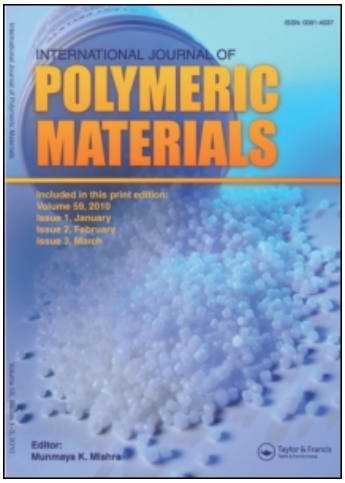

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FACTORS AFFECTING THE PARTICLE SIZE AND SIZE DISTRIBUTION OF POLYUREA MICROCAPSULES BY INTERFACIAL POLYMERIZATION OF POLYISOCYANATES

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FACTORS AFFECTING THE PARTICLE SIZE AND SIZE DISTRIBUTION OF POLYUREA MICROCAPSULES BY INTERFACIAL POLYMERIZATION OF POLYISOCYANATES

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The interfacial polymerization method was used to prepare fragrant microcapsules. The wall material was a polyurea formed by the reaction of triphenyl methane triisocynate (JQ-1) and TDI (2,4-toulene diisocyanate) with amines that were the reaction results of isocyanates with water. During the preparation, An emulsifier (GPE2040), protective colloid (PVA) and catalyst (dibutyltin dilaurate) were used. The influences of the phase ratio (organic/aqueous), core/wall ratio, the amounts of emulsifier and protective colloid and the radio of triphenyl methane triisocyanate (JQ-1)/TDI (2,4-toluene diisocyanate) on particle size and size distribution of the microcapsules prepared were studied. A mechanism of the process of wall forming is suggested i.e. it might be that the isocyanate migrates outwards through the forming microcapsule's wall and reacts there with water to form amines, which in turn react with isocyanate groups nearby, resulting in the formation of polyurea and the polyurea formed accumulates on the wall of surface.

Keywords: interfacial polymerization, microcapsule, particle size, size distribution, wall forming

INTRODUCTION

The micro encapsulation technology began in the 1950s. Barret Green et al. in National Cash Register CO. (NCR) in the U.S.A. first originated it. Microcapsules were prepared successfully in 1954 and applied to preparing the so-called carbonless copy paper. Thus this started the epoch of micro encapsulation technology [1, 2]. In the

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1960s, some substances were encapsulated in polymer materials using the phase separation technique and thus the controlled release microcapsules were prepared successfully. After this, in some countries, England, for example, Western European nations and Japan, heavy investments and many theoretical breakthroughs were made. In the meantime, the application of micro encapsulation technology extended to the fields of pharmaceuticals, domestic chemicals, photosensitive materials, food, biologic products, etc. which made the micro encapsulation technology develop more rapidly [2, 3, 4]. The application of micro encapsulation technology improved the quality of the traditional products. Micro encapsulation technology has been listed as one of the subjects of high-tech that would be researched and developed extensively in the 21st century.

In this article, an interfacial polymerization method was used for micro encapsulation. During the encapsulation, some isocyanate groups were hydrolyzed at the interface, gradually forming amines, which in turn reacted with unhydrolyzed isocynates to form a polyurea wall [5]. One characteristic feature of this method is that neither the process nor the end products face the formaldehyde problem, while traditional micro encapsulation techniques, for example gelatin method, gelatin-arabic gum combined coagulation, etc. encounter the free formaldehyde or formaldehyde release problems to varying extents. The average particle size and size distribution of the microcapsules were very important, since they affected the application characteristics of the microcapsules. We have investigated the effect of catalyst and core materials on particle sizes of microcapsules [6]. Hence, in this work, other factors influencing the particle size and size distribution of microcapsules were investigated.

EXPERIMENTAL

1. Chemicals

The perfume was from the Perfume Institute, Shanghai. Dibutyltin dilaurate served as the catalyst; sodium hydroxide (25%) was used in regulating the pH; poly(vinyl alcohol)(PVA) was used as protective colloid; these were available in the market, GPE2040 provided by Gaoqiao Fine Chemicals Co., Ltd., Shanghai was used as the emulsifier. The wall forming materials were TDI (2,4-toluene diisocyanate) and JQ-1 (triphenyl methane triisocyanate), which were purchased from Chemical supply house.

2. Apparatus

The high-speed mixer BME 1001 was from Weiyu Mechanical-electronic Co. Ltd., Shanghai. The JB90-D heavy electrical agitating machine was from Shanghai Specimen Model Factory. The TSM micro-size particles analytical instrument was from Shanghai University of Science and Engineering. The CAM-SCAN-4 scanning electron microscope was from Cambridge, England.

3. Test Methods of Average Size and Size Distribution of Microcapsules

The microcapsules prepared were spread on a microscope slide and covered with a cover glass. The microcapsules were observed under the microscope, some representative areas were defined as the statistic areas, and the statistic number was over 300. The average size and size distribution of microcapsules were determined by UV-M imaging analytical system.

4. The Micro Encapsulation

The micro encapsulation process consisted mainly of five steps: (a) preparing an aqueous phase containing the emulsifier, the protective colloid and water, an amount of sodium hydroxide (25% aqueous solution) was added under stirring; (b) preparing an organic phase containing the core material, the wall forming material and the catalyst; (c) emulsification (for 5 minutes) by stirring at 9000 rpm and, during emulsification, the organic fine particles were dispersed into the aqueous phase; (d) the system was transferred immediately into a reactor with a stirrer and stirred at room temperature for 3 hours, and (e), the microcapsules were obtained by filtration, then washed and dried at room temperature.

RESULTS AND DISCUSSION

There are a lot of elements that affect the particle size and size distribution of microcapsules. Here, the effects of phase ratio (organic/aqueous), the amounts of the emulsifier and the protective colloid, core/wall ratio and the ratio of JQ-1/TDI on average size and size distribution are discussed. The effects of shear rate, emulsifying conditions and the nature of emulsifiers on the micro encapsulation will be discussed in a separate paper.

TABLE 1 Average Particle Size of Products at Various Phase Ratios

Phase ratio (or./aq.)	Average size (μm)
8:92	Not available
10:90	2.691
12:88	2.930
14:86	3.347
16:84	3.781

1. Organic/Aqueous Phases Ratio

The experiments on different phase ratios were conducted and the corresponding results are shown in Table 1 and Figure 1.

From Table 1 and Figure 1, it is clear that the average particle size increased and the size distribution gradually broadened with increase in the organic phase portion. Figure 2 shows the SEM pictures of microcapsules prepared at different phase ratios. They show that the particle size of most microcapsules increased with increase in organic phase. Namely, in this study the higher portion of organic phase resulted in a larger particle size. It is obvious that at a given concentration of emulsifier, the increase in the organic phase will exceeds the dispersion capabilities of the system. Thus, the phase ratio of organic/acqueous should not be too high.

2. The Concentration of Emulsifier

The particle size of each microcapsule depends on the size of the dispersed droplet, which is determined by the emulsifiers used and the

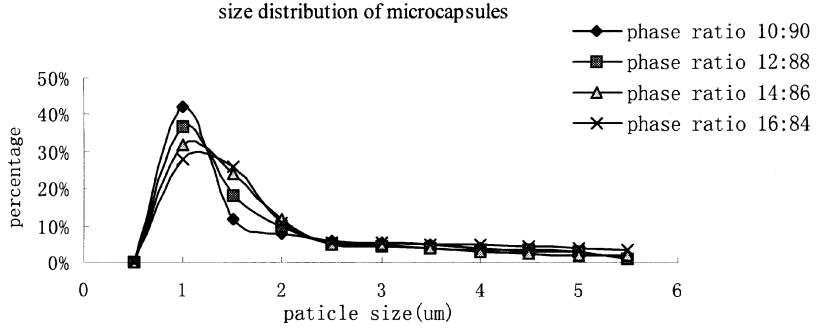

FIGURE 1 Size distribution of microcapsules prepared at various phase ratios core/wall ratio = 1:1, JQ-1: TDI = 2:1, GPE2040: 2.0%, PVA: 1.0%, catalyst: 0.1%.

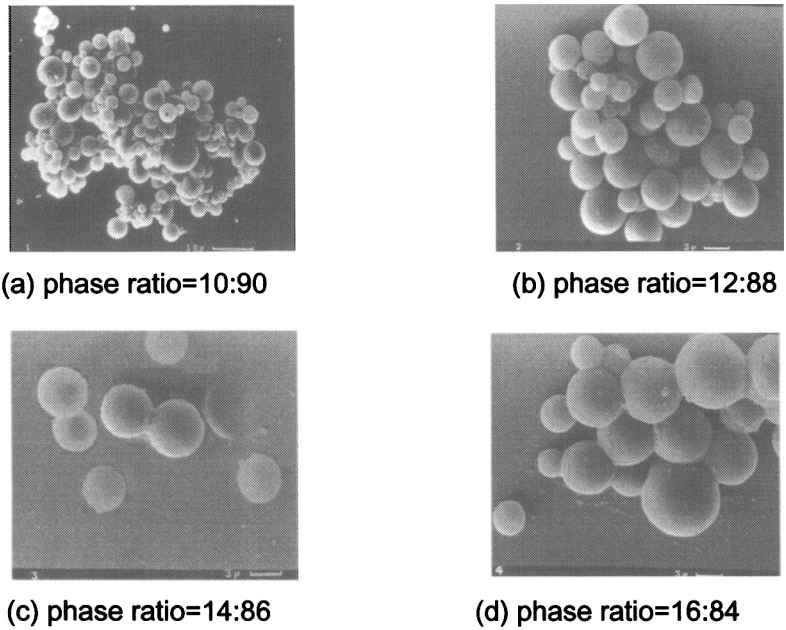

FIGURE 2 The SEM pictures of microcapsules from various phase ratios.

emulsifying conditions. Here an alcohol derivative of polyether GPE2040 was used as the emulsifier. Table 2,Figure 3 and Figure 4 show the particle size and size distribution of microcapsules obtained at various concentration of emulsifier.

From Table 2 and Figure 3, it can be seen that with increased concentration of GPE2040, the average size of microcapsules became

TABLE 2 The Average Particle Size of Microcapsules at Various Concentration of GPE2040

The amounts of GPE2040 (%)	Average particle size (μm)
0.5	3.538
1.0	3.363
1.5	3.011
2.0	2.691
2.5	2.548
3.0	2.425
3.5	2.412
4.0	2.393

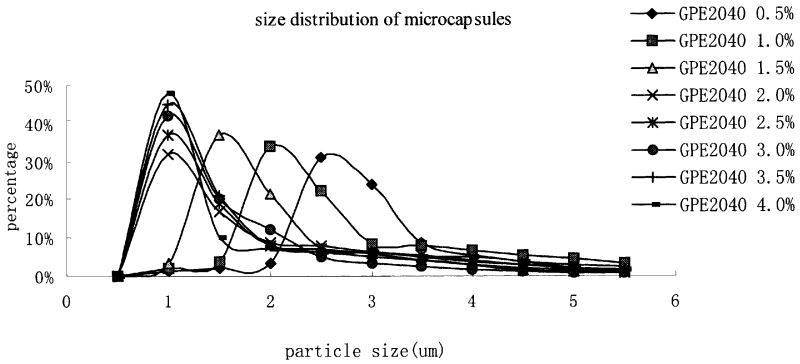

FIGURE 3 The size distribution of microcapsules at various concentration of GPE2040 phase ratio = 10:90, core/wall ratio = 1:1 JQ-1: TDI = 2:1, PVA: 1.0%, catalyst: 0.1%.

smaller and the size distribution became narrower. At higher concentrations of emulsifier, the organic phase is easily dispersed into finer droplets, owing to the higher activity of the surfactant, which would result in a lower free energy of the system, and lead to a smaller particle size and narrower size distribution. It is clear, from Figure 3, that when the concentration of GPE2040 was over 2.0%, the size distribution could become very narrow. Thus, the amount of GPE2040 should be 2.0% or more under the conditions of our experiment. Figure 4 shows SEM pictures of the microcapsules at various concentrations of GPE2040.

3. The Concentration of Protective Colloid

In order to increase the stability of the dispersion system, the use of suitable protective colloid was necessary. In this work, PVA (polyvinyl alcohol, 1788) was used.

The hydrophilic PVA dissolved in water, forming a stable viscose system as the outer phase. The higher viscosity of the outer phase hindered the movement of particles and hence prevented them from collision coagulation. The average size and size distribution of microcapsules from different concentrations of PVA are shown in Table 3 and Figure 5. Evidently, the average size became smaller and the size distribution became narrower as the concentration of PVA increased (Figure 5). Another conclusion can also be drawn from Figure 5, namely the concentration of PVA should not be less than 1.0%.

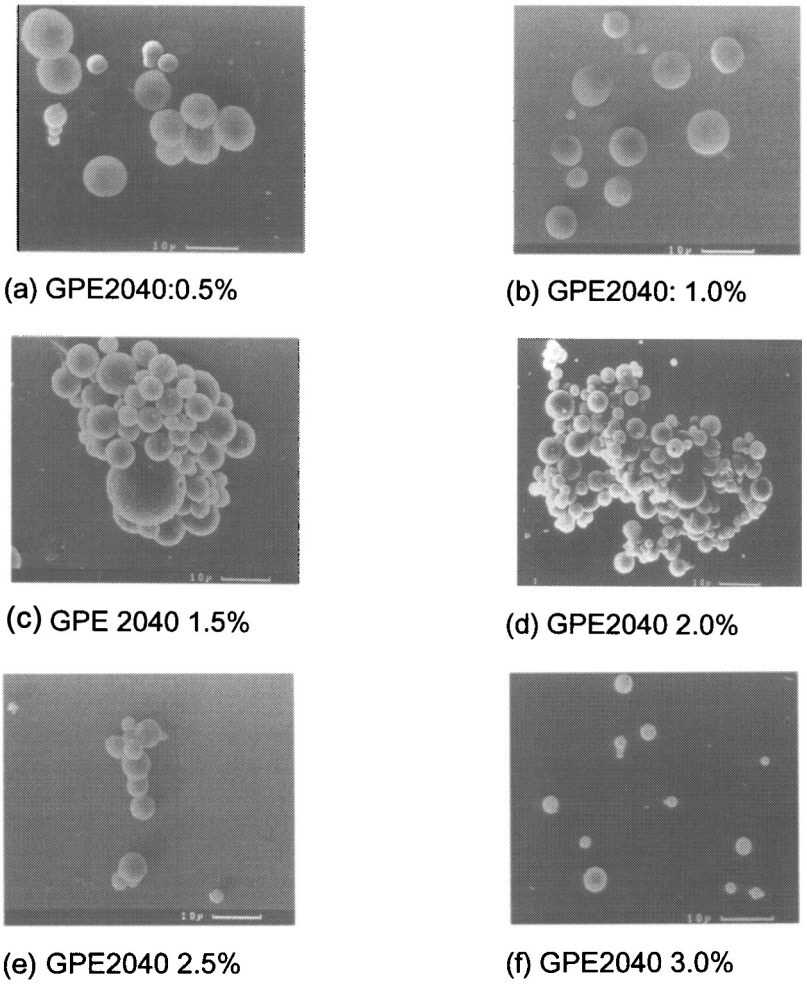

FIGURE 4 The SEM pictures of microcapsules from different amounts of GPE2040.

4. Core/Wall Ratio

The wall thickness, which was decided by the core/shell ratio and the particle size as well, decisively influences the performance of microcapsules. In order to seal the core material inside the microcapsules better, experiments with various core/wall ratios but at roughly the same original particle (droplet) size were carried out. In the cases of

TABLE 3 The Average Size of Microcapsules From Different Concentrations of PVA

Amount of PVA (%)	Average size (μm)
0.5	3.037
1.0	2.691
1.5	2.554
2.0	2.362
2.5	2.318

core/wall ratios of 3:1 and 2:1, the experiments could not be conducted successfully. Results listed in Table 4 indicate that as the core/wall ratio became smaller, i.e. the shell portion became larger, the particle size of the final product became larger and the size distribution became correspondingly wider. When the size of original droplet with that of the final particle was compared it could be concluded that the isocyanates might migrate outwards through the formed wall of the microcapsules and part of them reacted there with water to form amines, which then reacted with additional isocyanates nearby to form polyurea, which accumulated on the wall surface. In this way, as the process continued, the wall became thicker and thicker and the diameter of the particle formed became larger and larger. That is, the mechanism of wall formation is due to the outward diffusion of the isocyanate through the wall, not due to inward diffusion of water.

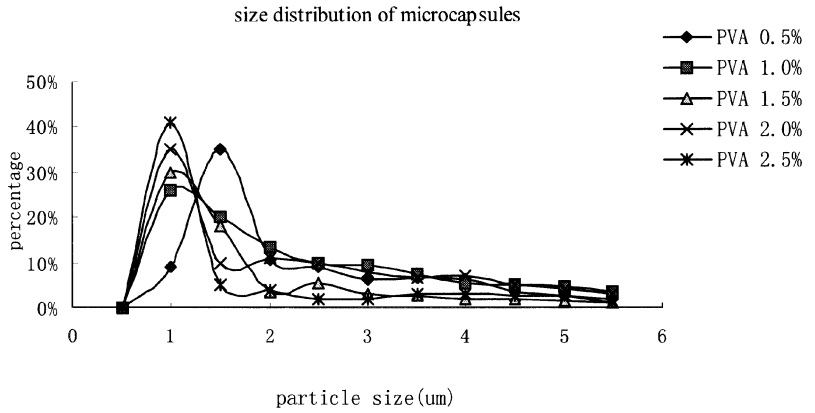

FIGURE 5 Size distribution of microcapsules at different concentrations of PVA phase ratio = 10:90, core/wall ratio = 1:1, JQ-1: TD1 = 2:1, GPE2040: 2.0%, catalyst: 0.1%.

TABLE 4 The Average Size of Microcapsules From Different Core/Wall Ratios

Core/wall ratio	Average size of final product (μm)	Size of original droplet (μm)
3:1	Not available	Not available
2:1	Not available	Not available
1:1	2.691	2.374
1:1.5	2.863	2.353
1:2	3.077	2.359
1:2.5	3.116	2.361
1:3	3.325	2.377

5. The Ratio of JQ-1/TDI

The wall forming materials were JQ-1 (triphenyl methane triisocyanate) and TDI (2,4-toluene diisocyanate). The ratio of JQ-1 to TDI could be changed to adjust the wall properties [7]. JQ-1 would mainly offer the flexibility and the TDI would mainly offer the rigidity of wall materials in this case. Therefore, the ratio of JQ-1 to TDI had important effects on the wall formation and structure of microcapsules. Table 5 showed the average sizes and Figure 7 showed the size distributions of microcapsules from different ratios of the two wall

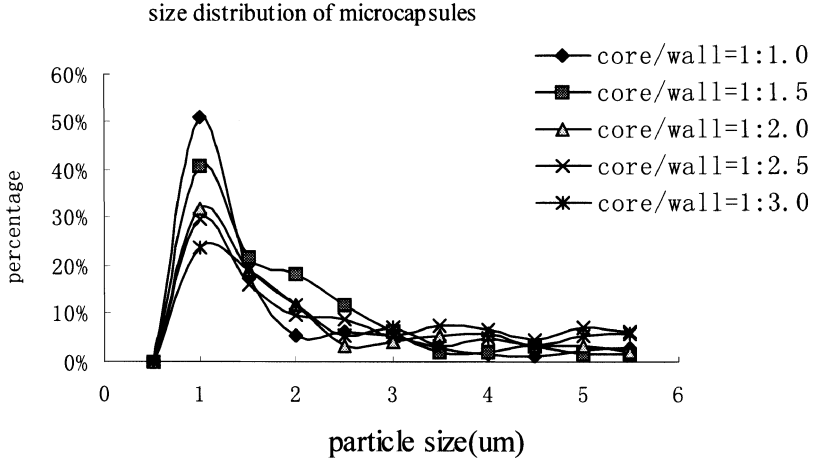

FIGURE 6 The size distribution of microcapsules from different core/wall ratio phase ratio = 10:90, JQ-1: TDI = 2:1, GPE2040: 2.0%, PVA: 1.0%, catalyst: 0.1%.

TABLE 5 The Average Size of Microcapsules From Different JQ-1/TDI Ratios

JO-1/TDI	Average size (μm)
3:1	2.468
2:1	2.691
1:1	3.427
1:2	3.861
1:3	4.384

precursors. The average size became larger and the size distribution became wider with increased TDI.

CONCLUSIONS

(1) With increasing concentration of GPE2040 and protective colloid (PVA), the average size of microcapsules became smaller and the size distribution became narrower.
(2) With smaller core/wall ratios, i.e., larger shell portion, the increment of organic phase portion and TDI, the particle size of microcapsules became larger and the size distribution became correspondingly wider.

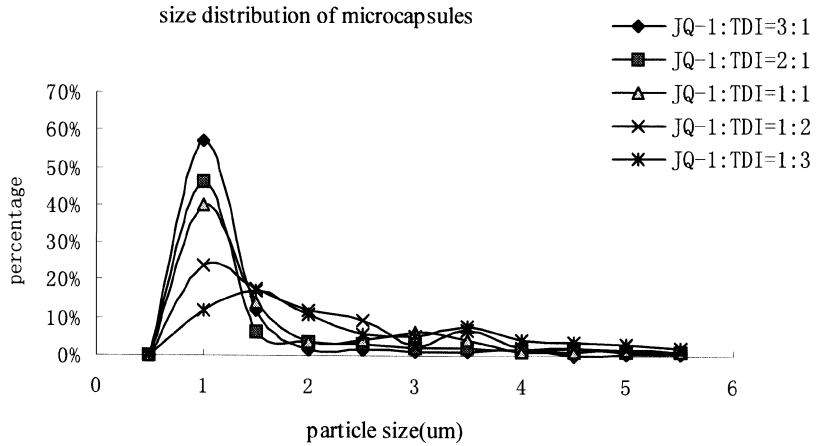

FIGURE 7 The size distribution of microcapsules from different JQ-1/TDO ratio phase ratio = 10:90, core/wall ratio = 1:1, GPE2040: 2.0%, PVA: 1.0%, catalyst: 0.1%.

(3) The process of wall formation might be that the isocyanates migrated outwards through the forming microcapsule walls and a part of them reacted there with water to form amines, which in turn reacted with additional isocyanate groups, resulting in the formation of polyurea that accumulated on the wall surface.

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