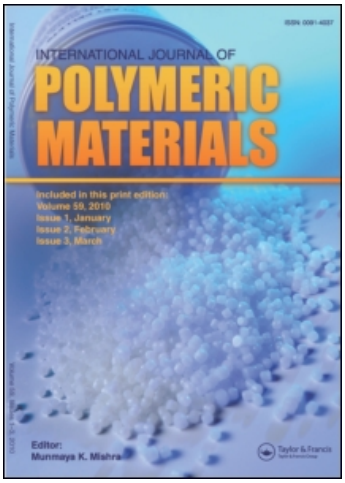


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

EFFECTS OF CATALYST AND CORE MATERIALS ON THE MORPHOLOGY AND PARTICLE SIZE OF MICROCAPSULES

Li Zhuo[a]; Chen Shuilin[a]
[a] Donghua University, Shanghai

Online publication date: 16 August 2010

To cite this Article Zhuo, Li and Shuilin, Chen(2004) 'EFFECTS OF CATALYST AND CORE MATERIALS ON THE MORPHOLOGY AND PARTICLE SIZE OF MICROCAPSULES', International Journal of Polymeric Materials, 53: 5, 385 — 393
To link to this Article: DOI: 10.1080/00914030490429898
URL: http://dx.doi.org/10.1080/00914030490429898

International Journal of Polymeric Materials, 53:385–393, 2004

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490429898

Taylor & Francis
Taylor & Francis Group

EFFECTS OF CATALYST AND CORE MATERIALS ON THE MORPHOLOGY AND PARTICLE SIZE OF MICROCAPSULES

Li Zhuo
Chen Shuilin
Donghua University, Shanghai, People's Republic of China

In this article, an interfacial polymerization method was employed for micro encapsulation. The wall material was polyurea and the core materials were diethyl (o-) phthalate, dibutyl (o-) phthalate and dioctyl (o-) phthalate. Poly (vinyl alcohol) (PVA) was used as protective colloid and GPE2040 was used as emulsifier. The effects of catalyst in different phases and core materials with different hydrophobicities on the morphology and particle size were studied. It was found that the surface of microcapsules form catalyst in aqueous phase were smoother and the average size was smaller than that with the catalyst in the organic phase and higher hydrophobicity gave smoother morphology.

Keywords: microcapsule, catalyst, core material, morphology, particle size

INTRODUCTION

Microcapsule are minute containers enclosing core materials such as drugs, pesticides, herbicides, dyes, fragrances, etc. within the wall material. The core material may be a liquid, a gas or a solid, while the wall material may be usually made of natural or synthetic polymeric membranes. Microcapsules have been used in numerous applications; for example, to separate active ingredients, to control odor, to mask taste, to control volatility and flammability, to moderate chemical reactivity, to provide slow release of contents and to protect the environment, etc. [1] Particle sizes of the microcapsules are usual within the range of 2–1000 μm. Theoretically, minimum microcapsules of 0.001 μm can be made. Now, capsules whose particle

Received 5 August 2001; in final form 15 August 2001.
Address correspondence to Li Zhuo, No. 1882, Yan an Road West, Shanghai 340, Donghua University, Shanghai 200 051, P. R. China. E-mail: lizhuo26@163.net

sizes are about 1–1000 nm have been made. Though the shapes of microcapsules are varied, most of them are spherical. Micro encapsulation processes can be roughly divided into three categories: chemical methods, physical-chemical methods and mechanic methods. Chemical methods include interfacial polymerization, in situ polymerization, etc. [1]. Although many methods for the preparation of microcapsule have been reported since Green and Schweitzer patented the first process in 1956 [2], the interfacial polymerization process has become an important, feasible, convenient and widely used technique that encapsulates a good variety of active principles. It offers the possibility of rapid production of polymers with high and specific molecular weight ranges under mild conditions of temperature and pressure [3]. In general, this procedure consists firstly of preparing an emulsion of two immiscible phases, each containing one complementary monomer. The polymeric shell of the microcapsule is then formed at the surface of the droplet of the dispersed phase through a polymerization reaction.

In the interfacial polymerization of isocyanates, the polymer was initially formed in the organic phase [4]; therefore, the morphology and particle size are highly affected by the composition of the organic phase. The morphology and the particle sizes of microcapsules are very important since they directly affect the behavior and applications of microcapsules [5]. Although there have been some reports on polyurea-microencapsulation, very few works relating the effect of catalyst and core materials on the morphology and particle size of microcapsule has been published so far. In this work, we have investigated the effect of catalyst and core materials on the morphologies and particle sizes of microcapsules. Three core materials with different hydrophobicities were specially selected.

EXPERIMENTAL

1. Reaction Mechanism

Naegeli [6] put forward that the reaction mechanism of isocyanate with water could be divided into several steps and finally generate the substituted urea. The reaction processes were shown as the following:

$$\mathrm{RNCO} + \mathrm{H_2O} \longrightarrow \mathrm{RNHCOOH} \xrightarrow{-\mathrm{CO_2}} \mathrm{RNH_2} \xrightarrow{\mathrm{RNCO}} \mathrm{RNHCONHR} \qquad (\mathrm{I})$$

$$\mathrm{RNCO} + \mathrm{H_2O} \longrightarrow \mathrm{RNHCOOH} \xrightarrow{\mathrm{RNCO}} (\mathrm{RNHCO})_2\mathrm{O} \xrightarrow{-\mathrm{CO_2}} \mathrm{RNHCONHR} \qquad (\mathrm{II})$$

$$\mathrm{RNCO} + \mathrm{H_2O} \longrightarrow \mathrm{RNHCOOH} \xrightarrow{-\mathrm{CO_2}} \mathrm{RNH_2}$$

$$\Big\downarrow \mathrm{RNHCOOH}$$

$$[\mathrm{RNHCO_{2^-}}][\mathrm{RNH_3^+}] \longrightarrow \mathrm{RNHCONHR} \qquad \text{(III)}$$

Sequence I would be favored in those cases in which the carbamic acid is very unstable, decomposing rapidly to the amine. When the carbamic acid is fairly stable, reaction sequence II could become increasingly important. Sequence III could be significant when the amine and the isocyanate react with each other very slowly.

In this work, an interfacial polymerization method using polyisocyanates was employed for micro encapsulation. The wall forming reaction follows that the isocyanate monomers are hydrolyzed at the interface to form amines, which in turn react with unhydrolyzed isocyanate monomers to form the polyurea microcapsule wall.

2. Apparatus

The high-speed mixer BME 100l is from Shanghai Weiyu mechanical-electronic Co. Ltd. JB90-D heavy electrical agitating machine is from Shanghai specimen model factory. TSM micro-size particles analytical instrument is from Shanghai University of Science and Engineering. CAM-SCAN-4 scanning electron microscope is from Cambridge, England.

3. Chemicals

The core materials of diethyl (o-) phthalate (Chemical Reagent), dibutyl (o-) phthalate (Analytical Reagent) dioctyl (o-) phthalate (Analytical Reagent) are purchased from the Shongkai Group Co Ltd. (Shanghai), Shenyang agent factory and the latter two were from Shanghai Feida industy and trade Co. Ltd., respectively. The Dibutyltin dilaurate acted as the catalyst; the sodium hydroxide (25% solution) was used to regulate the pH; poly (vinyl alcohol) (PVA) was used as protective colloid; Gaoqiao fine chemicals Co. Ltd. Shanghai provided GPE2040 used as the emulsifier. The wall forming materials were TDI (2, 4-toluene diisocyanate) and triphenyl methane triisocyanate, which were purchased from the chemicals shop.

4. Micro Encapsulation Process

The micro encapsulation process is illustrated in Figure 1. The micro encapsulation process consisted mainly of four steps: (a) preparing an aqueous phase (200 g) containing emulsifier (4 g), protective colloid (2 g) and water, stir-homogeniting them and adding Sodium hydroxide (25% aqueous solution); (b) preparing an organic phase containing core material (20 g), wall material (40 g) and catalyst (0.1%) (c) emulsification (for 5 minutes) under stirring of 9000 rpm and, during emulsification, the organic phase was dispersed into the aqueous phase with the aid of the emulsifier under high speed agitation; (d) the system was transferred immediately into a reactor with a stirrer and stirred at room temperature for 5 hour; and (e) finally, the microcapsules were recovered by filtration washed and dried at room temperature.

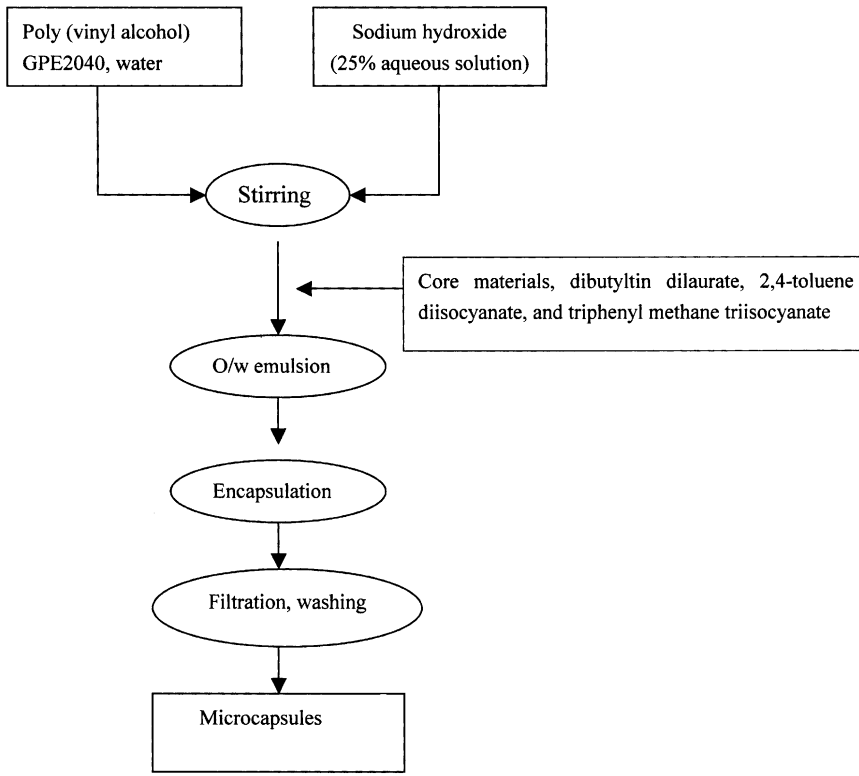


FIGURE 1 The micro encapsulation process used.

RESULTS AND DISCUSSION

1. Effects of Catalyst in Different Phases on Morphology and Particle Size

The effects of the catalyst, which was selectively added in organic phase, in aqueous phase and in both phases (half of each), on the morphology, the particle sizes and size distribution of microcapsules were studied.

(I). On the Morphology

The surface of the microcapsules whose core material was diethyl (o-) phthalate with catalyst in the organic phase only became rougher compared with the other samples prepared with catalyst in the aqueous phase only and in both phases as shown in Figure 2 (here, only are the former tow cases listed). It might be due to the active reaction in the dispersed globules by the addition of catalyst. Since the polymer was formed initially in the organic phase [4], the nature of this phase should affect the course of the polymerization reaction directly. Catalysts have been described as promoter of the formation of high molecular weight polymers [5]. Catalyst in the organic phase significantly promoted the reaction of TDI and led to an increase of the rate of polymer formation and precipitation of the polymer at the surface of the dispersed droplets during the early stage of the formation of the microcapsule wall [5]. These factors of rapid and random polymerization and precipitation on the globules surface would have led a very rough surface.

(II). On the Particle Sizes and Size Distribution of Microcapsules

Figure 3 shows the TSM micro-size particles analytical graphs of diethyl phthalate microcapsules. It can be seen that where the catalyst

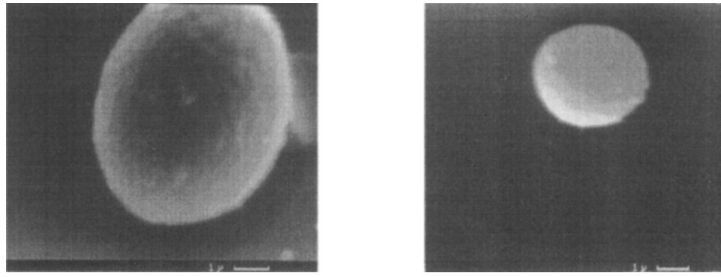
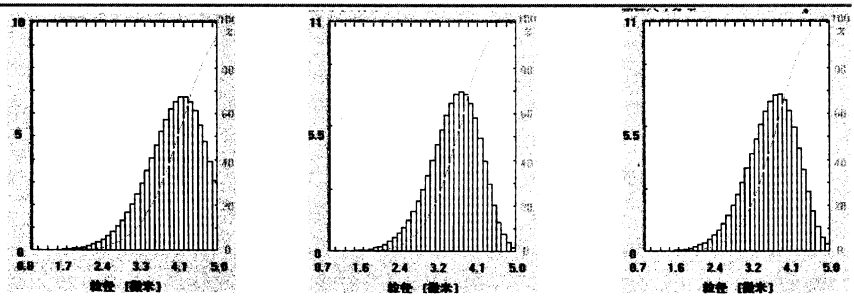


FIGURE 2 The surface morphological structure of the microcapsules formed under different conditions of catalysts. (a) Catalyst in the organic phase, (b) Catalyst in the aqueous phase.



(a) (b) (c)

FIGURE 3 Particle size distribution. Catalyst in the organic phase, Catalyst in the both organic phase (Half) and aqueous phase, and Catalyst in the aqueous phase.

was in the aqueous phase, the particle size became very small. In the case where the catalyst was in the organic phase, the particle size became bigger and the distribution became wider. This may be related to the roughness of microcapsules. Because of the fast wall-formation enhanced by catalyst in the same, homogeneous organic phase, microcapsule formed had a rough surface and probably bigger particle sizes. In the case of catalyst added into both phases (each half), the particle size lies in the middle. Table 1 shows the average particle sizes or microcapsules. Figure 4 showed the scanning electron micro-photographs of diethyl (o-) phthalate microcapsules. The results of scanning electron photographs are basically consistent with that of the particle distribution measurement.

2. Effect of Different Core Materials on the Morphology and Particle Size

(I). On the Morphology

The effect of different core materials on the morphology are shown in Figure 5 where the catalyst is in the aqueous phase. It was noticed

TABLE 1 The Average Particle Size of Microcapsules from Catalyst added to Different Phases

Catalyst	Average particle size (μm)
In organic phase	3.759
In both phase (each half)	3.342
In aqueous phase	3.211

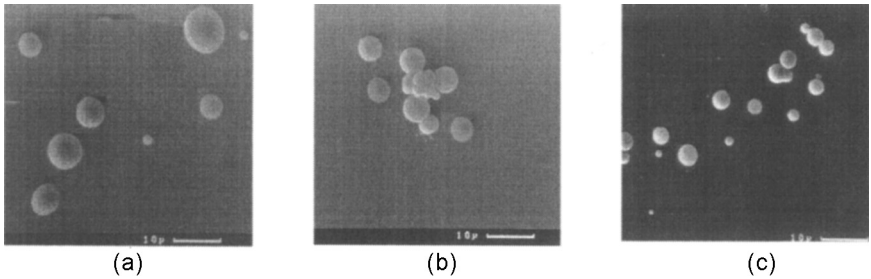


FIGURE 4 Scanning electron microphotographs of catalyst in different Phases. (a) Catalyst in the organic phase (b) Catalyst in the both organic phase (Half) and aqueous phase, and (c) Catalyst in the aqueous phase.

that in all the three cases of core materials the morphology of diethyl (o-) phthalate microcapsule was the roughest, while the morphology of dioctyl (o-) phthalate microcapsule was the smoothest and the situation of the morphology of dibutyl (o-) phthalate microcapsules was in the middle. This figure demonstrates clearly that the nature of core materials does affect the morphology of microcapsules. These different core materials might have significantly affected the course of the polymer wall formation during the micro encapsulation process. Comparing the hydrophobic properties of the core materials, the obvious differences in the morphological structure might result from the different length of hydrophobic groups denoting different hydrophobicities in the core materials. One likely reason is that the core materials containing shorter hydrophobic groups tended to diffuse towards the aqueous phase more easily and thus increase the difficulty of wall forming. Dioctyl (o-) phthalate is the most lipophilic one of them, and the shell formed is the clearest and smoothest one.

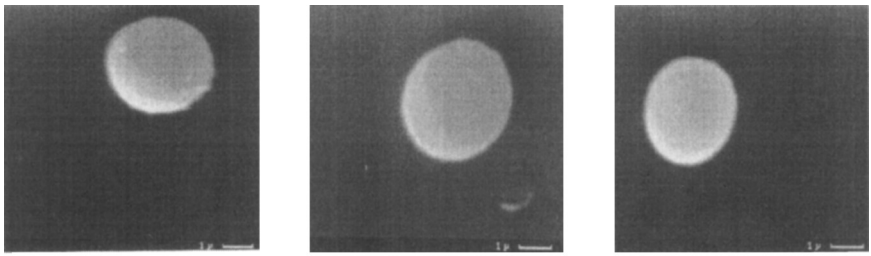


FIGURE 5 Scanning electron microphotographs of Microcapsules with different core materials. (a) Diethyl (o-) phthalate, (b) dibutyl (o-) phthalate, and (c) dioctyl (o-) phthalate.

TABLE 2 The Average Particle size of Microcapsules with Different Core Materials

Core materials	Average particle size (μm)
Diethyl (o-) phthalate	3.211
Dibutyl (o-) phthalate	2.910
Dioctyl (o-) phthalate	2.741

(II). On the Particle Size and Size Distribution of Microcapsules

From Table 2 and Figure 6, it can be seen that in the three cases, the average size of diethyl (o-) phthalate microcapsule was the biggest and the size distribution was the widest, dioctyl (o-) phthalate microcapsule's average size was the smallest and the size distribution was the narrowest and the case of dibutyl (o-) phthalate was in the middle. It was found that the viscosity of the emulsions increased with the increase in the length of the hydrocarbon chain. Increased viscosity would result in higher stability of the emulsion. Another reason might be that the emulsifier (HLB13.5) used matches better the core material with the longest hydrocarbon chain (HLB13). These reasons would result in smaller average particle size.

CONCLUSIONS

1. The catalyst in different phases affects the morphology and the particle size and size distribution of microcapsules. The surfaces of

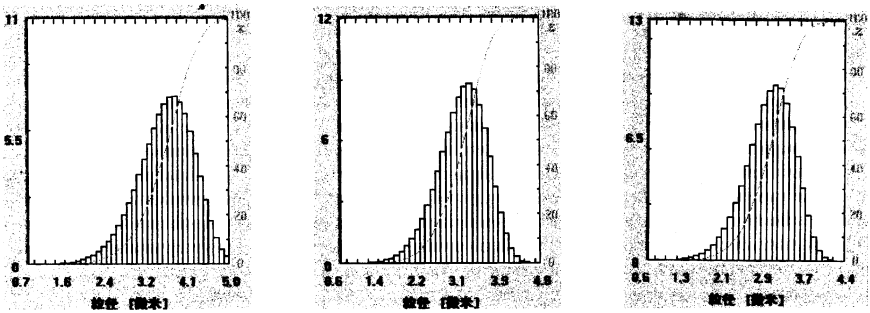


FIGURE 6 Particle distribution with different core materials. (a) Diethyl (o-) phthalate, (b) dibutyl (o-) phthalate, and (c) diocty (o-) phthalate.

microcapsules from catalysts in aqueous phase were smoother and the average size was smaller than that with the catalyst in the organic phase.

2. The core materials containing different hydrocarbon groups affect the morphology and particle size of microcapsules, and higher hydrophobicity gave smoother morphology.

REFERENCES

[1] Sche Herbert, B. (1987). US Patent 4673,764.
[2] Green, B. K. and Schleicher, L. (1956). US Patent 2,730,456.
[3] Pense, A. M., Vauthier, C., and Benoit, J. P. (1994). *Colloid & Polymer Science*, **272**, 211–219.
[4] Hong, K. (1999). *Journal of Materials Science*, **34**, 3161–3164.
[5] Yadav, S. K., Khilar Kartic C., and Suresh, A. K. (1996). *AIChE Journal*, **42**, 2616–2626.
[6] Naegeli, C., Tyabji, A., Conrad, L., and Litman F. (1938). *Helvetica Chimica Acta*, **21**, 1107.