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Conductometric titration studying on hollow microspheres preparation

Summary — Hollow microspheres were prepared *via* osmotic swelling. In order to study preparation process, a series of latex particles with different core/shell weight ratio were prepared by seeded emulsion polymerization. The content of surface carboxyl groups in the latex particles obtained from conductometric titration curve was used to determine the threshold core/shell weight ratio for hollow microspheres. Additionally, the rheology and opacity were studied. The results showed that the optimal core/shell weight ratio obtained from the conductometric titration curve was in agreement with the ratio acquired from transmission electron microscopy (TEM) analysis, the rheology and opacity studies.

Key words: hollow microspheres, core/shell weight ratio, conductometric titration, carboxyl groups content.

BADANIE ZA POMOCĄ MIARECZKOWANIA KONDUKTOMETRYCZNEGO PROCESU OTRZYMYWANIA PUSTYCH MIKROKULEK

Streszczenie — Puste mikrokulki były otrzymane za pomocą pęcznienia osmotycznego. Metodą polimeryzacji emulsyjnej z zastosowaniem różnych stosunków wagowych składników typu rdzeń/powłoka otrzymano dwie serie cząstek różniących się ilością użytego lateksu (tabele 1—3). W celu określenia granicznej wartości stosunku wagowego rdzeń/powłoka zapewniającego otrzymanie pustych mikrokulek zaproponowano nową metodę miareczkowania konduktometrycznego. Porównawczo zastosowano typową metodę elektronowej mikroskopii transmisyjnej (TEM) uzyskując podobne wyniki. Dodatkowo zbadano lepkość (tabela 5) i współczynnik nieprzezroczystości (tabela 6) uzyskanych próbek.

Słowa kluczowe: puste mikrokulki, stosunek wagowy rdzeń/powłoka, miareczkowanie konduktometryczne, zawartość grup karboksylowych.

Hollow microspheres have been widely used in coating applications. They reduce or remove the need of use of conventional pigments (such as titanium dioxide) or extenders without adding excessive and undesirable weight to the coating. Hollow microspheres provide excellent opacity in respect to the fact that the voids in the microspheres can scatter light more efficiently than corresponding particles of uniform density.

Recently, a large number of emulsion polymerization techniques are used to prepare the hollow microspheres, and the most commonly used synthetic approach named osmotic swelling has been developed by Kowalski and colleagues [1—8]. The osmotic swelling included making a structured particle with carboxylated core polymer as well as one or more outer shells, and then ionization of the carboxylated core at the glass transition temperature (T_g) of the shell polymer. The ionization causes swelling of the carboxylated core and results in water

filled microspheres, and the water can be removed by drying. Usually, the process was very complicated to reach thermodynamic and kinetic equilibrium, because it was unfavorable in energy for hydrophobic shells polymerizing onto the hydrophilic core. Many factors such as composition, core/shell weight ratio and network structure were crucial to obtain the stable hollow microspheres. However, the available information about the hollow microspheres was limited to the patents due to the strong commercial interest. Most of publications concentrated on their properties and applications, and scarcely considered the preparation, except the work by Okubo et al. [9—11], Vanderhoff [12], McDonald et al. [13] and Pavlyuchenko and Sorochinskaya [14]. The preparation of the hollow microspheres consist in the core-shell structure formation that could affect the morphology of the microspheres during the base neutralization process. But the process was often studied only through transmission electron microscopy (TEM) method. As credible it might be, time-consuming affects that sometimes it may not be necessary. We took a simple and convenient method that was conductometric titration to study the preparation process, along with rheology and opacity study.

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EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), methacrylic acid (MAA), acrylic acid (AA), and n-butylacrylate (n-BA) were AR grade, and were purified before use. Potassium persulfate (KPS) was used as initiator and sodium dodecylbenzenesulfonate (SDBS) was used as a stabilizer. NH_4OH diluted in water was used to swell the particles.

Synthesis

The latex syntheses were carried out in 500 mL, four-neck round-bottom flask equipped with a stirrer, thermometer, reflux condenser and nitrogen/reagent inlet tube. Step 1 (carboxylated core copolymer synthesis) included a seed latex preparation to control of the particle size and the carboxyl groups distribution. This process was conducted as a batch process by simultaneous charging all of the seed monomers at 85 °C for 180 min. The amounts of substrates used for synthesis are listed in Table 1. The seeds showing solid content of 20 wt. % and a number-average particle size of 104 nm were obtained. Then two different amounts of seeds for the same amounts of other substrates (series C₁ and C₂ in Table 2) were taken to prepare carboxylated core at 80 °C for 180 min. The monomers for the carboxylated core preparation were pre-emulsified, and two thirds of the initiator was added into the seed-latex, and the rest was added into monomers.

Table 1. Formulation for the synthesis of seed copolymer latex

Amounts of substrates, g					
MMA	MAA	BA	KPS	SDBS	H ₂ O
32.0	1.0	47.0	0.3	0.6	320.0

Table 2. Formulations for the syntheses of carboxylated core

Sample of carboxylated core	Amounts of substrates, g					
	Seeds	MAA	MMA	KPS	SDBS	H ₂ O
C ₁	6.0	18.0	42.0	0.36	0.8	240.0
C ₂	24.0	18.0	42.0	0.36	0.8	240.0

Step 2 (synthesis of hydrophobic shell onto carboxylated core particles) was carried out at 80 °C by constant feeding of the pre-emulsified shell monomers to the carboxylated core latex. The process was implemented at various core/shell weight ratios and with different polymerization time as it was listed in Table 3.

Step 3 (carboxylated core neutralization) was carried out in the presence of diluted NH_4OH for 1 h at 90 °C.

Table 3. Formulations for the polymer shell formation onto carboxylated core

Core/shell weight ratio ^{*)}	Amounts of substrates, g				
	St	KPS	SDBS	H ₂ O	Time, min
1/3	24.0	0.25	0.018	143.0	120
1/6	48.0	0.50	0.035	162.0	150
1/9	72.0	0.75	0.053	181.0	180
1/12	96.0	1.00	0.070	200.0	210
1/15	120.0	1.25	0.090	225.0	240

^{*)} Syntheses were carried out using 40 g of 20 wt. % suspension of carboxylated core particles.

Method of characterizations

The number-average diameter (\overline{D}_n) and the weight-average diameter (\overline{D}_w) of the particles were measured by Mastersizer 2000 (Malvern, Great Britain). The polydispersity of the particles was expressed as $n = \overline{D}_w/\overline{D}_n$ and the particle morphology was characterized by TEM (JEM-100CX, Japan) at an accelerating voltage of 100 keV. In carboxylated latex, the carboxyl groups may be distributed in three forms (serum, surface, or buried in the latex). The distribution of the carboxyl groups in the latex particles with different core/shell weight ratios can be determined by conductometric titration according to the method described by Hen [15] as follows: 5.000 g of latex was diluted with 40 mL of water and its solid content was measured by gravimetry. The pH value of the diluted latex was first adjusted to 11.0 ± 0.1 using NaOH solution, and then the latex was titrated with 0.2017 mol/dm³ HCl solution under the monitor of a DDS-11A⁺ conductometer (China). Then the amount of surface carboxyl groups (c_{COOH}) not screened by polystyrene shells could be calculated directly from conductometric titration curve.

The rheological properties of the latex were studied by a Brookfield viscometer (Japan).

The obtained hollow microspheres were also studied with respect to their opacity. The property of the hollow microspheres as polymeric pigment was estimated using a reflectometer C84-II (China) by measuring of the contrast index:

$$\Delta R = \frac{R_b}{R_w} \quad (1)$$

where: R_b and R_w were the reflection coefficients for the hollow polymer latex disposed on a black support and on a white support, respectively.

RESULTS AND DISCUSSION

Seeds in the emulsion polymerization

Water-soluble carboxyl-containing monomers create some problems in emulsion polymerization. Usually this type of latex cannot adsorb surfactant well, which therefore often lead to aggregation, and the water-soluble monomers might result in second nucleation in water

phase that should be avoided. The problems were solved by taking the seeded emulsion polymerization and pre-emulsifying of the monomers.

Table 4. Characteristic of carboxylic copolymer latex samples obtained using different quantity of seeds

Sample of carboxylated core used	Seeds, g	\bar{D}_n , nm	n
C ₁	6	169	2.22
C ₂	24	129	1.42

The seeds were the polymerization sites. It can be seen from Table 4 and Figure 1 that the amount of seeds used in the seeded emulsion polymerization has great impact on the control of \bar{D}_n and n . When dropping of the pre-emulsified monomers to the emulsion, the monomers were promptly absorbed by the seeds and polymerized immediately, which decreased the chance for

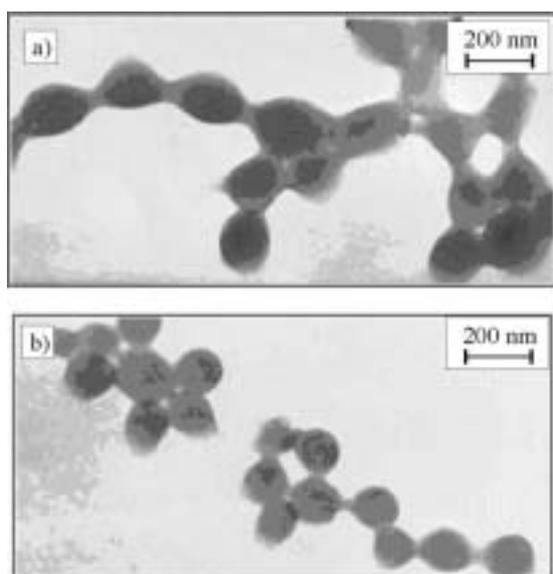


Fig. 1. Transmission electron micrographs of carboxylic copolymer latex obtained for samples: a) C₁, b) C₂

second nucleation in water. The more seeds used in the seeded emulsion polymerization, the more swift absorption of the monomers by the seeds would be, and the monodisperse latex particles could be obtained in return.

Surface carboxyl groups analysis

The hollow formation at the third stage generally proceeds *via* the osmotic mechanism. The base molecules diffuse into the carboxylated particle core and interact with the carboxyl groups. The arising carboxylate anions

promote a strong polyelectrolyte swelling of the polymer chain that leads to the voids in the latex particles. The hollow volume first depends on the ionization and hydration abilities of the carboxylated copolymer, and second on the shell polymer ability to deform under the pressure arising in the core. So in this case the core/shell weight ratio is crucial for the void formation. During the hydrophobic shell monomers polymerization onto the carboxyl-containing core, the hydrophilic carboxyl-containing chains have a tendency to move towards particle surface due to their hydrophilicity. Therefore, the optimal core/shell weight ratio for hollow microspheres is when all the carboxylated chains of the core are completely covered by the shell. As the core is completely encapsulated by the shells, the shells get enough strength to keep integrity under the pressure of the core. The amount of surface carboxyl groups (c_{COOH}) of the core not screened by the shells can be detected by conductometric titration [15].

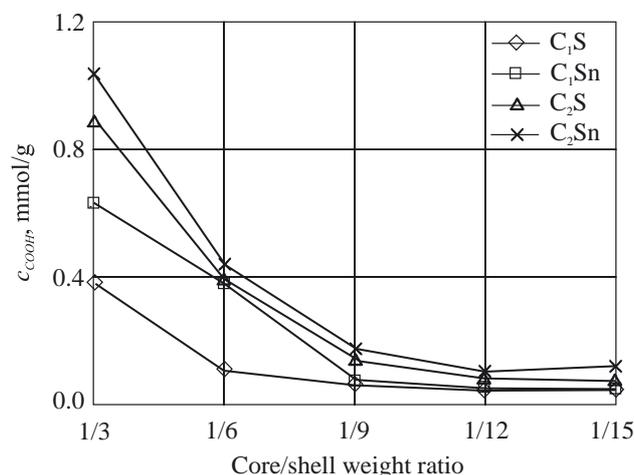


Fig. 2. Effect of core/shell weight ratio on the amount of surface carboxyl groups (c_{COOH}) of the latex particles denotations of curves are the same as denotations of series described in the text

Figure 2 shows c_{COOH} of the core-shell particles synthesized using different core/shell weight ratio before and after alkali neutralization. The series of samples obtained using carboxylated core C₁ or C₂ are denoted C₁S and C₂S, respectively. The letter "n" is added to symbols of series after alkali neutralization samples (C₁Sn and C₂Sn). As the diagram shows, with the increase in the shell coverage of carboxyl-containing core, c_{COOH} sharply decreases and then keeps constant ($-SO_4^{2-}$ generated by initiator KPS adsorbed to the surface of the latex could also react with HCl, so c_{COOH} revealed constantly). For the series C₁S and C₁Sn the surface carboxyl groups reach the minimal values for core/shell weight ratio equal 1/9 but for the series C₂S and C₂Sn this value stabilize for ratio 1/12. Stabilization of c_{COOH} indicate that the surface of the core is completely covered by the

shell at that ratio. When the shells entirely cover the core, the shells thus have enough strength to keep uniformity when the core is neutralized under high temperature. So C₁S and C₂S series can get perfect hollow microspheres when the core/shell weight ratios are 1/9 and 1/12, respectively, as it is clear from the diagram. Comparing c_{COOH} of the particle before alkali neutralization with that after alkali neutralization, there is an evident trend that the interior carboxyl chains tend to move towards water interface due to the carboxylate anions being more hydrophilic than carboxylic acid after alkali neutralization. The data also demonstrate the fact that the impulse to hollow particles formation comes from the movement of the carboxylated chains. No matter before and after the alkali treatment, the surface carboxyl groups content of C₂S series is higher than that of C₁S series. In seeded emulsion polymerization, series C₂S used more seeds than C₁S. However the shell monomers used are the same. Under this condition, the particles' number of C₂S series should be longer than of C₁S series, whereas the diameter of particle of C₂S series should be smaller than that of C₁S series (see Fig. 1), because there was no second nucleation. So the overall particle surface of C₂S should be larger than that of C₁S, which leads to higher surface carboxyl groups content than in C₂S. Oppositely, we can primarily judge which latex particle diameter is larger by contrasting c_{COOH} with each other from the conductometric titration curve.

Viscosity of latex

The viscosity of the latex listed in Table 5 is low, because the method we took for the preparation can confine the carboxylic monomers polymerization to the seeds not to water phase. The diversity in the viscosity between series C₁Sn and C₂Sn maybe result from the difference in particle diameter and the amount of surface carboxyl groups.

Table 5. Viscosity of latex particles obtained using different core/shell weight ratio

Serie	Viscosity, cP				
	core/shell weight ratio				
	1/3	1/6	1/9	1/12	1/15
C ₁ Sn	9.0	9.5	25.5	24.8	7.0
C ₂ Sn	80.0	100.5	81.7	64.5	60.0

Opacity of latex particles

The opacity of hollow microspheres is seriously related to the morphology of the particles and the diameter of the voids. When the core-shell particle is neutralized, the void is filled with water, and then the water moves out of the particle after drying. Usually the alkali neutralization is at the glass transition temperature (T_g)

of the shell polymer, and at that time the carboxyl chains are prone to moving to the surface. If the carboxylated core is not entirely covered by the shell, the force confining the movement of chains is not strong enough to retain the sphericity after drying. So the core/shell weight ratio will affect the opacity of hollow microspheres. The data presented in Table 6 show that the opacity of hollow microspheres gradually improved with increasing of the shell dosage to the core. Series C₁S and C₂S acquire excellent opacity at the core/shell weight ratio of 1/9 and 1/12, respectively, which are just the weight ratios at the conductometric titration curve considering for entirely shell coverage to the core. It is seen from the Table 6 that the particles before alkali treatment also show some opacity, sometimes even close to or higher than those after neutralization at lower shell thickness. It is because the carboxyl groups in the core can retain water amount that completely or partially remains inside the particle after shell synthesis, forming the small voids. Despite the fact that small voids can afford limited opacity it grows better with the shell coverage increase. The pressure in the core will force the small voids to grow bigger. At less shell coverage, the core-shell particles after alkali treatment might have lower opacity than those before alkali treatment due to their distortion. The change of the opacity before and after alkali neutralization illustrated the expansion of the voids in the latex particles.

Table 6. Opacity of particles obtained using different core/shell weight ratio

Serie	Opacitying ability				
	core/shell weight ratio				
	1/3	1/6	1/9	1/12	1/15
C ₁ Sn	0.734	0.926	0.968	0.967	0.984
C ₁ S	0.752	0.929	0.927	0.927	0.949
C ₂ Sn	0.201	0.724	0.856	0.949	0.929
C ₂ S	0.100	0.802	0.899	0.919	0.921

TEM analysis

The transmission electron micrographs in Figure 3 demonstrate the characteristics of the hollow microspheres obtained by neutralization of the core-shell particles at various core/shell weight ratios with ammonia solution. The diameter of particles are very small and polydispersity is observed for the core/shell weight ratio of 1/3 and 1/6, and the voids are broken up with the morphology distorted. Although the voids are formed in the particles for the core/shell weight ratio of 1/9, the shape is a little distorted for smaller shell coverage. For core/shell weight ratio of 1/12 and 1/15, the hollow microspheres are perfect with one large void in the middle, which is in accordance with the conductometric titration analysis. The conductometric titration showed that the C₁S could make fine hollow microspheres when

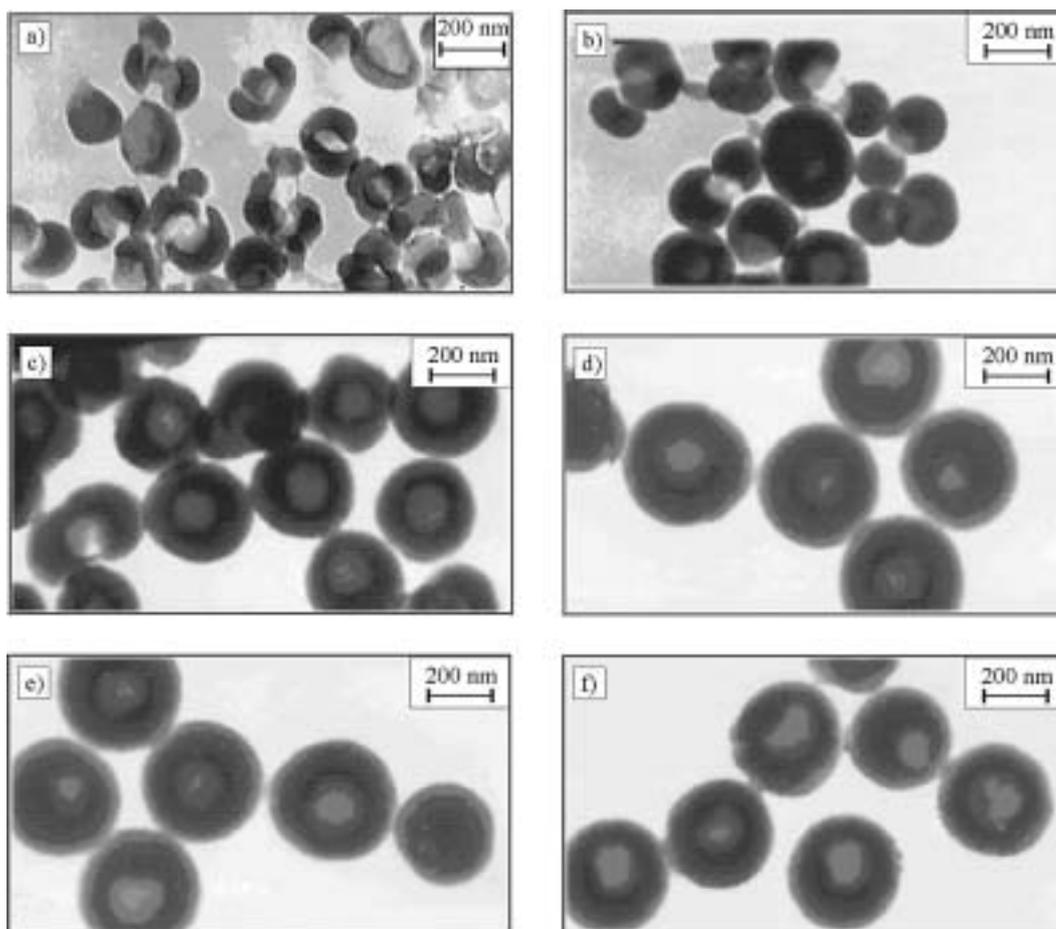


Fig. 3. Transmission electron micrographs of hollow microspheres in C_2Sn samples obtained using the core/shell weight ratio of 1/3 (a), 1/6 (b), 1/9 (c), 1/12 (d), 1/15 (e) and C_1Sn sample obtained at the core/shell weight ratio of 1/9

the core/shell weight ratio reached 1/9. Figure 3f shows that hollow microspheres with defectless morphology are obtained at that threshold ratio.

CONCLUSIONS

Three steps are involved in the preparation of hollow microspheres, and most significant factors are related to the synthesis conditions and core-shell particles as hollow microsphere precursors. The core/shell weight ratio is crucial factor to prepare hollow microspheres. The threshold ratio can be typically determined by TEM analysis. In this study, we alternatively determined this core/shell ratio for hollow microspheres preparation from conductometric titration curve. The rheology and opacity of the latex were also studied. The results were in agreement with each other, and also proved by TEM analysis.

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