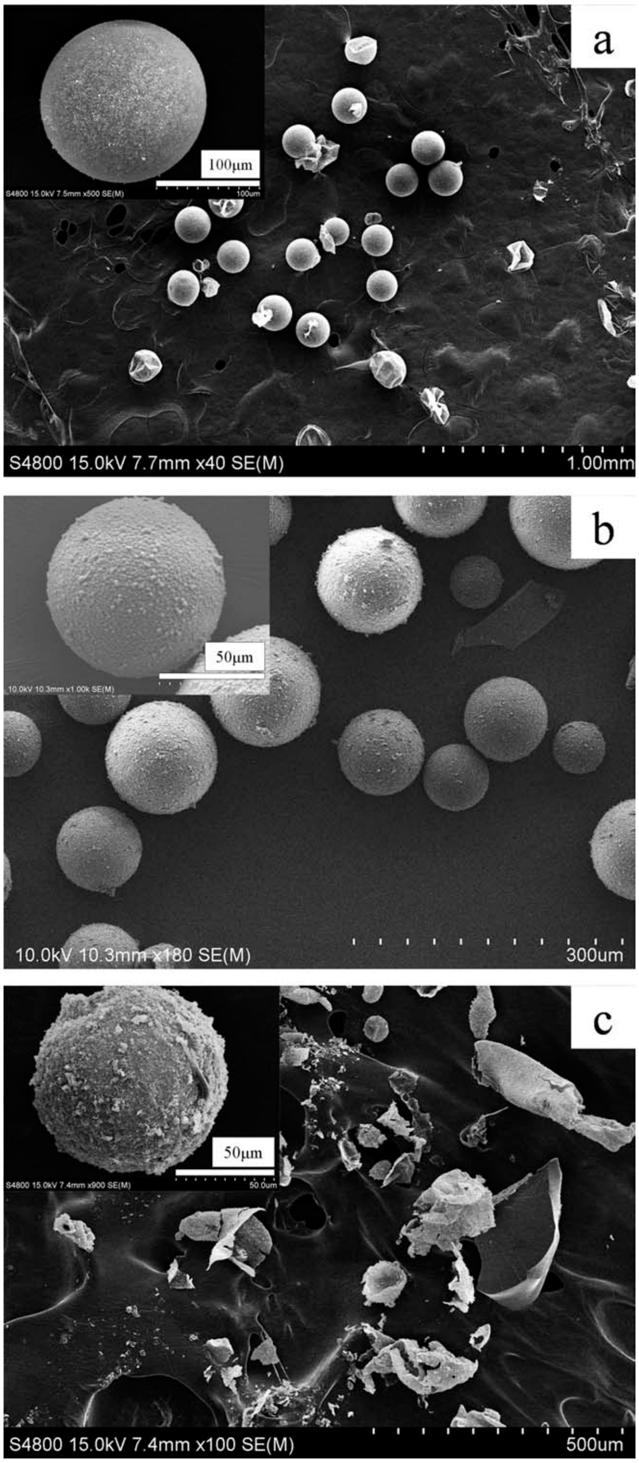


Figure 3 SEM images of microcapsules prepared with different concentrations of TiO_2 nanoparticles: (a) 0, (b) 0.2, and (c) 0.4 wt % oil core.

Effect of the TiO_2 nanoparticle content

Figure 3 shows the SEM of the microcapsules prepared with different concentrations of titanium dioxide. The surface morphology of the UF mircapsules obtained without titania was the smoothest among

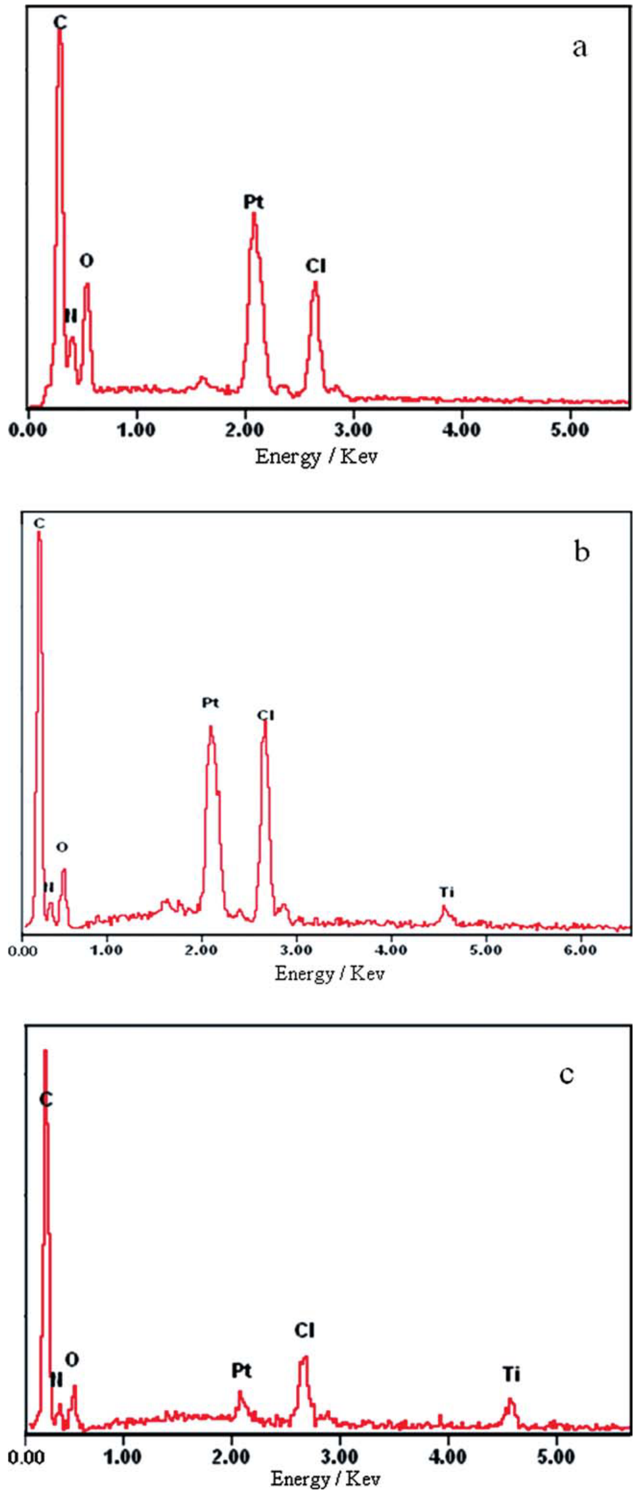


Figure 4 EDX spectra of the (a,b) outer and (c) inner surfaces of microcapsules (b,c) with and (a) without TiO_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the three samples, but some of microcapsules were obviously deformed and attached to the adjacent intact ones [Fig. 3(a)] because of the diffusion of core materials out of the shell and the contraction of the shell.[29] With the incorporation of 0.2 wt % TiO_2 nanoparticles of oil core into the shell, the microcapsules became robust and compact and had few microprotuberances on the surface but still had a relative smoothness [Fig. 3(b)]. This observation indicated that a small amount of TiO_2 nanoparticles was inserted into the UF shell, which could have increased the robustness and compactness of the microcapsules. It was reported that there are many unsaturated residual bonds and different binding states of hydroxyl on the surface of nano-TiO_2, which can form hydrogen bonds or van der Waals forces with hydroxyl or amino group of UF resin. Moreover, nano-TiO_2 particles are disposed to bond with the active groups of UF resin because of its high surface energy and insufficient coordination on the surface.[26] Thus, TiO_2 nanoparticles were not simply mixed with the UF resin, but intertwisted with the UF polymer chains[27] and thus could have been embedded into the shell of the UF microcapsules. Therefore, the robustness of the UF microcapsules could be increased because of the reinforcement and toughening effect of the nano-TiO_2 particles.[30] Simultaneously, the compactness of the UF microcapsules could also be increased in the existence of nano-TiO_2, which could have reduced the micropores in the surface of the microcapsules.[28] However, the surface morphology turned rough, and plenty of crack microcapsules not microencapsulated completely emerged when the concentration of TiO_2 nanoparticles was increased to 0.4 wt % oil core [Fig. 3(c)]. Additionally, a number of floc particles adhered to the surface of the microcapsules [insert of Fig. 3(c)]. This phenomenon was attributed to the fact that excessive nanoparticles, tending to aggregate because of the increase of their surface energy, inhibited the

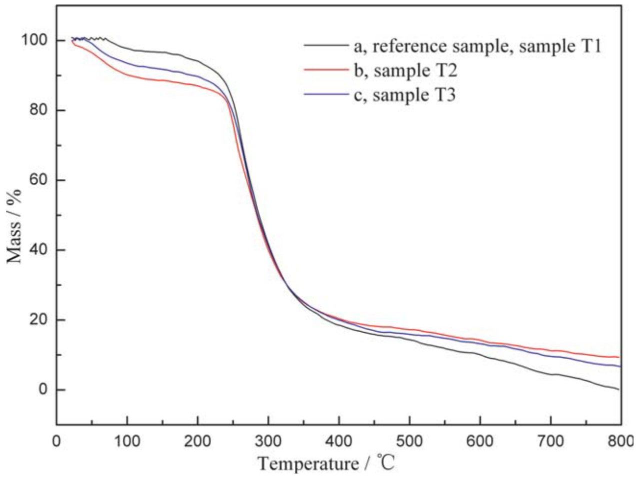
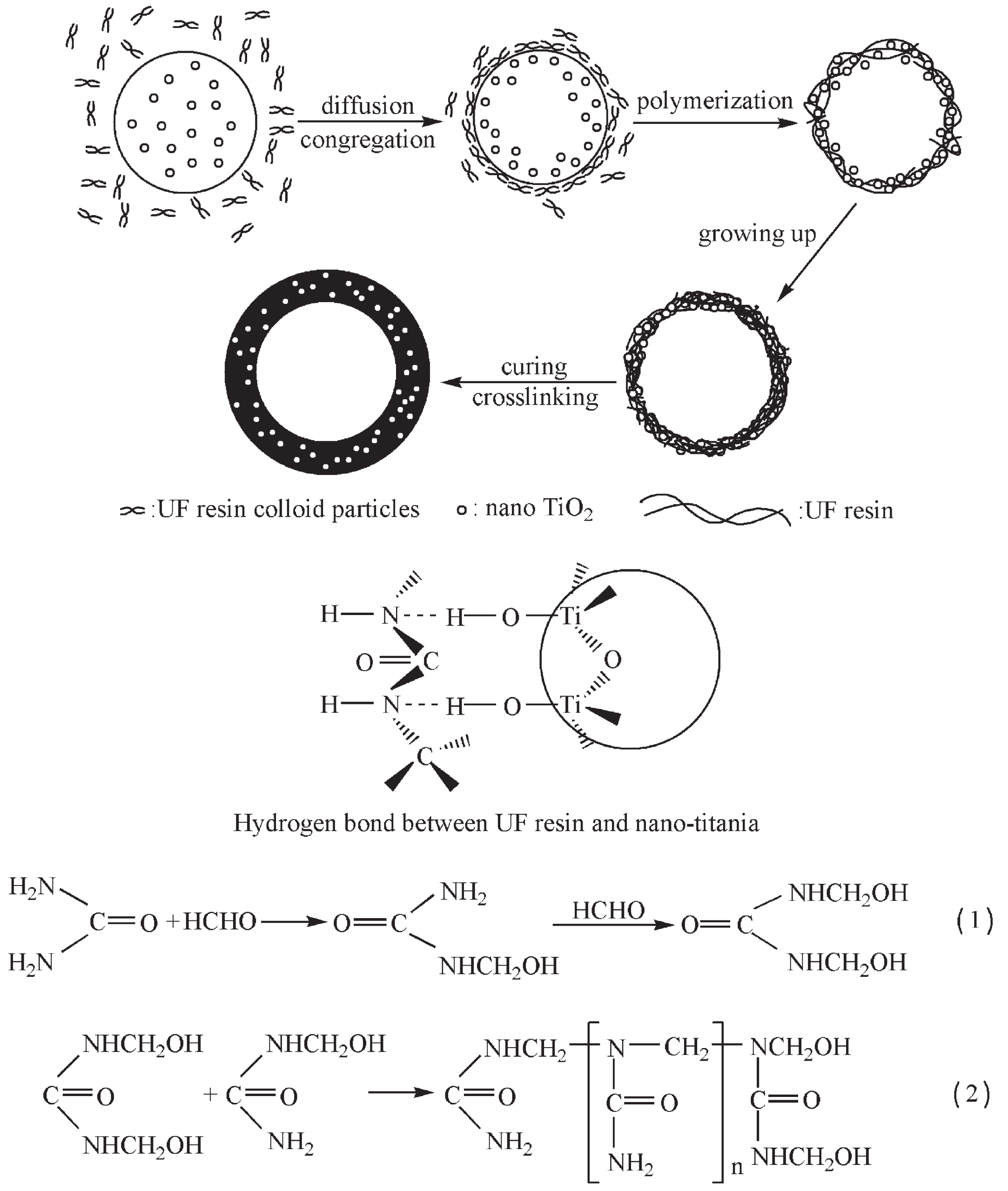


Figure 5 TG curves of microcapsules prepared with different concentrations of TiO_2 nanoparticles: (a) 0, (b) 0.2, and (c) 0.4 wt % oil core. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.



$$4NH_4Cl+6HCHO \rightleftharpoons (CH_2)_6N_4+4HCl+6H_2O \qquad (3)$$

Figure 6 Schematic illustration of the forming mechanism of microcapsules doped with nano-TiO_2.

process of microencapsulation.[28] As a result, many aggregations of UF resin colloidal particles formed in the solution, and some of them, together with some TiO_2 nanoparticles, which were not completely wrapped into the capsule shell, attached to the surface of the intact microcapsules.

To analyze the TiO_2 in the microcapsules, energy-dispersive X-ray spectroscopy (EDX) was used as an effective means to characterize the elemental composition. For sample T2, a broken microcapsule was found under the SEM observation; the outer and inner surfaces of the broken microcapsule were chosen as two typical regions for EDX testing [Fig. 4(b,c), respectively]. When the EDX spectra of the reference sample [sample T1, Fig. 4(a)] was compared, Ti signals were detected both in the outer [Fig. 4(b)] and inner [Fig. 4(c)] surfaces of the microcapsules [sample T2, the same sample as measured in Fig. 3(b)], which confirmed the presence of titania in the shell of the microcapsules, whereas Pt and N were introduced from platinum-sputtering and UF, respectively. The observed Cl signal was due to the

NaCl and NH_4Cl in the synthesis step and the curing step of the UF resin microcapsules.

TG analysis

When the microcapsules containing TiO_2 and oil blue N in TCE were used for TG testing, the right TG curves were never obtained, even after several tries. The results show that the mass loss ratio in the TG curves decreased dramatically from the initial 100% to −2220% to −2689% at about 210°C. The possible reason for the wrong curves have been that the crucible cover fell down because the TCE solution of oil blue N in the microcapsule was completely and suddenly gasified at 210°C, similar to an explosive minibomb on heating, as a compact wall structure prohibited the oil cores from leaking out below 210°C. To solve this problem, the microcapsules were cracked advisedly by pressing down and washed with acetone before TG analysis. The microcapsules without TiO_2 (reference sample, sample T1) were treated the same way.

Figure 5 shows the TG curves of the reference and doped microcapsules with different concentrations of TiO_2 nanoparticles. The mass loss before 120°C was attributed to the free water contained in the samples. The initial decomposition temperatures for microcapsules with 0.2 wt % (sample T2) and 0.4 wt % (sample T3) TiO_2 nanoparticles of oil core were observed at 241 and 239°C, respectively; these temperatures were a little higher than that of reference sample (231°C, sample T1). This indicated that the existence of TiO_2 nanoparticles slightly improved the thermal stability of the UF resin. All of the samples lost weight significantly at 240°C, and about 80% of the total mass was lost when the temperature was increased to 400°C. With the further increase of temperature to 800°C, the reference microcapsules (sample T1) were decomposed completely, whereas samples T2 and T3 still remained at about 9.3 and 6.7 wt %, respectively. The mass difference between the remains further confirmed the presence of TiO_2 in the shell of microcapsules. The final residue of sample T2 was a little heavier than that of sample T3; this was attributed to the loss of aggregated TiO_2 nanoparticles not completely wrapped into the capsule shell in sample T3.

On the basis of possible chemical reactions and interactions existing in the previous system, we propose a model for the formation of the microcapsule wall, as shown schematically in Figure 6. The prepolymer, composed of 1-hydroxymethyl urea and 1,3-dihydroxymethyl urea formed under alkalescent conditions [chemical eq. (1), Fig. 6], first condensed in weak acidic conditions ($pH = 4.0$) to form a low-molecular-weight polymer [chemical eq. (2), Fig. 6; the n value was small].[31] Simultaneously, numerous UF colloids emerged in the water phase. Then, emulsified droplets were produced with the addition of the nano-TiO_2/TCE dispersion under intensive stirring. UF colloids could congregate at the O/W interface to reduce the interfacial tension and form a thin film.[20] Meanwhile, TiO_2 nanoparticles could also diffuse into the O/W interface because of its hydrophilicity. With increasing stirring time, both the UF colloids and nano-TiO_2 gradually aggregated to grow up slowly in the O/W interface. During the curing process, the addition of the curing agent, NH_4Cl, induced a rapid decrease in the pH value [chemical eq. (3), Fig. 6], which dramatically accelerated the polymerization. In this case, more and more UF colloids associated with nano-TiO_2 deposited onto the O/W interface to form a thicker microcapsule shell. Under continuing condense polymerization, the TiO_2 nanoparticles intertwisted with the polymer chains via hydrogen bonds, van der Waals forces, and so on to form an inorganic–organic hybrid crosslinking composite film. Finally, reinforced microcapsules doped with nano-TiO_2 were obtained.

CONCLUSIONS

Leak-proof and optically transparent UF resin microcapsules with enhanced mechanical strength and doped with TiO_2 nanoparticles were prepared by *in situ* polymerization. The effects of different concentrations of NH_4Cl of UF prepolymer and of TiO_2 nanoparticles on the morphologies and mechanical strength of UF microcapsules were comprehensively investigated. NH_4Cl played an important role in the curing process, but a high concentration caused the emergence of colloidal particle agglomerations. The transparency of the microcapsules was improved by a reduction of the amount of UF resin prepolymer. TiO_2 effectively enhanced the compactness and robustness of the microcapsules. However, the process of microencapsulation was inhibited by the higher concentration of TiO_2 nanoparticles, which was more than 0.2 wt % of the mass of the oil core.

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