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Effect of the intermediate layer-core ratio on the morphology and opacity ability of hollow latex particles

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ABSTRACT: In this study, well-monodispersed hollow latex particles were synthesized through semicontinuous seed emulsion polymerization, and the effect of the hollow latex particles' intermediate layer–core ratios on their morphology and opacity ability were studied. The results show that when the intermediate layer–core ratios increased from 6 to 10, the swelling degree of the hollow latex particles decreased, and the intensity gradually increased, but the opacity ability increased first and then decreased. When the intermediate layer–core ratio was 8, the opacity ability of the hollow latex particles was the best. When the intermediate layer–core ratios were 6 and 7, the surface of the hollow latex particles was rough, and they showed a great swelling degree, big cavity, and thin shell, and few of latex particles collapsed or ruptured. When the intermediate layer–core ratios were 9 and 10, the hollow latex particles had a smooth surface, thick shell, and small swelling degree and cavity, and roughly, there was no collapse or rupture of the hollow latex particles. When the intermediate layer–core ratio was 8, the swelling degree of the hollow latex particles was moderate. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42268.

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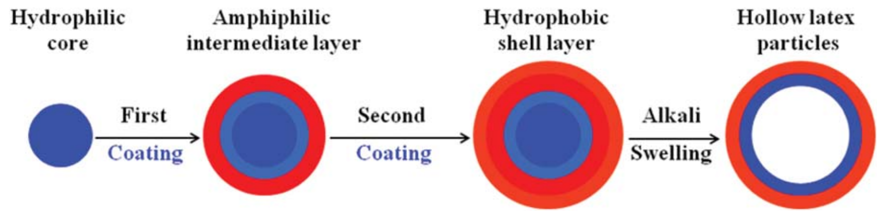
INTRODUCTION

In recent years, the research and development of products with special functions are currently attracting considerable attention in the coating and paint industries. Recently, latex particles with special morphologies have received increasing attention on the basis of particle design theory and emulsion polymerization theory. Hollow latex particles can refract light effectively because of differences in the refractive index of external shells and internal cavities. Therefore, hollow latex particles have good applications in high-quality coatings as paint or padding; for example, they provide opaqueness and surface glossiness in automobiles, construction, and papermaking.[1,2] Moreover, hollow latex particles have potential applications in medicine release, medicine carriers, medicine delivery, and other fields.[3,4]

In the reported preparation methods of hollow latex particles, the method of alkali swelling seed emulsion polymerization has been the best choice because of its well-known process flow, low cost, and easy industrialization.[5] This method was first developed by Rohm and Haas in 1984.[2] They synthesized the hydrophobic shell with a hydrophilic core first and then added alkali for swelling to get the hollow latex particles.[6,7] However, the hollow latex particles synthesized in this way will rupture, collapse, or form reverse-order core–shell structures.[8,9] To solve this problem, Blankenship *et al.*[10] developed a method for forming an amphiphilic intermediate layer between the hydrophobic shell and the hydrophilic core. The size of the core latex particles containing carboxyl swelled and increased 10s or even 100 times by neutralizing with alkali in the aqueous solution. During this period, great expansion tension was generated on the intermediate layer. Therefore, the key factors influencing the final morphologies and opacity ability of the hollow latex particles included whether the intermediate layer had enough stiffness when it suffered from the expansion tension of the core latex particles and swelled properly to form a hollow structure. The thickness of the intermediate layer was one of the important factors that influenced its stiffness, and it has not been reported.

Herein, hollow latex particles with different intermediate layer–core ratios were synthesized through semicontinuous seed emulsion polymerization, and the influence of the intermediate layer–core ratios on the morphology and opacity ability of hollow latex particles were studied via scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible (UV–vis) spectrophotometry, and other characterization methods. Meantime, the mechanism was investigated.



Scheme 1. Formation process of the core–intermediate layer–shell structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and styrene (St; all AR grades, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) were purified by distillation under reduced pressure and stored in a refrigerator. Sodium dodecyl sulfate (SDS; AP grade, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) and Sorbitan fatty acid ester (Span-80; Tianjin Fuchen Chemical Reagent Factory, Tianjin, China) were used without further purification. Sodium persulfate (SPS; AP grade, Tianjin Ke Miou Chemical Reagent Co., Ltd., Tianjin, China) was purified by recrystallization twice in water before use. Ammonia (25.0–28.0 wt %, AP grade, Guangzhou Reagent Chemical Factory, Guangzhou, China) and RS-998A St–acrylic emulsion (48 wt %, BATF Industrial Co., Ltd., Shunde, China) were used as received. Deionized water was used throughout.

Preparation of the Hollow Latex Particles

The polymerization was carried out in a four-necked, 1000-mL, round-bottomed flask equipped with an inlet of nitrogen gas, a reflux condenser, a glass stirrer, and a pressure-equalizing funnel. The procedure included three steps: the synthesis of the core, the synthesis of the intermediate layer, and the synthesis of the shell layer. The formation process of the core–intermediate layer–shell structure is shown in Scheme 1. The typical formula is listed in Table I, and the detailed steps are shown in the later.

Synthesis of the Core. Amounts of 157.5 g of deionized water and 0.375 g of SDS, a mixture of 0.15 g of MAA and 7.35 g of MMA, and an aqueous solution of SPS (0.4658 g of SPS dissolved in 10 mL of water) were added to the reactor sequentially and polymerized at 80°C for 1 h. Then, the mixture of monomers (33.7 g of MAA and 62.4 g of MMA) were emulsified by 0.7865 g of SDS and 1.6135 g of Span-80 in 57.6 g of deionized water and were added simultaneously and dropwise to the reactor for 3 h. Afterward, the system was heated to 90°C and maintained at this temperature for 1 h. After that, the system was cooled down to room temperature.

Synthesis of the Intermediate Layer. A certain amount of the core latex particles was diluted to less than a 30 wt % solid content, and the initiator aqueous solution were added to an another reactor at 80°C. After that, the intermediate monomers mixture of MAA, MMA, BA emulsified by SDS, and Span-80 in deionized water were constantly fed into the reactor in 4 h. Then, the reactor was kept at 90°C for 1 h. At last, the system was cooled down to room temperature.

Synthesis of the Shell Layer and Alkali Treatment. As shown in the formula, a certain amount of core–intermediate latex particles were diluted to a less than 10 wt % solid content in the third reactor at 80°C. Then, the shell monomer emulsified by SDS in deionized water and the initiator aqueous solution were fed into the reactor for 2 h, during which the ammonia was added to the system to swell the particles. After that, the reactor

Table I. Random Choice Formulas for the Preparation of the Hollow Latex Particles

Ingredient (g)	Seed	Core	Intermediate	Shell
MAA	0.15	33.7	4.68	0
MMA	7.35	62.4	79.53	0
BA	0	0	9.36	0
St	0	0	0	93.32
SDS	0.3750	0.7865	0.4599	1.3998
Span-80	0	1.6135	0.9436	0
SPS	0.4658	0	0.4678	0.3733
H2O	167.5	57.6	181.5	186.7
Ammonia	0	0	0	3.6427
Seed	0	175.84	0	0
Core latex	0	0	50	0
Intermediate–core latex	0	0	0	80

Table II. Various Formulas for the Synthesis of the Intermediate Layer

Intermediate layer-core	6	7	8	9	10
MAA (g)	4.68	4.72	4.68	4.70	4.68
MMA (g)	79.53	80.17	79.53	79.93	79.53
BA (g)	9.36	9.43	9.36	9.40	9.36
SDS (g)	0.4599	0.4636	0.4599	0.4622	0.4599
Span-80 (g)	0.9436	0.9511	0.9436	0.9483	0.9436
H2O (g)	171.46	171.87	171.46	171.72	171.46
SPS (g)	0.4678	0.4716	0.4678	0.4702	0.4678
Core latex (g)	50.0	43.2	37.5	33.5	30.0
V (%)	87.12	78.34	47.05	30.03	22.52

was heated to 90°C and maintained at this temperature for 1 h. At last, the system was cooled down to room temperature.

Characterizations

Solid Content. We determined the solid content by baking 2-g samples at 120°C in an oven for 1 h and weighing the residue; then, we calculating the result by determining the percentage of residue remaining after baking.

Cavity-Relative Volume (V). V of the hollow latex particles was obtained. When the hollow polymer latex particles were prepared, the latex particles obtained average particle sizes without alkali swelling (d1) and with alkali swelling (d2). The formula for calculating V of the final hollow latex particles is as follows:

$$V=\frac{d_2^3-d_1^3}{d_2^3}\times 100\%$$

Acid Value (AV). The acid value was measured by the dilution of 1 g of core–intermediate latex particles in 50 g of water and then by titration by a KOH standard aqueous solution. AV could be calculated with the following formula:

$$A_V=56.1\times\frac{(V_1-V_2)c}{m}\times 100\%$$

where AV is the acid value of the latex particles (mg of KOH/mg of sample), V1 is the volume of KOH solution consumed in a normal test (mL), V2 is the volume of KOH solution consumed in the blank test (mL), c is the concentration of the KOH standard solution (mol/L), and m is the mass of the sample (g).

Particle Size. Malvern Zetasizer Nano ZS (ZS Nano-S, United Kingdom) was used to measure the average particle size of the samples.

Viscosity. The viscosity of the emulsions was measured by a rotary viscometer (DV-2+PRO digital viscometer, China) at 30°C with 100 rpm.

Electron Microscopy. TEM (JEM-2100F, Japan) and SEM (LEO-1530VP, Germany) were used to observe the external and internal structure of the hollow latex particles.

Opacity. The opacity of the hollow latex particles were determined by measurement of the transmittance of the film formed by the mixing of the samples with St–acrylic emulsion with a weight ratio of 1 : 4 by UV–vis spectrophotometry (U-3010, Japan).

RESULTS AND DISCUSSION

Synthesis of the Hollow Latex Particles

To prepare the hollow latex particles, composites of a hydrophobic shell with a hydrophilic core, which contained carboxyl, were synthesized. However, because of the strong hydrophilicity of carboxyls, the molecular chain of the polymer containing carboxyl will move to the aqueous phase and finally distribute in the surface of the latex particle core, whereas the hydrophobic shell tends to distribute in the oleic phase. As a result, when hollow latex particles are prepared, the core and shell interpenetrate easily and form an inverted core–shell structure. One method is to synthesize a hydrophilic and oleophilic intermediate layer in the hydrophilic core and the hydrophobic shell as the transition layer. The other method is to adopt starving polymerization, which maintains a relative high conversion rate of the monomer in the system, to make it polymerize when the monomers reach the surface of the core latex particles but have not entered them, and the polymer in the intermediate layer covers the surface of the latex particles core constantly. What is more, this method can effectively prevent the occurrence of secondary nucleation. The typical formulas for preparing hollow latex particles and intermediate layers with different thicknesses are listed in Table II, where the intermediate layer–core was ratio of the weight of the intermediate layer to the solid content weight of the core latex.

In this experiment, the conversion rate of the monomer was greater than 98%; this was calculated when the solid content was tested after the reaction and obtained by theoretical calculation, respectively. This indicated that the reaction was carried out completely. The feeding rate of the intermediate layer was constantly 0.6101 g/min. The test results of the acid value and diameter of the core latex particles and the intermediate layer–core latex are shown in Table III. As shown in the Experimental section, the carboxyl content in the core latex particles was greater than its content in the polymer of the intermediate layer. So, the theoretical value of the core latex particles was greater than that of the intermediate layer–core latex when the core latex particles were effectively covered by the intermediate layer and formed the intermediate layer–core latex. As shown in Table

Table III. Acid Value and Particle Size of the Latex Particles in Each Step

Latex particles	Acid value (mg of KOH/g)		Particle size (nm)	PDI
	Theoretical value	Actual value		
Core latex	67.8	64.3	120.5	0.023
Core-intermediate latex	26.7	25.1	170	0.015
Hollow latex particles	—	—	430.1	0.028

III, the actual acid value of the intermediate layer–core latex particles was extremely close to its theoretical value and was much less than the actual acid value of the core latex particles. This indicated that the core latex particles was well-covered by the intermediate layer latex particles in the experiment. The particle distribution index (PDI) reflected the homogeneity of the particle size distribution of the polymer latex particles. If its value was smaller, the particle size distribution of the latex particles was more uniform.[11] Also, the PDI of the intermediate layer–core latex particles was smaller than that of the core latex particles; this proved that there was not secondary nucleation in the process of the intermediate layer coating of the core latex particles. The degree of swelling of the hollow latex particles prepared from different intermediate layer–core values were calculated by the relative volume of the cavity of the hollow latex particles, as shown in Table II. When the intermediate layer–cores were 6 and 7, the cavity volume of the hollow latex particles was relatively larger; when the intermediate layer–core was 8, the cavity volume of the hollow latex particles was relatively moderate; and when the intermediate layer–cores were 9 and 10, the cavity volume of the hollow latex particles was relatively small.

Morphology of the Hollow Latex Particles

Particle Size and Viscosity Analysis. The hydrophilicity of an acrylic resin increases greatly after being neutralized by alkali, and the size swells dramatically. This phenomenon is called the alkali thickening effect.[12] During this period, the average particle size and the viscosity of the emulsion also increases greatly. Hence, one can examine the swelling degree of the hollow latex particles by examining its particle size and the viscosity of the emulsion. What is more, the swelling degree of the hollow latex particles directly determined the morphology of the latex particles. For this reason, the morphology and opacity ability of the hollow latex particles can be studied by the inspection of its swelling degree. The effects of the intermediate layer–core ratios on the viscosity of the emulsion and the diameter of the hollow latex particles are shown in Figure 1, and the solid contents were all 30 wt %.

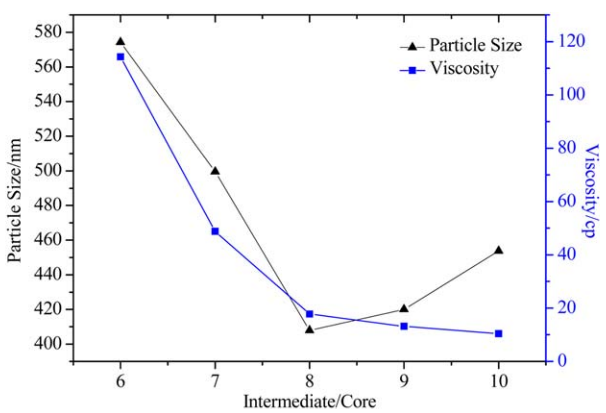


Figure 1. Effect of the intermediate/core ratio on the viscosity and diameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 1, the viscosity of the emulsion decreased gradually with increasing intermediate layer–core; this indicated that the swelling degree decreased gradually. Meantime, the diameter of the hollow latex particles decreased dramatically first and then increased slightly with increasing intermediate layer–core. Two factors determined the change trend of the diameter of the hollow latex particles because of the increase in the intermediate layer–core. One was that the increase in the thickness of intermediate layer increased the particle size of the latex particles. The other was that as the thickness of the intermediate layer increased, the swelling degree of the hollow latex particles decreased gradually; this decreased the particle size of the latex particles. When the intermediate layer–core ratios were 6, 7, and 8, as the thickness of intermediate layer increased, the swelling degree of the hollow latex particles decreased greatly; as a result, the decrease in the particle size of the latex particles occupied the leading role. As a consequence, the particle size of the latex particles decreased. When the intermediate layer–core ratios were 8, 9, and 10, with increasing thickness of the intermediate layer, the swelling degree of the hollow latex particles decreased slightly; as a result, the increase in the particle size of the latex particles increasing occupied the leading role. As a consequence, the particle size of the latex particles increased. When the intermediate layer–core ratio was 8, the particle size of the hollow latex particles was at a minimum.

SEM Analysis. The surface morphology of the hollow latex particles was analyzed through SEM images, and the SEM images of the hollow latex particles with different intermediate layer–core ratios are shown in Figure 2.

Figure 2(a–c) shows that when the intermediate layer–core ratios were 6, 7, and 8, the surface of the hollow latex particles was relatively rough, and wrinkles appeared. This roughness degree decreased as the increase of the intermediate layer–core ratios. There were quite a few of latex particles collapse or rupture; and the quantity of latex particles collapsed or ruptured also decreases as the increase of the intermediate layer–core ratios. Figure 2 (d) and (e) showed that when the intermediate layer–core ratios were

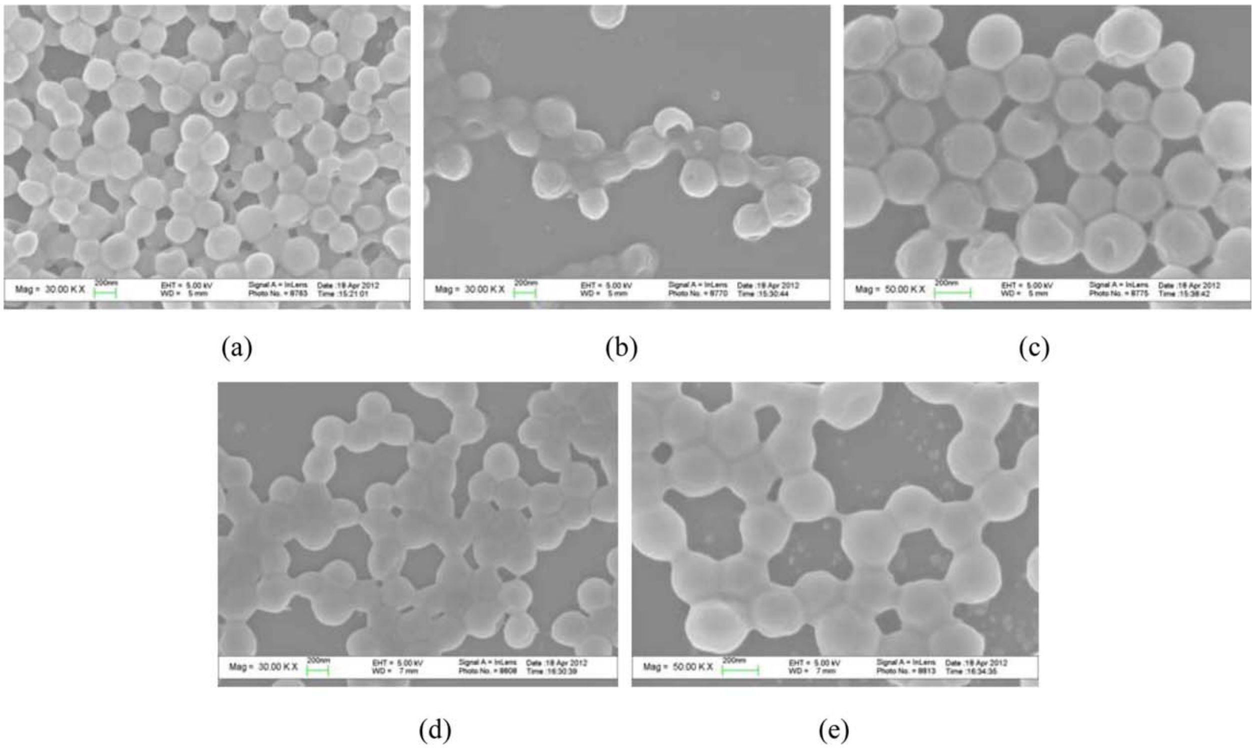


Figure 2. SEM images of the hollow latex particles prepared with various core–intermediate ratios of (a) 6, (b) 7, (c) 8, (d) 9, and (e)10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

9 and 10, the surface of hollow latex particles becomes smooth, and there was not collapse or rupture of latex particles roughly. It can be known from literatures that the surface of polystyrene latex particles presents smooth structure, and when there was polar group or ion distributed in the surface of latex particles, the smooth degree of the surface will decrease.[12] The wrinkles on the surface of latex particles were mainly because the hydrophilicity of carboxyl in the core increases greatly after being neutralized by alkali and becoming carboxylate radical ions, and the final part of carboxylate radical ions distribute on the surface of hollow latex particles. This indicated that when the intermediate layer–core ratios were 6, 7 and 8, the intermediate layer lacks enough intensity to constraint the expansion tension generated by the neutralized latex particles effectively, and finally the hollow latex particles have collapse or rupture because the swelling degree was too big, or the carboxylate radical ions in ruptured latex particles distribute on the surface of hollow latex particles as lacking constraints. When the intermediate layer–core ratios were 9 and 10, the intermediate layer of the latex particles was thicker and had enough intensity, the swelling degree decreased, the situations of collapse or rupture of the latex particles decreased greatly, and the carboxylate radical ions were covered effectively. Therefore, the surface of the hollow latex particles was relatively smooth.

TEM Analysis. The internal morphologies of the hollow latex particles were analyzed through TEM images, and the TEM images of the hollow latex particles with different intermediate layer–core ratios are shown in Figure 3.

The latex particles presented a cavity structure, as shown in Figure 2. When the intermediate layer–core ratios were 6 and 7, the cavity of the latex particles was relatively big, the shell was thin, a lot of latex particles were distorted, and there were quite a few latex particles that were collapsed or ruptured, as shown in Figure 3(a,b); this was in line with the analysis results of Figure 2(a,b). When the intermediate layer–core ratios were 8, 9, and 10, the internal cavity of the latex particles decreased greatly, and the shell was complete. There were few latex particles that were collapsed or ruptured, and as the intermediate layer–core increased, the internal cavity of the latex particles decreased gradually, as shown in Figure 3(c–e). Figure 3 further proves that with increasing intermediate layer–core, the swelling degree of the hollow latex particles decreased gradually, and the intensity of the latex particles was bigger and bigger. Therefore, with increasing intermediate layer–core, the coverage of the intermediate layer on the core was thicker and thicker, and when the intermediate layer–core ratios were 6 and 7, the latex particles swelled excessively, so the cavity was relatively big, and there were quite a few collapsed or ruptured latex particles. When the intermediate layer–core ratios were 9 and 10, the swelling degree of latex particles was relatively small, so the cavity was relatively small, and there were few collapsed or ruptured latex particles. When the intermediate layer–core was 8, the swelling degree of latex particles was moderate, and there was some collapse of latex particles.

UV–Vis Spectrophotometry Analysis. The opacity ability of hollow latex particles was determined through measurement of the transmittance of the films formed by the mixture of the hollow latex particles with the St–acrylic emulsion at a weight ratio of 1 : 4, and the transmittances of the films formed by the

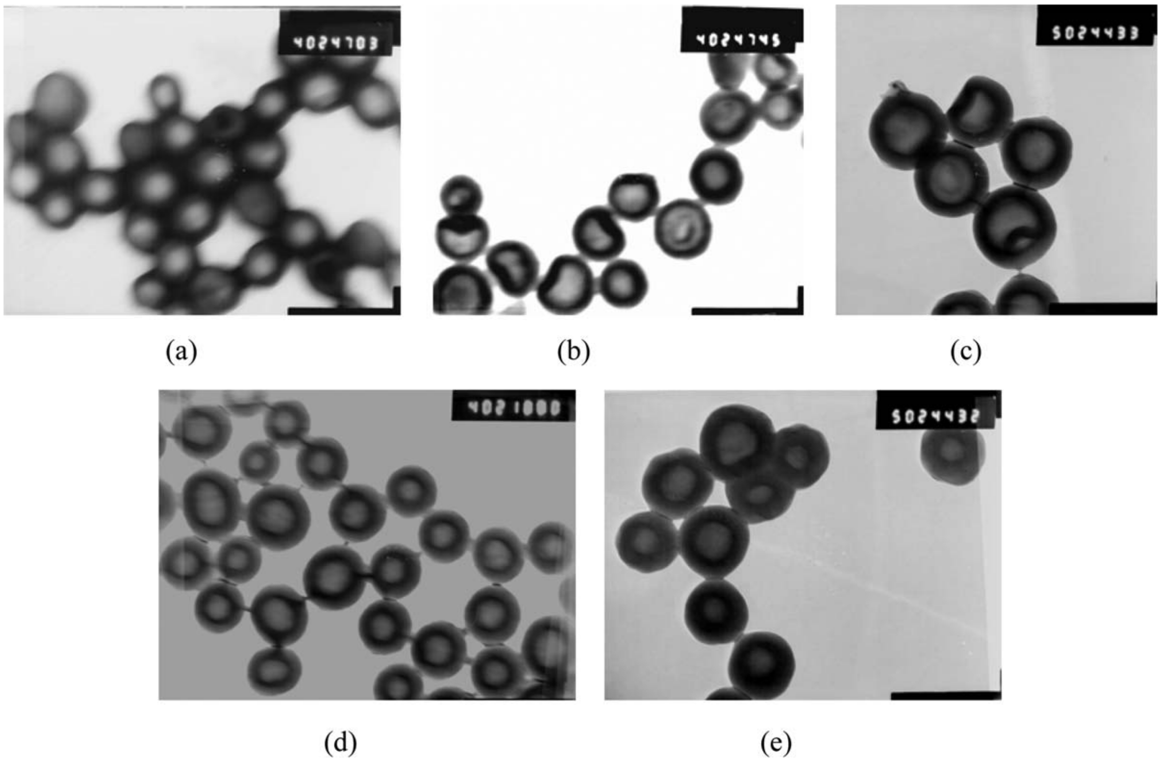


Figure 3. TEM images of the hollow latex particles prepared with various core–intermediate ratios of (a) 6, (b) 7, (c) 8, (d) 9, and (e) 10.

mixture of the hollow latex particles, which had different intermediate layer–core ratios with the St–acrylic emulsion, are shown as Figure 4.

As shown in Figure 4, with increasing intermediate layer–core, the opacity ability of the hollow latex particles increased first and then decreased, and when the intermediate layer–core ratio was 8, the opacity ability of latex particles was the best. This was mainly because when the intermediate layer–core ratios were 6 and 7, the swelling degree of the latex particles was too big, the cavity was relatively big, the shell was relatively thin, the intensity of the latex particles was not great enough, and quite a few of latex particles collapsed or ruptured. This influenced its opacity ability. When the intermediate layer–core ratios were 9 and 10, the swelling degree of the latex particles was smaller, the cavity was smaller, and it could not refract the light effectively, so the opacity ability decreased. When the intermediate layer–core ratio was 8, the swelling degree, cavity size, and shell thickness of latex particles were moderate, and there were fewer collapsed or ruptured latex particles, so the opacity ability was the best. Therefore, to prepare the hollow latex particles with the highest opacity ability, the best intermediate layer–core ratio was 8.

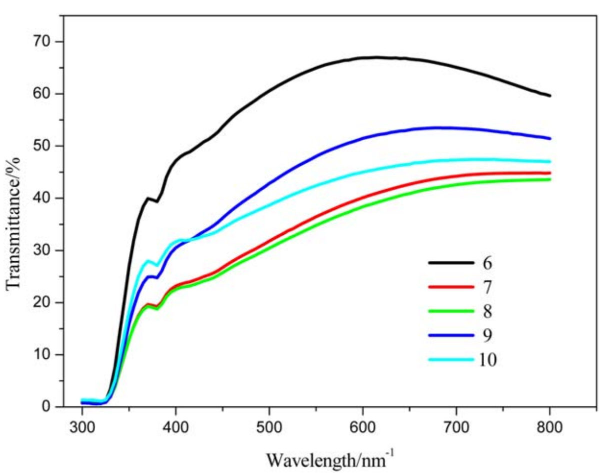


Figure 4. Transmittance of the films formed by the mixture of the hollow latex particles with the St–acrylic emulsion at a weight ratio of 1 : 4. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

CONCLUSIONS

In this study, well-monodispersed hollow latex particles through the semicontinuous seed emulsion polymerization were synthesized, and the effect of the hollow latex particles' intermediate layer–core ratios on their morphologies and opacity ability were examined. From the results, we drew the following conclusions:

1. As the intermediate layer–core ratios increased between 6 and 10, the swelling degree of the hollow latex particles decreased, the intensity gradually increased, and the opacity ability increased first and then decreased. When the intermediate layer–core ratio was 8, the opacity ability of the hollow latex particles was the best.

2. When the intermediate layer–core ratios were 6 and 7, the surface of the hollow latex particles was rough, the swelling degree was relatively great, the cavity was relatively big, the shell was thin, and quite a few of latex particles collapsed or ruptured.
3. When the intermediate layer–core ratios were 9 and 10, the surface of the hollow latex particles was relatively smooth, the swelling degree was small, the cavity was relatively small, the shell was relatively thick, and roughly, there was no collapse or rupture of the hollow latex particles.
4. When the intermediate layer–core ratio was 8, the swelling degree of the hollow latex particles was moderate.

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