

Synthesis of SBR/PMMA Core/Shell Latices: The Role of Initiator and Surfactant on Particle Morphology and Instability Performance

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ABSTRACT: Poly(butadiene-stat-styrene)/poly(methylmethacrylate), SBR/PMMA, structural latices were synthesized by using equal moles of different kinds of surfactants: anionic, nonionic, and anionic/nonionic mixture in a two-stage emulsion polymerization. The results indicate that the application of anionic surfactants for the first stage, accompanying sodium persulfate initiator, KPS, for both stages led to core/shell and raspberry morphologies depended upon the hydrophilic lipophilic balance (HLB) of the surfactant. On the other hand, a core/shell structure was observed for structural latices which were synthesized via application of nonionic or anionic/nonionic mixed surfactants along with azobisisobutyronitrile, AIBN, and KPS as first and second-stage initiators, respectively. The surface polarity and wettability of the seed particles

and finally the tendency of the systems to gain the minimum surface free energy change are the basis for the observed morphologies. On the other hand, the stability of core/shell particles was investigated via incremental addition of an electrolyte, ammonium acetate, at temperature close to the glass transition of PMMA shell, 85°C. The particle size measurement on destabilized samples showed that the core/shell latex only stabilized by anionic surfactant was considerably microagglomerated with increasing the electrolyte content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1412–1419, 2007

Key words: SBR/PMMA core/shell particles; microagglomerates; electrolyte; seeded emulsion polymerization; particle morphology

INTRODUCTION

For several decades, composite latex particles with different morphological features have been synthesized via seeded emulsion polymerization.^{1–8} These latex particles with core/shell structure are widely used for preparing advanced engineering plastics with high impact strength, and for toughening other matrix polymers.^{9–16} In rubber-toughened glassy polymers with core/shell particles, the toughening behavior and processability are mainly affected by particle size, grafting density, grafting degree, and shell structure, which control the state of dispersion of particles in the melt and solid states.^{17–20} Therefore, many research scientists have investigated the role of crucial preparation parameters, initiator and surfactant type, on the final morphology of two-stage emulsion particles.^{21–32} Jönsson et al.² reported the role of second-stage initiator, potassium persulfate, KPS, and *tert*-

butyl hydroperoxide (*t*-BHP), on the seeded emulsion polymerization of styrene in the presence of poly(methylmethacrylate) (PMMA). They showed that the seed containing polymer anchored sulfate end groups could produce core/shell particles having graininess and smooth interface structure between core and shell regions dependent upon the type of second-stage initiator. They also concluded that the above difference in shell structure causes a large difference in the tendency of the core/shell particles to undergo phase inversion when swollen with a good solvent for the shell.²¹ Other publications have also emphasized the critical role of the initiator and surfactant type on controlling the particle morphology in a two-stage emulsion polymerization.^{25–27} By changing the surface polarity of the seed particles via employing various initiators and surfactants, the surface charge density and consequently the capability of the seeds to adsorb shell polymer chains can be varied. On the other hand, the thermodynamically preferred morphology of the composite latex particles is the one with the lowest interfacial free energy change. A useful thermodynamically based mathematical model has been developed to describe the free energy changes corresponding to various possible morphologies in structural latices.²⁶ The model could predict the crucial role

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TABLE I
The Characteristics of Various Surfactants Used in the Two-Step Emulsion Polymerization of SBR/PMMA Core/Shell Latices

Emulsifier	Type	Mole ($\times 10^{-3}$)	M_w (g/mol)	HLB ^a
Lithium stearate	Anionic	3.8	290	16.1
Potassium abeitate	Anionic	3.8	351	19.3
SLS/Triton X-100 ^b	anionic/nonionic	3.8	288/690	19.6
Tween 20	Nonionic	3.8	1227	19.0

^a The HLB number of nonionic surfactants were calculated by Griffin's method, and for the anionic surfactants by Davies' method.²⁵

^b The HLB of mixed surfactant was calculated via mixture law.

of second-stage initiator type on the final particle morphology for a few prepared samples. In other research works, the effect of various surfactants were investigated on the size and morphology of the core/shell particles in a two-stage emulsion polymerization.^{28–31} Sundberg et al.³⁰ investigated the influence of the surfactant type on the interfacial tension between incompatible components, an oil and synthesized PMMA, and hence on the morphology of stabilized structural particles in the aqueous media. The effect of the amount of added emulsifier in the second stage and its addition method on the final morphology of the composite latex particles were studied by a separate group.²⁹ The type and amount of emulsifier are critical parameters that control the size and morphology of core/shell particles. Merkel²⁸ investigated the effect of different nonionic surfactants on the characteristics of rubbery core and core/shell latices. They selected suitable nonionic surfactants having HLB number ranging from 16 to 19, to produce monodisperse core and core/shell particles. Conversely, the amount of surfactant has indicated a crucial effect on the grafting efficiency, G_e , and grafting degree, G_d , in the second stage emulsion polymerization.^{6,27,28} An excess of emulsifier causes secondary particle formation and concomitant reduction of G_d and G_e , while its insufficiency leads to more coagulation.

The surfactant and initiator types not only affect the morphology of core/shell particles in a seeded emulsion polymerization, but also may contribute to their performance in a coagulation process.³² Wills and Roebing³³ used ammonium acetate as an electrolyte to microagglomerate acrylic core/shell latex particles, 60 nm in diameter, which were stabilized by sodium lauryl sulfate (SLS). Their results showed a success in making microagglomerated particles at 90°C.

In this research work various surfactants—anionic, nonionic, and anionic/nonionic mixture—were used in equal number of moles and HLB ranging from 16 to 20 to produce SBR/PMMA core/shell latices. The main interest was to investigate the role of surfactant and initiator types on the morphology of the composite particles along with their destabilization probability by using an electrolyte at the temperatures close to the glass transition of the shell. Therefore, our final goal, the preparation of microagglomerated SBR/

PMMA core/shell particles with different sizes and shapes, artificial morphologies, for investigation of the role of the state of particles agglomeration on final properties of a toughened plastic can be accomplished. This part of our ongoing research will appear in another paper.³⁴

EXPERIMENTAL

Materials

Methyl methacrylate (Merck, Germany) was freshly distilled, while styrene (Merck) was distilled after its washing with sodium hydroxide aqueous solution, 10 wt %, to remove their inhibitors. Butadiene (Merck) was purified through an ascarite (sodium hydrate-asbestos absorbant) filled gas tower bed and passed over an anhydrous calcium sulfate bed prior to use. Azobisisobutyronitrile (AIBN) which was used after its recrystallization from methanol, and potassium persulfate (KPS), both were purchased from Merck. Sodium lauryl sulfate (SLS), Triton X-100 (both from Merck), Tween 20 (Fluka), stearic acid, and lithium hydroxide (both from Merck) were used as surfactant in the first stage emulsion polymerization. The characteristics of the surfactants are presented in Table I. Tertiary dodecyl mercaptan (TDM) from Merck Co. was used as chain transfer agent. Aqueous ammonium solution, 25 wt % (Fluka, USA), and acetic acid (Merck) diluted with twice-distilled water, 50 wt %, were used. The solvents: toluene, acetone, and methyl ethyl ketone all were supplied from Merck. Distilled deionized water was prepared in our laboratory and used in the polymerization process.

Emulsion polymerization of the seed

The poly(butadiene-stat-styrene), SBR, seed latices were synthesized via batch emulsion polymerization in 200-mL stainless steel pressure vessels based on predesigned recipes (Table II). Water, emulsifier, initiator, and styrene were added to each vessel and purged with Argon gas for 15 min and then cooled down in an ice-salt mixture before adding the chain transfer. Later, liquid butadiene was added to the vessel and its excess amount vented, the vessel capped

TABLE II
Recipes for Preparation of SBR Seed Latices

Ingredients	Recipes ^a			
	1	2	3	4
Butadiene	90.00	90.00	90.00	90.00
Styrene	10.00	10.00	10.00	10.00
Water	180.00	180.00	180.00	180.00
TDM	0.10	0.10	0.10	0.10
KPS	0.40	0.40	–	–
AIBN	–	–	0.80	0.80
Lithium hydroxide	0.09	–	–	–
Stearic acid	1.08	–	–	–
Potassium hydroxide	–	0.21	–	–
Abietic acid	–	1.11	–	–
SLS	–	–	0.21	–
Triton X-100	–	–	2.10	–
Tween 20	–	–	–	4.63

^a The weights of ingredients are in grams.

with metal crown cap lined by rubber gasket and teflon tape. The charged vessels were tumbled end-over-end in a thermostatically controlled water bath at 65°C and 60 rpm for 24–36 h. To prepare the cores with intermediate gel content, the polymerization in each case was stopped at 60% conversion by adjusting the reaction time. The residual butadiene was removed by flash evaporation for at least thrice. The free emulsifier was consumed during the second-stage emulsion polymerization; therefore no extra surfactant was added.

Seeded emulsion polymerization

Seeded emulsion polymerization was carried out to graft PMMA chains on the SBR seeds. The second-stage polymerization was performed in 100-mL glass bottles based on predesigned recipes (Table III). The SBR latex, and other components except MMA monomer were charged into the bottles and purged with Argon gas for 15 min, then MMA was added to the bottles and capped with metal crown caps lined with neoprene gaskets. The bottles tumbled end-over-end for equilibrium swelling time, 15 h and 40 rpm at room temperature in a thermostatically controlled water bath, and then the temperature was raised to 65°C and kept for 3 h.

Characterization

Gel content of the SBR latex

The degree of conversion was measured gravimetrically at the end of the reaction. Emulsion polymerization of SBR latex, especially in higher conversions and temperatures has a self-crosslinking essence. The gel content of seed particles was measured via solvent extraction method. Three samples of dried SBR film, 0.25 g, were added to 25 mL toluene and stirred at 300 rpm and room temperature for 48 h. Then samples

were centrifuged at 5000 rpm for 1 h. The sediment gel phase was separated from the sol phase and dried in a vacuum oven at 50°C. The gel fraction was determined gravimetrically based on the total weight of the sample.

Grafting degree

To determine grafting efficiency, the core/shell latices were freeze-dried to a fine powder, and placed in a vacuum oven at 40°C for 3 h to remove the trace amount of water. Then, three samples of powder, 1 g each, were dispersed in 25 mL acetone/methyl ethyl ketone mixture, 50/50, and were stirred at room temperature and 300 rpm for 48 h. The dispersions were centrifuged at 10,000 rpm for 2 h. The gel phase at the bottom of the cell was separated from supernatant phase, and both fractions were dried to remove solvents under vacuum at 40°C for 24 h. The grafting degree, the weight ratio of ungrafted PMMA to rubber particles, G_d , was measured gravimetrically.

Particle size and size distribution

The size and size distribution of the seed and core/shell latices were measured via laser light scattering (photon correlation spectroscopy), SEM-633, with wavelength 632.8 nm and laser source light He and Ne gas.

Morphology of core/shell particles

Transmission Electron Microscopy, TEM, Zeiss CEM 902A, was used to observe the morphology of structural latex particles. The latices were further diluted with distilled water, and then dilute droplets was transferred onto the copper grids, mesh 200, and dried in open air. Then, the samples were stained by osmium tetroxide vapor, OsO_4 , before microscopy to distinguish the core and shell regions.

TABLE III
Recipes for the Preparation of Core/Shell Latices

Ingredients	Recipes ^a			
	1	2	3	4
Latex no. 1a ^b	100.00	–	–	–
Latex no. 2	–	100.00	–	–
Latex no. 3	–	–	100.00	–
Latex no. 4	–	–	–	100.00
KPS	0.14	0.14	0.14	0.14
Water	60.00	60.00	60.00	60.00
MMA	20.00	20.00	20.00	20.00

^a The solid content of SBR latices was 20 %wt and the weights of ingredients are in grams.

^b The SBR latex no. 1a was synthesized at 70 °C.

TABLE IV
The Characterization of the Synthesized Core and Core/Shell Particles

Seed latex	Gel content (%)	Mean size (nm)	PDI ^a
No. 1	–	211	1.22
No. 1a	58	112	1.07
No. 2	5	71	1.16
No. 3	67	101	1.09
No. 4	55	113	1.00
No. 4a	–	158	1.06
Core/Shell	Grafting degree (%)	Mean size (nm)	PDI ^a
C.S. No. 1a ^b	48	130	1.05
C.S. No. 2	57	95	1.13
C.S. No. 3	46	117	1.09
C.S. No. 4	43	132	1.16

^a PDI: Polydispersity index of latex particles, which was measured by LPS device.

^b The core/shell latex was prepared by application of seed latex no.1a, which was synthesized at 70 °C.

RESULTS AND DISCUSSION

Equal moles of various kinds of surfactants with HLB values in the range of 16–20 were used in emulsion polymerization to prepare the SBR seed and SBR/PMMA core/shell particles with different surface characters. The surfactants were anionic, anionic/nonionic mixture, and nonionic, which were only added for the first stage of emulsion polymerization. Conversely, AIBN was used as initiator when the ionic surfactants were substituted by the anionic/nonionic and nonionic ones. Because emulsion polymerization of butadiene/styrene was not stable using KPS as initiator and nonionic or anionic/nonionic surfactants. The results indicate that the size and size distribution index of the rubbery seed particles decrease as the HLB value of the anionic surfactant is raised (Table IV). In addition, the size of the rubbery seed particles increase while its polydispersity decrease as the anionic surfactants are substituted by nonionic one with the same HLB value. The main difference among the surfactants with different polarity but the same solubility is the number of formed micelle arising from the difference in the number of surfactant molecules used per micelle. Furthermore, the reaction temperature increment has reverse effect on size and size distribution of latices stabilized with anionic and nonionic surfactants. On contrary of the nonionic stabilized latex, in anionic stabilized latex the size of the particles decreases and the distribution increases as the reaction temperature is raised (Table IV).

The observed changes can be attributed to the nature of nonionic surfactants, which affect the size and shape of final emulsion particles. Using the nonionic surfactant compared to the anionic one caused the number of micelles and consequently the latex particle

size to increase. In fact, for nonionic surfactants the number of surfactant molecules per micelles is much higher than that of the anionic surfactants. On the other hand, the nature of the interaction forces between colloidal particles stabilized with nonionic surfactants is steric repulsion compared to electrostatic for anionic types.

The crucial role of anionic initiator, KPS, along with anionic surfactants in the recipes should be considered. In fact, the presence of anchored sulfate ion on the particle surface as *in situ* surfactant, in addition to added surfactant can enhance the surface polarity and improve the colloid stability of the produced latices.

On the other hand, the seed latices produced by the nonionic surfactant, Tween 20, for example, showed the narrowest particle size distribution, recipe 4, compared to other surfactants. But, this observation depends on the specific condition of emulsion polymerization. By changing the process temperature from 65°C to 70°C, the performance of both nonionic and anionic surfactants will change too (Fig. 1). By raising the polymerization temperature for the recipes based on Tween 20 the size of rubbery seed changed from 113 to 158 nm, and its distribution broadened (Table IV). The observed change can be attributed to the nature of nonionic surfactant. As the temperature increases, the hydrogen-bonding interaction between the hydrophilic polyethyleneoxide segments of the nonionic surfactant with aqueous media deteriorates, and causes the CMC reduction that produces micelles with bigger size. Thus, latices synthesized at higher temperatures need more concentrations of nonionic surfactants for colloidal stability. The worst situation will be observed if the reaction is performed at a temperature close to the cloud point of the surfactant, where the colloid may sediment. The behavior of lithium stearate, an anionic surfactant, was *vice versa* in

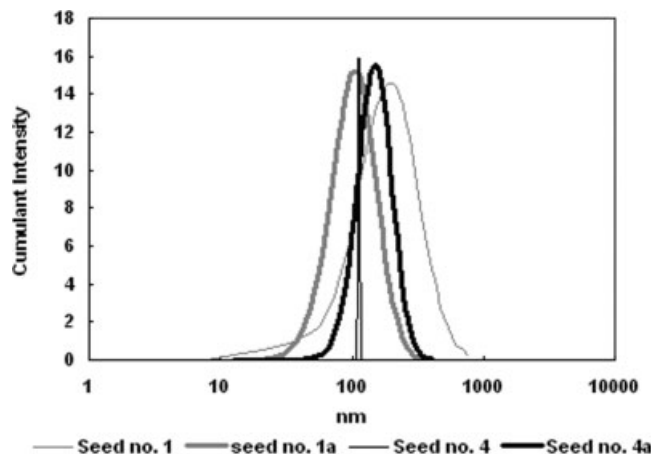


Figure 1 The effect of polymerization temperature on the particle size and size distribution of SBR latices prepared via lithium stearate and Tween 20.

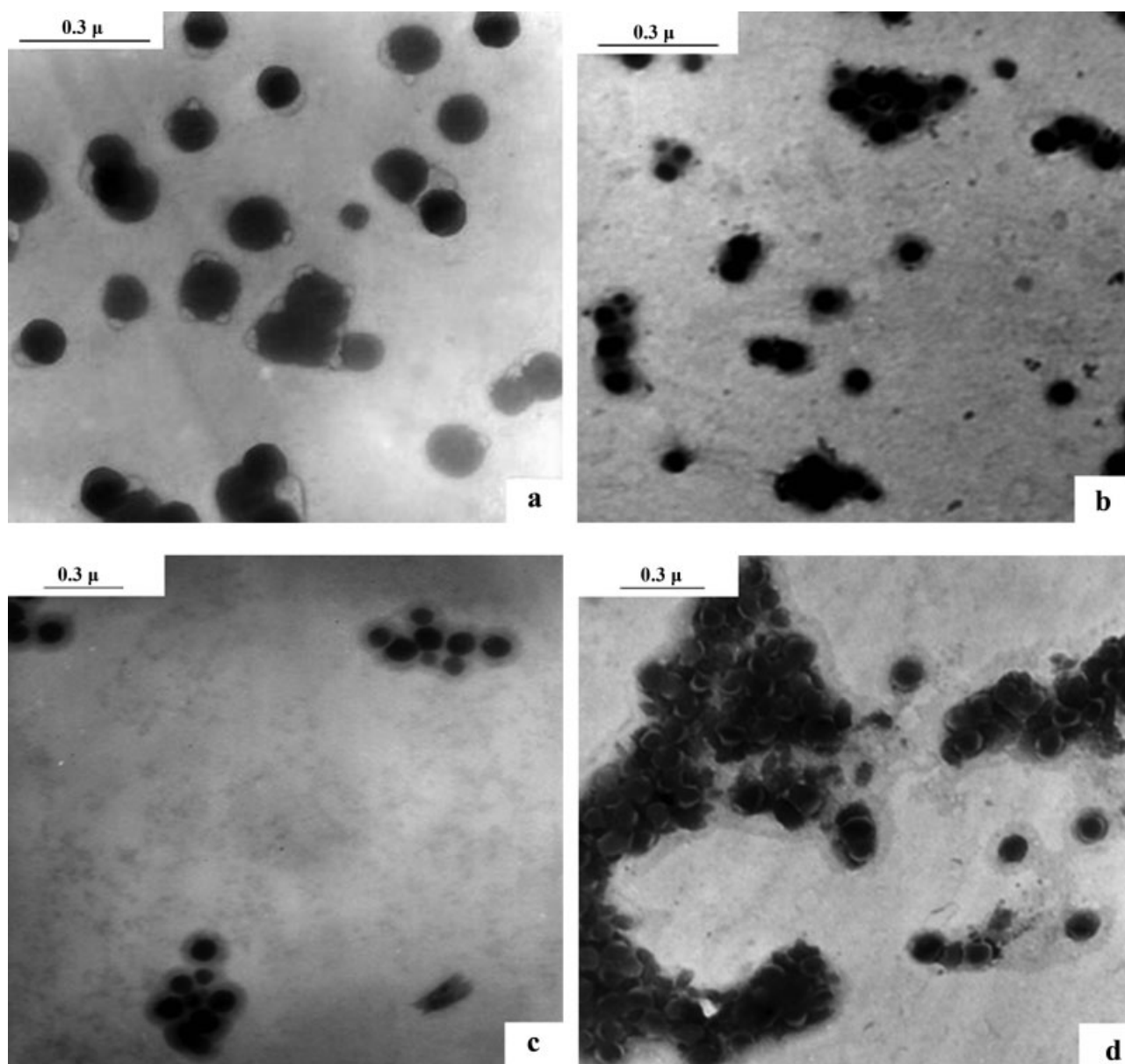


Figure 2 TEM micrographs of SBR/PMMA core/shell particles prepared via different surfactants, (a) lithium stearate, (b) potassium abietate, (c) SLS/Triton X-100 mixture, and (d) Tween 20.

comparison to Tween 20. The result showed the decrease of rubber particle size from 211 to 113 nm by increasing the temperature from 65°C to 70°C (Table IV). The CMC of anionic surfactants increases with temperature, and so smaller latex particles may form. Also, lower temperature, 65°C, may not be enough for dissolution of crystalline stearate molecules to form smaller micelles.

To investigate the role of surfactant on the morphology of structural particles with intermediate gel content, the first stage emulsion polymerization was continued to 60% conversion. Thus, after removal of excess monomer, the free surfactant from Step 1 was used for second stage polymerization without adding extra surfactant. It was assumed that (i) the amount of

free surfactant of all types was not sufficient enough to stabilize the newly formed particles during shell formation and (ii) the amount of surfactant was just enough to prevent coagulation of the system, in which the polymer/water interfacial area was growing as the polymerization proceeded. The same polymer/monomer, SBR/MMA, ratios were selected in all recipes (Table III). No coagulum was observed in all synthesized SBR/PMMA latices after second-stage polymerization. On the other hand, TEM micrographs indicated discrete core/shell particles without generation of any new particles (Fig. 2). Different particle morphologies were observed in the structural latices synthesized via application of anionic surfactants accompanying KPS as initiator in the first and second

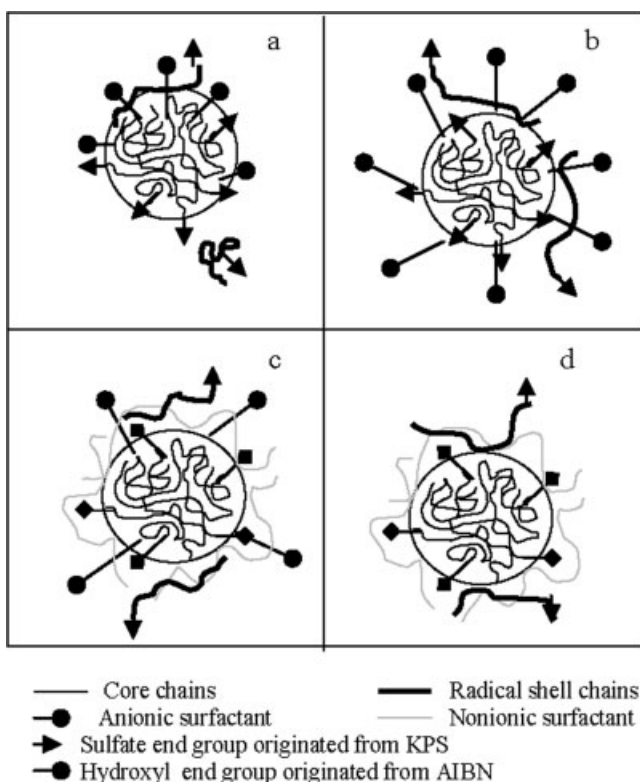


Figure 3 The schematic illustration of the role of surfactant and initiator types on the adsorption of shell macroradicals: (a) KPS initiator with low HLB anionic surfactant, (b) KPS initiator with high HLB anionic surfactant, (c) AIBN initiator with anionic/nonionic mixed surfactant, and (d) AIBN initiator with nonionic surfactant.

part of reaction [Fig. 2(a,b)]. The seed surface stabilized via the surfactant having lower HLB formed the raspberry composite particles, whereas higher HLB surfactant led to core/shell morphology. The more wettability of seed surface generated via more hydrophilic surfactant can decrease the interfacial free energy between the incompatible Stage 1 and Stage 2 polymers and so more coverage of SBR seed by PMMA shell (Fig. 3). However, this criterion alone can not establish a full coverage core/shell structure because the interfacial between each polymer with aqueous media can affect the interfacial surface free energy of the system. Thus, the stabilized SBR/PMMA core/shell latex produced via potassium abietate, besides having lower interfacial tension between SBR and PMMA phases, has the minimum interfacial surface free energy change compared to other morphologies. Nevertheless, the core/shell morphology was observed for the seed latices, which were produced using nonionic and anionic/nonionic blend surfactants accompanying first-stage initiator, AIBN, and second stage initiator, KPS, [Fig. 2(c,d)]. The SBR seed with low surface polarity originated due to application of AIBN initiator can adsorb the polymeric radicals having sulfate ion end-groups produced during

the second stage polymerization (Fig. 3). The size and size distribution of the SBR latices, which were used as seed in the subsequent stage of emulsion polymerization, are shown in Figure 4. As one can see, the synthesized SBR/PMMA particles via Tween 20 show a higher particle size distribution compared to its primary SBR seed. In contrast, when the SBR latex produced by lithium stearate in second stage polymerization, the polydispersity index of synthesized structural particles decrease. The increase of particle size distribution in former case can be attributed to deficiency of nonionic surfactant in the second-stage polymerization. Low surfactant content results in nonsuitable coverage of the growing particle surface, and reduces the interface between particles and polymerization media. So, the absence of enough surfactant and particle instability in the presence of second monomer can lead to the flocculation of the core/shell particles. In contrast, the polymerization of PMMA in the presence of SBR seed prepared using lithium stearate, led to core/shell particles with narrow particle size distribution compared to its primary seed (Fig. 4). This can be attributed to the formation of SBR/PMMA particles with nonuniform shell thickness. Thus, the small core/shell particles engulfed via the thicker shell layer than the large particles.

Stability of core/shell latices

The stability of as synthesized core/shell latices was investigated via application of ammonium acetate solution. The electrolyte solution was added incrementally as separate streams of ammonium hydroxide, 29 wt %, and aqueous acetic acid, 50 wt %, to all core/shell latices at 85°C and 250 rpm. In fact, increasing temperature toward the glass transition of the shell material can lead to irreversible flocculation phenomenon and formation of more stable microagglomerates.

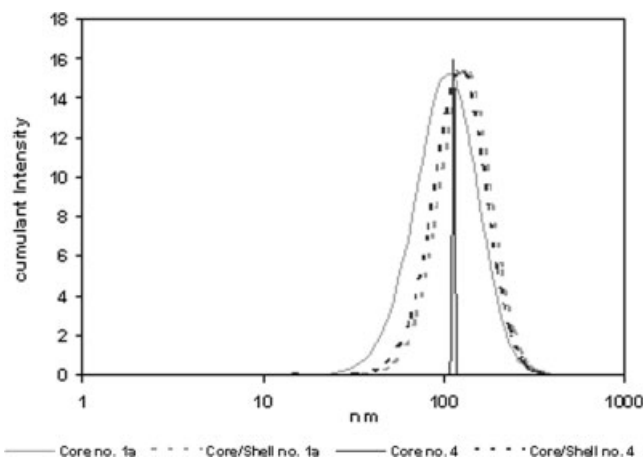


Figure 4 The variation of particle size distribution of SBR seed latices which were used in second stage emulsion polymerization.

TABLE V
The Effect of Electrolyte Content on the Particle Size of SBE/PMMA Core/Shell Latices

Latex	Surfactant	Electrolyte ^a (%)	Mean size (nm)	Agglo. in. N_p	Coagulum ^a (%)
C.S. No. 2	Anionic	0.0	95.0	1.0	0.8
		5.0	122.0	2.0	3.5
		10.0	286.0	27.0	13.0
		20.0	308.0	34.0	28.5
C.S. No. 3	Anionic	0.0	120.5	1.0	0.5
	Nonionic	5.0	117.2	1.0	1.2
		10.0	120.7	1.0	0.8
		20.0	156.3	2.0	2.7
C.S. no. 4	Nonionic	0.0	131.7	1.0	2.5
		5.0	125.6	1.0	3.6
		10.0	131.6	1.0	1.9
		20.0	132.6	1.0	2.8

^a The added electrolyte and coagulum percent were accounted based on the dried core/shell.

At temperatures above 85°C, the gelation of the latices would occur in electrolyte concentration above 20%. This can be attributed to the rapid coagulation as a result of reduction of the performance of the surfactants, especially for nonionic ones near their cloud point. As one can observe, the core/shell latices show diverse responses to the added electrolytes (Table V). The decrement of C.S. no.2 latex stability with increasing the electrolyte concentration and subsequently growing the particle size seems mainly due to the increase in ionic strength of latex and adsorption of the monovalent counterion on the core/shell particles. The results indicate that the agglomeration index, N_p , of SBR/PMMA particles increases considerably as a function of electrolyte concentration for latex, which is stabilized by anionic surfactant. The agglomeration index, N_p , was defined as the volume of primary particles over the rubber particle agglomerates^{20,33}; that is,

$$N_p = \frac{V_A}{V_P} = \frac{D_A^3}{D_P^3} \quad (1)$$

where V_A and V_P are the volumes of agglomerated rubber particles and primary particle, respectively. D_A and D_P are weight-average particle diameters for agglomerated and primary unagglomerated core/shell latices, respectively, which were measured by laser particle size device.

Figure 5 shows that the particle size distribution curves shift to higher particle size and broaden by increasing the electrolyte percent. Thus, the enhancement of electrolyte amplifies the rate of coagulation, and so produces the heterogeneous microagglomerates in size. On the other hand, no alteration in particle size was observed for the core/shell particles synthe-

sized using Tween 20 and SLS/TritonX-100 blend surfactants. Only, a microagglomerated structure as doublet was observed for core/shell latex prepared using SLS/TritonX-100 blend surfactants in the maximum electrolyte concentration. The stability of core/shell latices against the electrolyte can be explained based on the interaction energy between the particles stabilized via different stabilizing materials. In another words, the origin of interfacial interaction energy between particle dispersions via anionic surfactant is electrostatic repulsion, whereas the force for nonionic stabilization is steric repulsion.

As the amount of coagulant in the original latex increases, the double layer around the particles shrinks and therefore the PMMA stabilized SBR par-

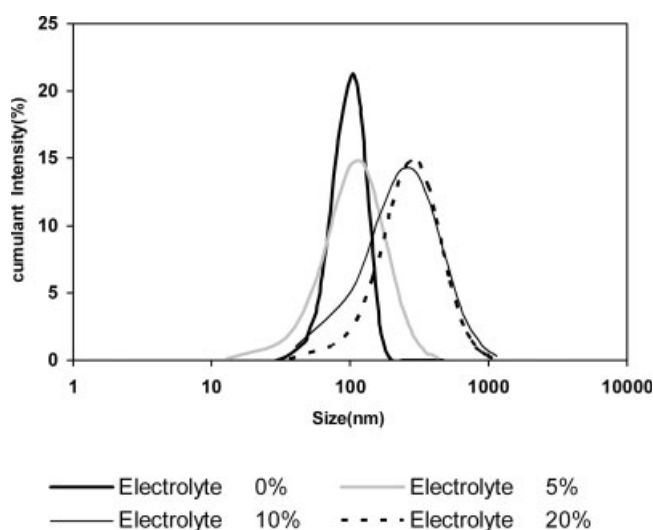


Figure 5 The effect of electrolyte percent, ammonium acetate, on the size and size distribution of SBR/PMMA core/shell particles prepared via potassium abietate surfactant.

ticles have the chance to overlap and make aggregates. Conversely, it can be expected that nonionic surfactant may destabilize and desorb from the surface of the particles as the temperature increases. The phase separation temperature of the nonionic surfactants from water depends on many parameters. For instance, the phase separation process may be a time consuming process. Therefore, the slow destabilization performance of nonionic covered core/shell particles can be attributed to their high phase separation temperature or its slow desorption or rupture kinetics.

CONCLUSIONS

SBR/PMMA latex particles made with an ionic initiator, KPS, in both core (SBR) and shell (PMMA) stage polymerization led to various particle morphologies, raspberry versus core/shell, depended upon the HLB value of the anionic surfactant used in emulsion polymerization. Nevertheless, the only core/shell structure was observed for the SBR/PMMA latices, which were prepared via the primary SBR seed using nonionic initiator, AIBN, in the first and ionic one, KPS, in the second stage polymerization accompanying the nonionic or nonionic/ionic mixed surfactant. In the former state, the role of surfactant is crucial in addition to applied initiator in both stages. The wettability of the seed surface made via application of more hydrophilic surfactant led to a favorable core/shell structure. In the latter state, the core/shell morphology was formed because of the polarity difference between the two polymers due to the absence and presence of ionic groups from their initiators on the SBR and PMMA surfaces, respectively. It seems that the initiator type rather than the surfactant type determines dominantly the final morphology of the SBR/PMMA latex particles. In overall, the tendency of the two-stage emulsion system involving various kinds of surfactants and initiators, to get the minimum surface free energy change dictates the morphology of composite particles.

Conversely, the results showed the crucial role of surfactant type on the stability of the produced core/shell latices against the added ionic electrolyte, ammonium acetate. SBR/PMMA latex made by ionic surfactant were microagglomerated considerably via increasing the electrolyte concentration, and no change was observed for the latices made with nonionic or nonionic/ionic mixed surfactants. This can be attributed to the specific interaction between monovalent counterion with ionic surfactant molecules on the

colloidal particles. Thus, the adsorption of electrolyte on the particle surface decreases the repulsive interaction energy among the particles.

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