Preparation of Raspberry-Shaped Styrene-Butadiene-Methyl Acrylate-Acrylic Acid Latex Particles by Emulsion Polymerization Followed by Alkali/Heating Method

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ABSTRACT: Monodispersed raspberry-shaped polystyrene-butadiene-methyl acrylate-acrylic acid particles were made by semi-batch emulsion polymerization followed by alkali and heat treatment. The particle sizes and size distributions were studied by hydrodynamic chromatography and transmission electronic microscopy. The morphology of the particles was observed by SEM, cryo-SEM, and TEM. Treatment temperature was found to have a significant impact on the particle size and morphology of the treated latexes. Higher temperatures lead to larger particle sizes and more discernible raspberry domains with sizes around 50 nm on the particle surfaces. Higher levels of alkali did not significantly change the particle size but did increase the total titratable acid amount, presumably due to the hydrolysis of methyl acrylate during the treatment. GPC results showed that higher amount of oligomers or polymers are produced in the serum for the heat-treated latexes. Divinylbenzene crosslinking agent at the levels of 0.05–3% limited the particle expansion and decreased the serum acid. A possible mechanism of raspberry particle formations was proposed, which involves migration of hydrophilic and hydrophobic species during the heat treatment. Lastly, potential applications for raspberry particles in paper coating were explored. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1276–1284, 2011

Key words: emulsion polymerization; polystyrene; morphology; raspberry-shaped particles; coatings

INTRODUCTION

The control of latex particle morphology either during the emulsion polymerization or through post-treatments has been an intensive area of research for several decades. A variety of structured particles such as core-shell, microdomain, hollow, and interpenetrating networks have been created.[1,2] These particles may also have unique surface morphologies such as raspberry or multilobes.

Tolue et al.[3] reported preparation of acrylonitrile-styrene-acrylate (ASA) structured lattices in two-stage seeded emulsion polymerizations. The ASA particles contain a soft poly (n-butyl acrylate) core and a hard styrene-acrylonitrile shell. Raspberry-shaped particles were produced when nonylphenol ethoxylated polyethylene glycol surfactant was used in the core emulsion polymerization and styrene and acrylonitrile monomers were batch fed in the second stage.

Qi et al.[4] reported synthesis and characterization of poly(butyl acrylate)/silica and poly(butyl acrylate)/silica/poly(methyl methacrylate) composite particles. Emulsion polymerizing butyl acrylate (BA) in the presence of silica particles preabsorbed with 2,2′-azobis(amidinopropane) dihydrochloride (AIBA) initiator produced PBA/silica composite particles. These particles exhibited a raspberry-like surface morphology with the silica particles adsorbed onto the surface of the PBA particles. Liu et al.[5,6] studied the dispersion of nanosilica particles in the in-situ emulsion polymerization of polyacrylate. A raspberry morphology was also observed with unmodified silica nanoparticles embedded in the polyacrylate latex.

An alkali/heating method can be used to make hollow particles either with a single or with multiple voids. Single void hollow particles are generally made with core/shell techniques that start with the synthesis of a carboxylated polymer core (acid or ester) and a thermoplastic polymer shell by emulsion polymerization. Subsequently, the produced core/shell particles are treated by the addition of alkali and heated at a high temperature. Hollow particles with water inside are believed to be produced by an osmotic mechanism.[7,8]

The preparation of submicron multiple void polymer particles can also be made by core/shell techniques similar to those for single-void hollow

particles.[9] Multiple void particles, however, are typically made using a single-step "homogeneous" styrene-carboxylic acid or methyl methacrylate-carboxylic acid copolymerization with subsequent stepwise alkali/acid or alkali/heating treatments.[10–13] Incorporating ionic and nonionic emulsifiers into the particles during the emulsion polymerization and then following with an alkali/heating treatment is a newly developed method.[14–17] Other techniques were also reported to make multiple void polymer spheres.[18–20] However, using one-step emulsion polymerization with subsequent alkali/heating treatment to make raspberry-shaped particles has not been reported.

In this study, raspberry-shaped styrene-butadiene-methyl acrylate-carboxylic acid particles were made using emulsion polymerization techniques with subsequent alkali/heating treatments. The impact of polymer composition and treatment conditions (e.g., crosslinker levels, pH, time, and temperature) on the resulting particle size and morphology were studied. The formation of raspberry-shaped particles was observed in a number of cases. The use of these morphologies in paper coating applications was also explored.

EXPERIMENTS

A commercial carboxylated styrene butadiene binder from Dow Chemical Company was used in this study. It has a particle size of 122 nm and a glass transition temperature (T_g) of 5°C.

A series of latices were produced using a semicontinuous emulsion polymerization, but with different levels of divinylbenzene (DVB) crosslinker. The basic properties are shown in Table I. Note that these four latices have similar particle sizes, but the glass transition temperatures and percentage gel content slightly increase with higher crosslinker levels.

After the polymerization, the pH of the latex was raised to 8–13 by adding 20% of sodium hydroxide. The latices were also diluted to a solids level of 20%. The emulsions with different pH were placed in 125-mL stainless steel pressure-resistant vessels having a polytetrafluoroethylene inner container. These vessels were put into a preheated oven with temperature ranging from 80 to 180°C for about 3.5 h. After the treatment, the vessels were cooled down to room temperature.

CHARACTERIZATION OF LATEXES

The particle size and particle size distribution was measured using hydrodynamic chromatography (HDC). The acid was quantified using Metrohm 809 Titrando and titrating with potassium hydroxide in the presence of ethanol and methyl ethyl ketone sol-

TABLE I
Latex Description and Properties

	Description	Particle size (nm)[a]	T_g (°C)[b]	Gel (%)
Latex A	0.05% DVB	368	105	86
Latex B	0.1% DVB	369	105	94
Latex C	1% DVB	376	111	95
Latex D	3% DVB	376	114	96

[a] Particle size is weight-average diameter by hydrodynamic chromatography.
[b] T_g is the half height point temperatures at the transition using DSC with a scan rate of 10°C/min.

vents. The aqueous phase (serum) of a latex was obtained by centrifuging the latex at 15,000 rpm at 10°C for 1 h. The acid in the serum was then titrated using the method mentioned earlier. The percentage gel is the fraction of dried film that is insoluble in the toluene solvent. The glass transition temperature (T_g) of dry latices was measured using differential scanning calorimetry (DSC) with a 10°C/min scan. The chromatograms of latex serums were analyzed with a Waters aqueous GPC.

The particle morphologies were observed with a FEI Nova NanoSEM 600 field emission scanning electron microscope (SEM) and a JEOL JEM-1230 transmission electronic microscopy (TEM). The latex particles were prepared by air-drying and staining with osmium tetraoxide. Particles sizes were also measured using the TEM and the Leica QWin and Microsoft Excel software.

Particle cross-sections were observed by SEM. Particles were sectioned in a JEOL SM-09010 Cross Section Polisher, coated with 10 nm of osmium and imaged using the FEI Nova NanoSEM 600 SEM.

Cryo-SEM was used to observe the latex particle morphologies in the wet state. The latex droplets were frozen, fractured, and imaged at −90 to −145°C using the FEI Nova NanoSEM 600 SEM.

The optical properties of produced particles in a styrene-butadiene binder at the binder/pigment ratio of 70/30 by weight were evaluated. Formulations were drawn down on Leneta opacity charts using a 10-mil drawdown bar. The films were dried at 80°C for 8 min then stored at 23°C and 50% relative humidity for 24 h. The opacity contribution of the particles was evaluated as a contrast ratio. The CIE-Y reflectance [lightness/darkness reading] over both the white and black sections of the coated Leneta charts was collected with D65/10° illumination using a Miniscan XE-Plus. The contrast ratio is calculated as the Y reflectance value over the black section (Y_{black}) divided by the Y reflectance value over the white section (Y_{white}). The 20° and 70° gloss was measured using a Zehnther ZLR 1050 glossmeter. Each formulation was drawdown three times. Each

TABLE II
Particle Size Measurement of Dried Latex B Particles by HDC and TEM

	Original latex B	80°C	140°C	160°C	180°C
Median size by HDC, nm	369	372	423	494	518
Median size by TEM, nm	363	369	375	369	367
Particle count	754	406	384	440	514
Volume increase by TEM, %	0	5	10	5	3

Expansion conditions: $1\times$ NaOH at different temperatures for 3.5 h (initial pH around 11.2).

drawdown was measured five times with the reported values being the average of the 15 readings.

RESULTS AND DISCUSSION

The polystyrene-butadiene-methyl acrylate-acrylic acid latices were made through semicontinuous emulsion polymerization. Then the pH of the latices was raised by adding sodium hydroxide. The pH-adjusted latices were heated at a high temperature for a period of time. The influences of base amount (pH), temperature, and expansion time on the particles of expanded latices were evaluated. For viscoelastic polymers, temperature and expansion time have some interactions. Higher temperature and shorter expansion time should have similar effects as lower temperature and longer expansion time. To maximize process efficiency, a short expansion time was desired, while the temperatures were varied. In this study, the expansion time was fixed at 3.5 h. The treatment temperatures and base amounts on the properties of expanded latices were studied.

Influence of expansion temperatures on properties of expanded latices

The base amount needed to 100% neutralize the acrylic acid in the latex was calculated and assigned

the designation of $1\times$. Addition of $1\times$ of sodium hydroxide into latex B increased the pH of the latex to around 11. This base treated latex was held at temperatures from 80 to 180°C for 3.5 h and then cooled to room temperature. This temperature range was selected to cover the ranges below and above the glass transition temperature of the latex polymer (around 105–114°C).

Following the expansion at different temperatures, the median particle sizes were measured by HDC and TEM. The results are shown in Table II. As expected, following the alkali-heating treatment, the latices generally expanded and became larger. The representative particle size distributions of the original and expanded latex B particles by HDC and TEM are shown in Figures 1 and 2, respectively. Both HDC and TEM showed the particle size distributions of the original and expanded latex particles are monodistributed with a bell shape.

For the original latex B, the median particle size by HDC is 369 nm, consistent with the median particle size result of 363 nm by TEM. However, the particle sizes of expanded latices measured by HDC are larger than those measured by TEM, especially as the treating temperature increased. For example, after treatment at 180°C, the median particle size by HDC is 518 nm, whereas the median particle size by TEM is 367 nm. This can be explained by the mechanisms of the measurement techniques.
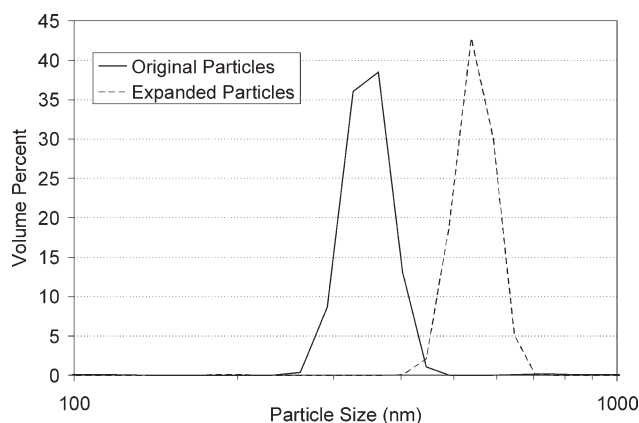

Figure 1 HDC particle sizes distribution of original (solid line) and expanded (dashed line) latex B particles.
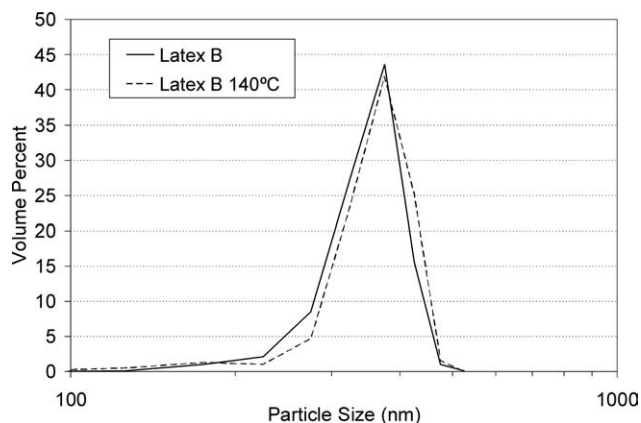

Figure 2 Particle size distribution of original (solid line) and expanded (dashed line) latex B particles by TEM.

TABLE III
Titration Results of Heat-treated Latex B and Their Serums

Treating temperatures (°C)	23	80	110	140	160	180
Total acid amount (%)	2.2	2.3	2.3	2.6	3.9	3.7
Serum acid amount (%)	0	0.3	0.3	0.3	0.5	0.6

Expansion conditions: 1× NaOH at different temperatures for 3.5 h (initial pH around 11.2).

HDC measures the particle sizes according to the hydrodynamic volume of latex particles in water, while TEM is a measure of dried latex particles. For latex particles with hydrophilic polymer chains on the surface, the hydrodynamic volume measured by HDC appears larger as it includes the extended hydrophilic polymer chains.

Table III shows the titration results of the latex and latex serum of the original and expanded particles. The acid amounts in the latex and latex serum are similar for expansion temperatures up to 140°C. At higher temperatures (160 and 180°C), the acid amounts significantly increase, indicating a significant amount of acid-containing compounds or oligomers are produced at these conditions.

Influence of base amounts on the expanded particles at 180°C

In this experiment, the levels of sodium hydroxide were varied from 0.5 to 4×. Note as discussed earlier, addition of 0.5× of sodium hydroxide is expected to neutralize 50% of acrylic acid in the latex and 4× of sodium hydroxide to neutralize 400% of acrylic acid (about three times extra base added). An excess of base is desirable as this allows for neutralization of the acrylic acid and hydrolysis of some of the methyl acrylate.

For this study, the expansion time was fixed at 3.5 h with a temperature of 180°C. The influences of base levels on the HDC median particle sizes and titratable acid amounts of expanded latex B were studied and the results are shown in Table IV.

With the base levels from 0.5 to 2×, the HDC particle sizes increased from 370 to 517 nm. Further increasing the base levels from 2 to 4× did not significantly increase the particle sizes.

The acid amounts in the treated latex serums continuously increased as the base amount increased. Specifically, treatment with 1× of NaOH resulted in 0.5% of acid while treatment with 4× of NaOH resulted in 0.7% acid. This is about a 50% increase in serum acid amount. The extra acid in the serum is expected from the acrylic acid-rich oligomers released from the latex particles.

Untreated latex B contains about 2% of acrylic acid and 5% of methyl acrylate. The titrated acid amount is around 2.2% with no detectable acid in the serum. After the base addition and heat treatment, the acid amounts of the treated latices are all significantly above the baseline 2%. This extra acid is assumed to come from the hydrolysis of methyl acrylate, which produces acrylic acid. If the 5% of methyl acrylate present in latex B is 100% hydrolyzed, it would produce about 4.3% of acrylic acid resulting in a total acrylic acid of about 6.3%. Examining the total acid data in Table IV of 5.3–7.0% for treated latices, it appears that a majority of methyl acrylate has been hydrolyzed when 2–4× of sodium hydroxide was used to treat latex B at 180°C for 3.5 h.

Influence of treatment conditions on aqueous compounds or oligomers

The increases in serum acid in the treated latices indicate that some acid-containing compounds, oligomers, or polymers dissolve into the aqueous phase during the heat treatment. Using titration, it is difficult to differentiate these acid-containing species. Therefore, GPC was used to compare the chromatograms of the latex serums before and after treatment. Note that quantification of the molecular weights of the serum phase species was not done due to the complexity such an analysis adds.

Figure 3 overlays the GPC spectra of both the original and treated latex B particles at different temperatures and base amounts. The top image is the RI response using refractive index detector and the bottom is the UV response. The higher the signal response, the more the compounds or polymers are in the serum. Figure 3 shows that latices treated at higher temperatures tend to have bigger peak areas for both RI and UV responses. This indicates a higher amount of oligomers or polymers present. A dramatic change in GPC curves is seen in the sample treated at 180°C with 2× NaOH. Note the broad peak at a retention time of 12–22 min for both RI and UV traces. This is not detectable in the untreated latex. This peak indicates that some medium to high molecular weight polymers are present in the serum of the treated latices.

TABLE IV
Basic Particle Properties of Heat-treated Latexes with Different Base Levels

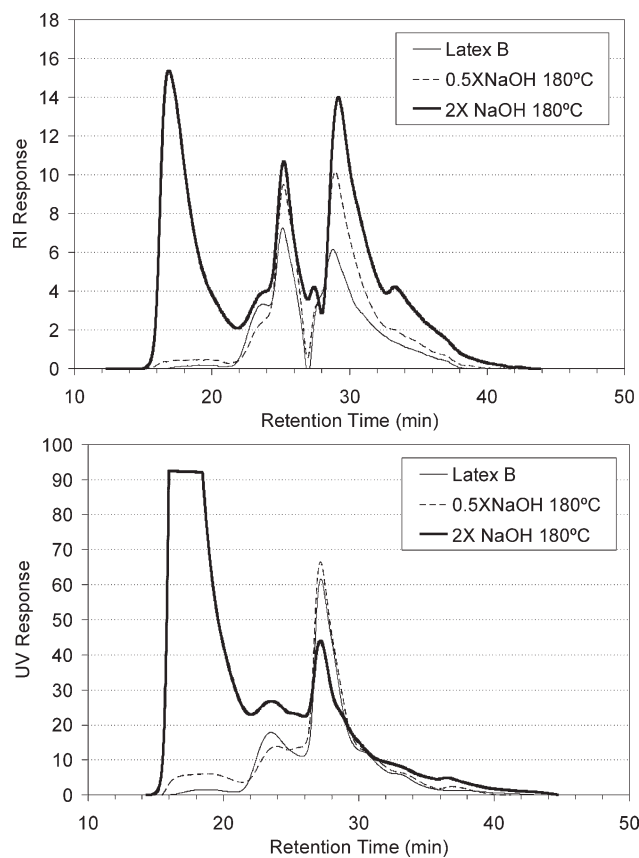| Base amount	0	0.5×	1×	2×	3×	4×
Final pH	2.5	8.2	11.2	12.0	12.3	12.7
HDC (nm)	369	370	490	517	535	520
Total acid amount (%)	2.2	2.4	3.1	5.3	7.0	6.0
Serum acid (%)	0	0.5	0.6	0.7	0.7	0.7

Expansion conditions: 180°C for 3.5 h.

Figure 3 Aqueous GPC spectra of original and treated latex B. Top: RI responses; bottom: UV responses at 260 nm.

Influence of crosslinker levels on expanded particles

Four latices with DVB crosslinker levels from 0.05 to 3% were made and treated at 180°C for 3.5 h after addition of 1× and 4× sodium hydroxide. The HDC particle sizes and serum acid amounts of expanded particles are summarized in Table V.

As expected, the HDC particle sizes and serum acid amount decreased with the divinylbenzene crosslinker levels increasing from 0.05 to 3%. Cross-linking the polymer creates a tight network structure which both reduces the ease of transport into the particle and makes it is more difficult for the osmotic pressure to expand the particle. In addition, because the acid-rich polymers are more tightly held within the structure, less makes it out into the serum phase. As shown in Table V, both the total acid amount and serum acid are highest when the DVB level is at 0.1%. Further, increasing the DVB levels reduced the titratable acid in the treated latices.

Influence of heating temperatures on particle morphologies

Figure 4 shows the SEM images of latex B particles before and after the alkali/heating treatments at dif-

ferent temperatures. The original latex particles have spherical shapes with smooth surfaces. Treatment at a temperature of 80°C, which is below the T_g of the latex polymer, resulted in the particle surfaces slightly rougher with a few bumps on the surface. At treatment temperatures above the T_g, the alkali/heat treated particles still have round shapes but have a much rougher surface (raspberry-like). Particles treated at even higher temperatures (160 and 180°C) show a more discernible raspberry-shape than particles treated at lower temperatures (80 and 140°C).

The TEM images shown in Figure 5 provided similar morphology information to the SEM images. The original particles are spheres with smooth edges. Treatment at 80°C did not change the particle surface textures. Treatments at higher temperatures (140–180°C) resulted in the particle surfaces having some small domains. At higher treatment temperatures, the number and size of domains on the particle surfaces increased.

Cross-section SEM and cryo-SEM of particle morphology of expanded latex

Dried samples were cross-sectioned at room temperature and observed by SEM. The primary interest was to observe the internal structure to investigate whether the voids or holes were present inside the particles. Figure 6 shows the internal structure of treated particles by cross-section SEM. This image also shows the raspberry domains on the particle surface and continuous uniform internal particle bodies. Note that no observable voids are seen inside the particles.

Cryo-SEM was also attempted in an effort to observe the internal particle structure in a wet state and exclude the potential influence of sample preparation. Unfortunately, when the latex droplets were frozen and fractured, they tended to fracture around the particles rather than through them. Figure 7 shows the resulting images. Similar to the dried SEM images, these particles were 400–500 nm in

TABLE V
Characterization of Expanded Particles of Latexes with Different DVB Levels

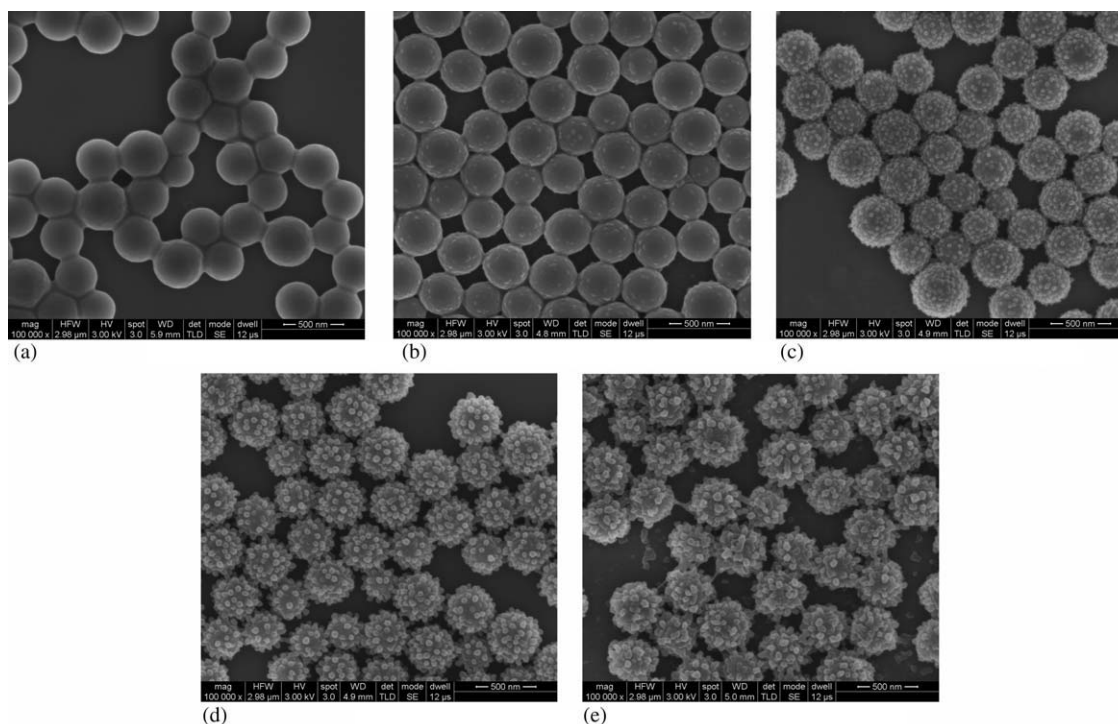| DVB levels, %					
	Base levels	0.05	0.1	1	3
HDC, nm	1×	613	530	506	455
	4×	618	520	498	454
Total acid amount, %	1×	1.8	3.1	2.3	2.2
	4×	3.5	6.0	3.0	2.4
Serum acid, %	1×	0.5	0.6	0.5	0.3
	4×	0.7	0.7	0.5	0.4

Treatment conditions: 180°C for 3.5 h.

Figure 4 SEM images of expanded latex B at expansion temperatures from 80 to 180°C (×1 NaOH for 3.5 h). A: latex B; B expanded at 80°C; C: expanded at 140°C; D: expanded at 160°C; E: expanded at 180°C.
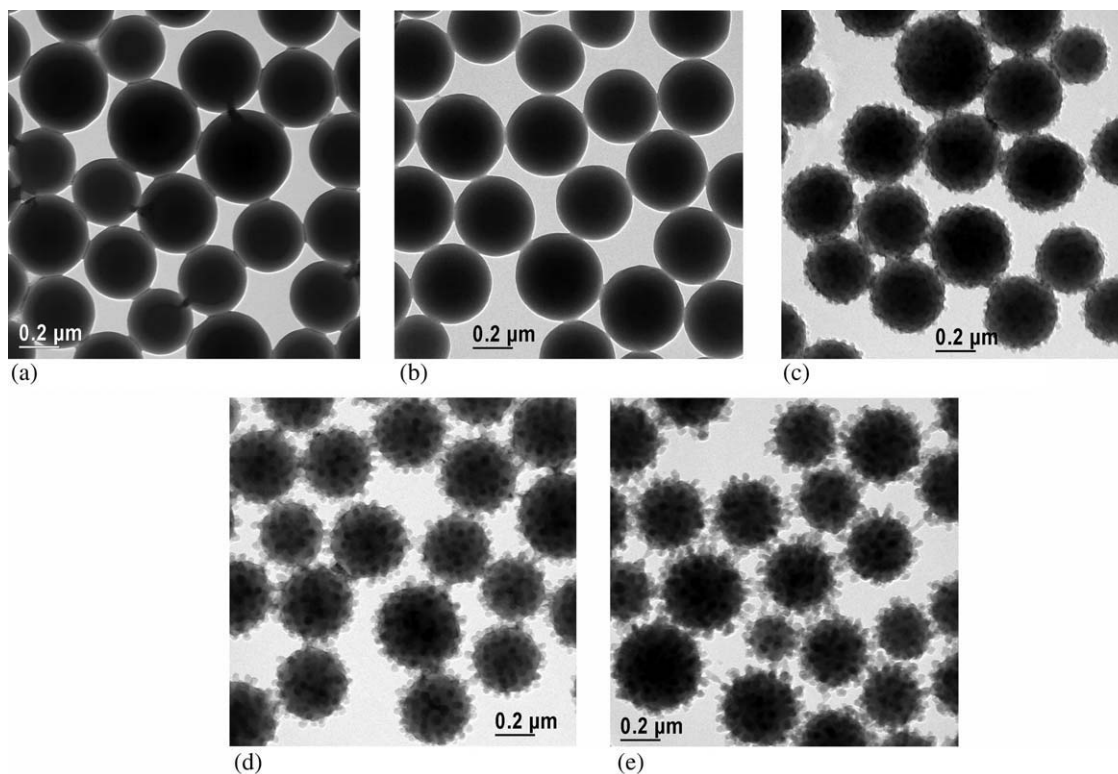

Figure 5 TEM images of expanded latex B at temperatures from 80 to 180°C (×1 NaOH for 3.5 h). A: latex B; B expanded at 80°C; C: expanded at 140°C; D: expanded at 160°C; E: expanded at 180°C.

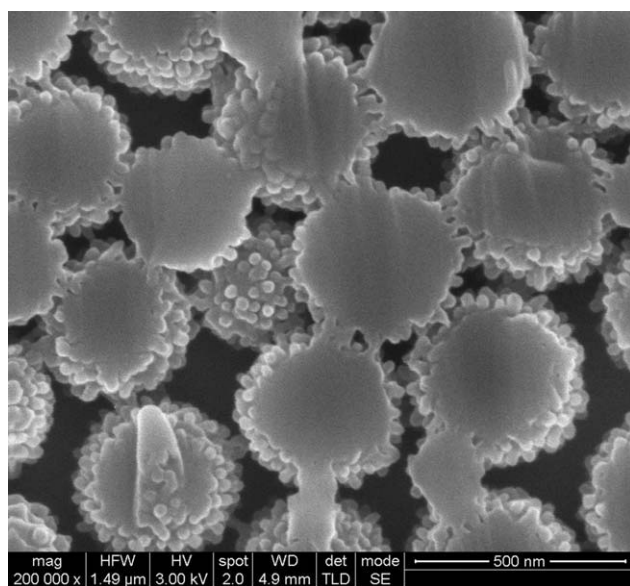**Figure 6** Cross-section SEM of expanded latex B (×1 NaOH at 180°C for 3.5 h).

diameter and covered by small (50 nm) round bumps or protrusions confirming the raspberry shape of the particles.

Potential mechanism of raspberry particle formation

The proposed mechanism for raspberry-shape particle formation is as follows. On addition of sodium hydroxide to the latex, the particles are swollen and the carboxyl groups are neutralized to acrylic salts. As this takes place during a heat treatment, especially if the temperature is above the T_g of the latex polymer, the more hydrophilic acrylic salt-rich domains tend to move toward the particle surface while the hydrophobic polystyrene segments prefer to move away from the surface. This leads to a rough or raspberry particle formation. Higher treatment temperatures facilitate neutralization of acrylic acid and hydrolysis of methyl acrylate as well as increase the movement of polymer chains. This results in more and larger domains on the particle surfaces. This mechanism is in agreement with the observation that raspberry morphology is more obvious for the treatment at 180°C than at 140°C or below.

Dozens of research papers report the formation of multivoids latices by an alkali/acid or alkali/cooling method.[21,22] The generally accepted mechanism of multivoid particle formation is that after the particles are swollen by alkalis and the carboxyl groups are neutralized,[23–26] osmotic pressure is generated from the existence of the neutralized carboxyl groups. These allow the water to enter inside the particles and form small domains. The multivoids

(water domains) particle morphology is fixed during cooling.[27–34]

The cross-section SEM results of the raspberry particles do not support the existence of multivoid formation in these particles. This could be due to the polymerization and treating conditions. For example, most literature reports using surfactant-free emulsion polymerization or nonionic surfactant during the emulsion polymerization while anionic surfactant was used in this study. In addition, the treatment temperature in this study went up to 180°C. This is much higher than those reported in the literature with treatment temperatures from 80 to 120°C. Higher treatment temperature facilitates polymer chain movement, allowing any water domains to be filled by polymer chains. Therefore, no detectable voids remain in the raspberry-shape particles.

Thermodynamic factors determine the equilibrium morphology of the final polymer latex particles, while kinetic factors determine the ease with which such thermodynamically favored morphologies come about. Formation of raspberry-shaped particles further indicates that differences in polymerization technique and treatment conditions (temperature, duration, and pH) will impact particle morphology even when the latex polymers have similar chemical compositions.

Optical properties of unexpanded and expanded latex B in a SB binder latex

The raspberry-shaped surface of the particles potentially opens up some new applications. One of these
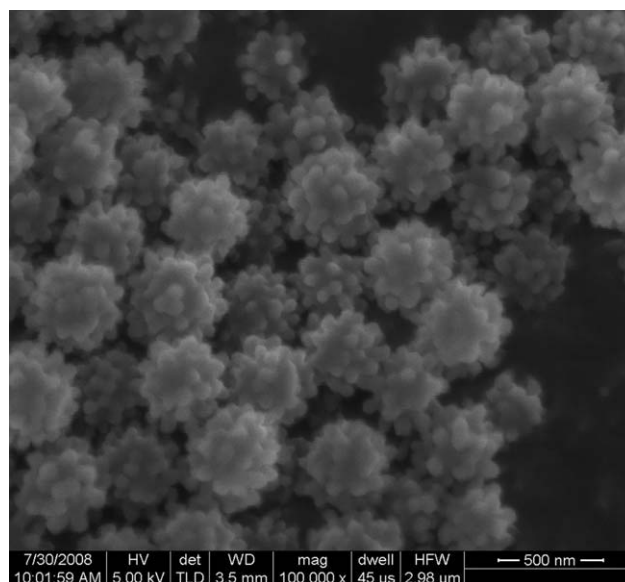

Figure 7 Cryo-SEM of expanded latex B (×1 NaOH at 160°C for 3.5 h).

Coating mixtures	Gloss at 20°		Gloss at 75°		Contrast (%)	
	Mean	Std. dev	Mean	Std. dev	Mean	Std. dev
SB binder/Unexpanded latex B (70/30)	16.6	2.2	89.6	1.2	2.1	0.2
SB binder/expanded latex B (70/30)	2.2	0.8	20.1	1.6	3.4	0.3

is its use as a low-gloss coating modifier for matte paper application. This effect was studied using some model coating formulations.

Original Latex B and heat-treated Latex B particles (1× NaOH at 140°C for 3.5 h) were formulated with a carboxylated styrene-butadiene binder latex at 30% by weight. The formulations were coated on Leneta opacity charts and dried at 80°C for 8 min. After storing at room temperature and 50% humidity for 24 h, the glosses at 20 and 75° and contrast of the coated sheets were measured. The results are shown in Table VI.

The heat-treated latex B particles show a significant reduction in the 20 and 75° sheet glosses. For example, the sheet gloss at 75° with treated latex B is 20.1, compared with 89.6 of the original latex B. The significant reduction in sheet gloss may be due to the raspberry shapes of the expanded latex particles on the coating surface increasing the surface roughness. It may also be due to the higher concentrations of acid and soluble oligomers in the treated latex serum. These may form a network in the wet-stage formulation or during the drying, causing the rougher surface. Both coated sheets are relatively transparent with low contrast level.

CONCLUSIONS

Monodispersed raspberry polystyrene-butadiene-methyl acrylate-acrylic acid particles were made by semibatch emulsion polymerization following alkali and heat treatments. The influences of latex compositions and expansion conditions on the treated particles were studied. Expansion temperature was found to have a significant influence on the particle sizes and morphology of treated latices. Higher expansion temperatures lead to larger particle sizes and more discernible raspberry domains. Higher levels of alkali did not significantly change the particle sizes but did increase the total titratable acid amount. Increasing DVB was found to decrease the particle expansion and decrease the serum acid.

The mechanism of raspberry particle formation was also discussed in the article. It is believed that the more hydrophilic acrylic salt-rich domains move toward the particle surface while the hydrophobic polystyrene segments tend to move toward the center of the particles. The raspberry particles could have used as low-gloss coating modifiers.

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