

Synthesis and Properties of Agglomerating Agent for High-Solids NBR Latices

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ABSTRACT: Agglomerating agents were synthesized in a latex form utilizing a seeded emulsion polymerization method to get high solid content NBR latex without exhibiting excessively high viscosity and unstability in the concentration process. An agglomerating agent synthesized with ethylacrylate in the core part and methacrylamide as the hydrophilic monomer in the shell effectively increased the average size of the NBR base latex when it was mixed with the NBR latex and settled for about 2 h. The NBR latex, treated with the proper amount of an agglomerating agent, could be concentrated up to 60.5 wt % solid, while an untreated NBR latex could only be concentrated to 45.0 wt % solid due to the viscosity buildup. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 276–282, 2002; DOI 10.1002/app.10325

Key words: agglomerating agent; high solid content latex; hydrophilic monomer; NBR latex; emulsion polymerization

INTRODUCTION

The rubber latex made by conventional emulsion polymerization has about a 40–150-nm average diameter with narrow size distribution and 25–50% total solid content. Latices with high solid contents have advantages of reduced manufacturing cost due to the low energy consumption and storage space demand. Therefore, active researches have been conducted to increase the solid content of latices both in the emulsion polymerization step and postemulsion treatment process.¹

Acrylonitrile–Butadiene–Styrene (ABS) rubber particles should have over a 200-nm particle size and polydisperse particle-size distribution to give high impact resistance and good processability.² Acrylonitrile–Butadiene–Rubber (NBR) latices for application to foam rubber and puff require high solid contents with low viscosity to make uniform cells in the foam.^{3–5} Several methods are known for increasing solid contents of latices by concentration after physical or chemical treatment, such as addition of electrolytes,⁶ subjecting the latex to freezing and thawing,⁷ addition of solvents,⁸ mechanical shearing,⁹ and the addition of agglomerating agents.^{10,11}

In this study, we synthesized agglomerating agents by seed emulsion polymerization with various hydrophilic monomers and investigated the physical properties of agglomerating latex and

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Table I Emulsion Polymerization Condition and Properties of Agglomerating Agent

Reaction Stage	Stage and Latex Property	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
Seed stage	EA	10	10	10	10	10	10	10	10	10
	ODS-Na	0.011	0.0225	0.045	0.09	0.135	0.18	0.225	0.27	0.315
	KPS	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Water	62.5	62.5	62.5	62.5	62.5	62.5	62.5	62.5	62.5
Second stage	EA	90	90	90	90	90	90	90	90	90
	MAAm	5	5	5	5	5	5	5	5	5
	ODS-Na	0.101	0.203	0.405	0.81	1.215	1.62	2.025	2.43	2.835
	KPS	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
	Water	200	200	200	200	200	200	200	200	200
Latex property	PS (nm)	353.4	207.8	171.7	136.5	120.4	109.4	119.8	101.7	115.0
	Conv. (%)	95.00	96.11	100	96.48	96.17	96.71	100	96.19	96.82
	Coag. (%)	1.3	0.51	1.37	0.09	0.09	0.05	0.03	0.07	0.12

EA: ethylacrylate, ODS-Na: emulsifier, KPS: initiator (unit: g) PS: Particle size, Conv.: conversion, Coag.: coagulum.

agglomerated NBR latex in the agglomeration and concentration process.

EXPERIMENTAL

Materials

Ethyl acrylate (EA) and methacrylic acid (MAAc) from the Junsei Chemical Company (Tokyo, Japan) were distilled under reduced pressure and stored in a refrigerator. Methacrylamide (MAAm) and acrylamide (AAm) from the Aldrich Chemical Co. were purified by recrystallization in metha-

nol. Emulsifiers such as sodium dodecylbenzene sulfonate (SDBS) and sodium lauryl sulfate (SLS) were reagent grade from the Junsei Chemical Company. Potassium salt of oleic acid (OLA-K) was prepared by saponification of oleic acid with potassium hydroxide. Sodium octadecyl sulfate (ODS-Na) was commercial sample and used as received. Potassium persulfate (KPS) from the Junsei Chemical Company was used as an initiator. Deionized water purified by passing through a Millipore system was used throughout the experiments.

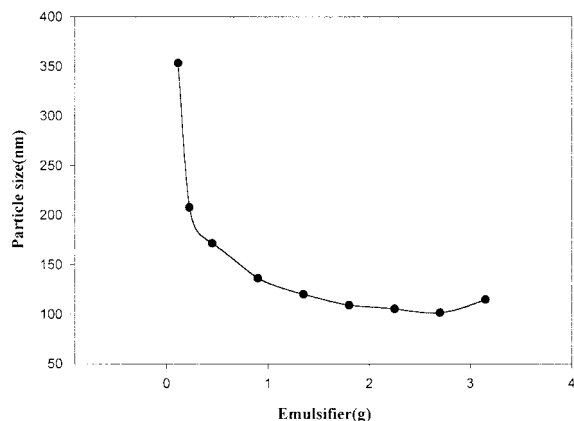


Figure 1 Plot of average particle size of the agglomerating agent vs. the amount of emulsifier (ODS-Na).

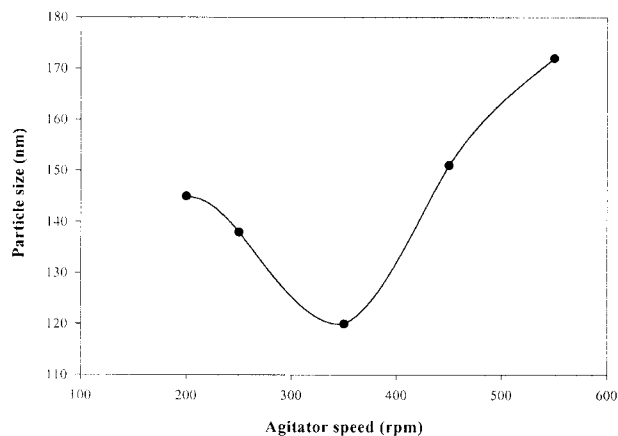


Figure 2 Effect of the agitator speed (rpm) on the particle size of the agglomerating latex.

Table II Particle Size and Conversion Data of Emulsion Polymerization with Various Emulsifier

Emulsion Polym.		B-7	E-1	E-2	E-3
Emulsifier		ODS-Na	DBS-Na	SLS	OLA-Na
Latex Property	Conv. (%)	100	94.28	91.83	91.04
	PS (nm)	119.8	127.8	182.6	593.7

Recipe: first stage EA/Emulsifier/KPS/Water = 10 g/0.225 g/0.1 g/62.5 g.
 Second stage EA/MAAm/Emulsifier/KPS/Water = 90 g/5 g/2.025 g/0.9 g/200 g.

Synthesis of Agglomerating Agents

Syntheses of agglomerating agents were carried out in a 500-mL four-neck reaction flask equipped with a mechanical stirrer, condenser, thermometer, nitrogen inlet, and a peristaltic pump. The temperature was controlled by a thermostatic bath within $\pm 1^\circ\text{C}$. The seeded emulsion polymerization method was used for the synthesis of the agglomerating agent.

For the preparation of seed latex, distilled water (62.5 g), ethyl acrylate (10.0 g), and ODS-Na (0.011–0.225 g) were added to the reaction flask, and the reaction mixture was purged with nitrogen gas and stirred at 350 rpm. When the monomer emulsion was at 80°C by heating, the aqueous initiator (KPS, 0.10 g) solution was added to start the polymerization. After about 2 h the seed latex was obtained with a conversion of 90%. To this seed latex were added 90.0 g of ethylacrylate through one dropping funnel and 5.0 g of methacrylamide (50 wt % aqueous solution), KPS initiator and ODS-Na (0.101–2.835 g) through another

dropping funnel for 3 h with stirring. The resulting agglomerating latex was stirred further for 1 h at 85°C for the complete reaction.

Agglomeration and Concentration of NBR Latex

NBR base latex (solid content 30.0%, avg. particle size 94.0 nm) was agglomerated and concentrated by the following procedure. First, the synthesized agglomerating agent was slowly added to the NBR latex and then stirred for about 5 min at room temperature. The amount of the agglomerating agent was about 4 wt % of NBR latex based on the solid content. The mixture latex was then stood still for 2 h. Emulsifier OLA-K corresponding to 0.2 wt % of NBR solid was then added as a stabilizer under stirring. The whole mixture was put in a rotary evaporator and then concentrated at 45°C under reduced pressure (700–750 mmHg) up to 60 wt % solid. During this process the stability of NBR latex was examined by optical microscope and viscosity was measured.

Table III Particle Size and Conversion Data of Agglomerating Latices Made with Various Hydrophilic Monomers

Reaction Stage and Latex Property		B-7	M-1	M-2	M-3
Seed stage	EA	10	10	10	10
	ODS-Na	0.225	0.225	0.225	0.225
	KPS	0.1	0.1	0.1	0.1
	Water	62.5	62.5	62.5	62.5
Second stage	EA	90	90	90	90
	MAAm	5			
	AAm		5		
	MAAc			5	
	AAc				5
	ODS-Na	2.025	2.025	2.025	2.025
	KPS	0.9	0.9	0.9	0.9
Water	200	200	200	200	
Latex property	Conv (%)	100	93.44	87.32	81.3
	PS (nm)	119.8	113.6	209.6	301.6
	pH	2.89	2.82	2.24	2.26

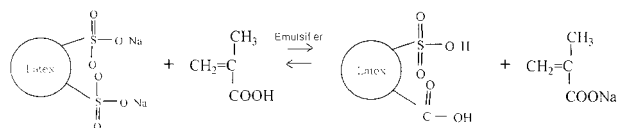


Figure 3 Schematic diagram of the exchange of counter ions between the latex particle and the acid monomer.

Analysis and Measurements

Polymerization conversion was determined by the following procedure. First, 3–4 mL of agglomerating latex was taken using a syringe and weighed in an aluminum dish. Second, 0.15 w/w % benzoquinone–methanol solution was added to it as an inhibitor. It was dried using an IR drier (Mirano Co., Model 6640) until constant weight. The conversion of monomer was determined by gravimetry.

Particle size and distribution of the agglomerating agent were measured by the light-scattering method using a Par-III (Otsuka Electronics Co., Japan) instrument and reported as the Z-average particle size. The latex particle was also observed by transmission electron microscope (JEOL 1200 EX 2, JEOL Co., Japan) at 60 KeV with 20,000–58,000 magnification. To take photographs, the latex sample was diluted to a proper concentration, stained with osmium tetroxide (OsO_4), and then coated with carbon.

ζ -Potential of agglomerating latex was measured using Zetasizer 3000HS (Marvern Co., England) after dilution to 1 g/L solid with water. Viscosity of the latex was measured with a Brookfield viscometer at 20°C.

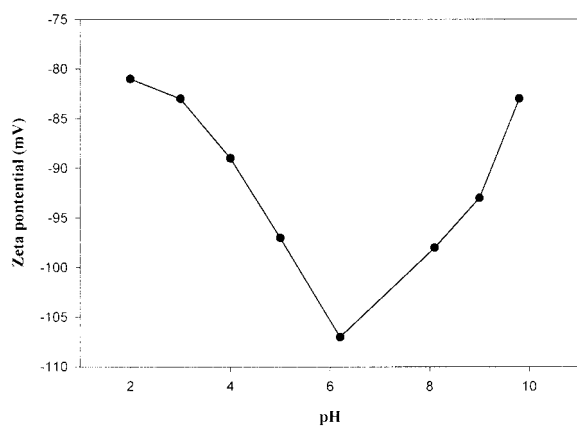


Figure 4 Zeta potential of the agglomerating agent vs. pH of the aqueous medium.

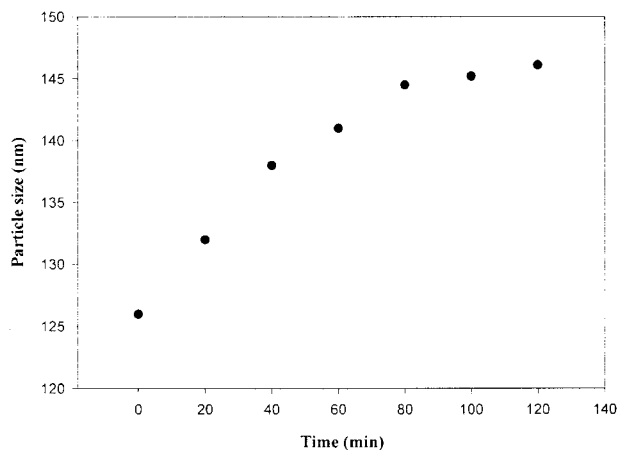


Figure 5 The change of average particle size of agglomerated NBR latex with settling time after agglomeration.

RESULTS AND DISCUSSION

Emulsion Polymerization of Agglomerating Agents

It is well known that the emulsifier affects the particle size, molecular weight, and other properties of the resulting latex in the emulsion polymerization. To determine the optimum amount of emulsifier, the agglomerating agents were synthesized by a seeded emulsion polymerization method with varying amounts of ODS-Na while keeping other reaction conditions constant such as amount of monomer, initiator, water, and stirring speed.

The recipe and properties of the agglomerating latex obtained are summarized in Table I and

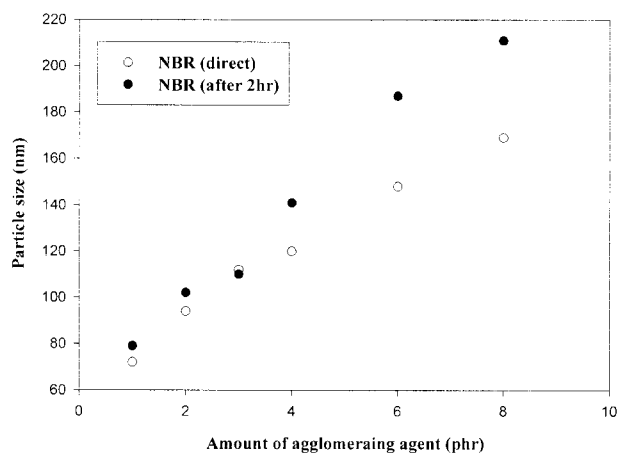


Figure 6 Average particle size of agglomerated NBR with the amount of agglomerating agent.

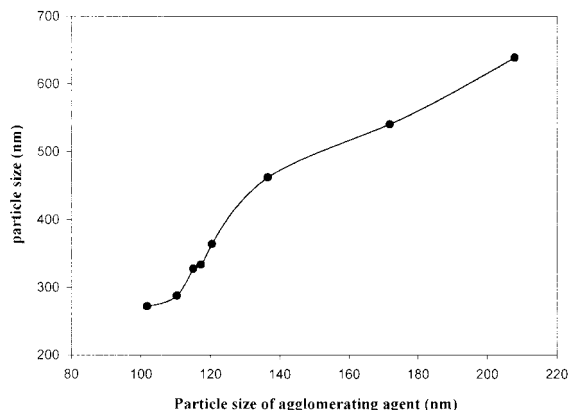


Figure 7 Change of particle size of agglomerated NBR latex with the particle size of agglomerating agent.

Figure 1. From these data, it was noted that the average particle size of THE agglomerating latex decreases as the amount of ODS-Na increases. Above about 1.35 parts of ODS-Na (sample B-5), the size of latex particles remained constant. The particle size, however, increased rapidly below 0.45 parts of emulsifier including both in the seed and second stage, as shown in the sample B-3. Batch B-7 exhibited the smallest amount coagulum and almost complete conversion. Therefore, this reaction was used as a reference recipe in the examination of other reaction conditions. The effect of rotating speed of agitator is shown in Figure 2. The particle size and amount of coagulum were lowest at the agitator speed of 350 rpm.

The effect of emulsifier type on the emulsion polymerization was studied utilizing the basic recipe. We used same amount of SDBS, OLA-K, and SLS emulsifier as the ODS-Na in reaction B-7 (Table I) both in the seed and second stage. As shown in Table II, the particle size of resulting latices increased in the order, ODS-Na < SDBS

< SLS < OLA-K. The conversion of monomer to polymer decreased in the same order. The use of OLA-K as emulsifier gave latex particles with large sizes. This seemed to be due to the reduced degree of ionization of carboxylate salt-type emulsifier compared to the sulfonate salt emulsifier, thus resulting in instability among the growing particles with less surface charge.¹²

We also employed different hydrophilic monomers in the second stage of seeded emulsion polymerization. As shown in Table III, the conversion decreased in the order of increasing solubility of hydrophilic monomer used in the second stage of emulsion polymerization, i.e., MAAM > AAM > MAAC > AAC.¹³⁻¹⁵ When monomers with carboxylic acid groups such as methacrylic acid and acrylic acid (MAAc and AAC) were used, the conversion decreased significantly and some large particles were formed. This instability may be due to the counter ion exchange reaction between the growing polymer particle and incoming carboxylic acid monomer as shown in Figure 3. To check this point, the zeta potentials were measured for an agglomerating agent (M-2) that was prepared with an acid monomer (MAAc) in the second stage. The zeta potential became highest at pH = 6.3 in the Figure 4 as the pH of the aqueous medium increased with dilute aqueous NaOH solution. As the pH was further increased, the surface charge of latex was neutralized screened due to the increased ionic strength of the medium. The neutralized acid monomers also tend to remain in the aqueous phase; thus, it showed a low conversion.

Agglomeration and Concentration of NBR Latices

The NBR base latex (30 wt % solid, avg. particle size 94.0 nm) was first agglomerated with the synthesized agglomerating latex and then concentrated to increase the solid contents. First, we

Table IV Particle Size, Total Solid Content (TSC), and the Amount of Coagulum after Agglomeration and Concentration of the NBR Latex

Agglomerating Agent		B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
Particle Size (nm)		353.4	207.8	171.7	136.5	120.4	109.4	119.8	101.7	115.0
NBR latex										
agglomerated										
and										
concentrated	TSC (%)	—	53.70	56.53	57.11	57.83	57.85	59.21	57.48	56.12
	PS (nm)	—	638.7	540.2	462.3	3636	335.6	327.3	272.1	327.3
	Coag.	gel	gel	large	large	small	none	small	none	small

Table V Synthesis of Agglomerating Agent with Different Amounts of MAAm in the Second Stage

		A-1	A-2	A-3	A-4	A-5	A-6	A-7
Seed stage	EA	10	10	10	10	10	10	10
	ODS-Na	0.225	0.225	0.225	0.225	0.225	0.225	0.225
	KPS	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Water	62.5	62.5	62.5	62.5	62.5	62.5	62.5
Second stage	EA	90	90	90	90	90	90	90
	MAAm	8	7	6	5	4	3	2
	ODS-Na	2.025	2.025	2.025	2.025	2.025	2.025	2.025
	KPS	0.9	0.9	0.9	0.9	0.9	0.9	0.9
	Water	200	200	200	200	200	200	200
Latex property	PS (nm)	111.5	113.5	115.2	119.8	118.1	124.1	119.2
	Conv. (%)	94.71	97.8	99.17	100	100	98.45	97.59
	Coag. (%)	0.17	0.18	0.16	0.12	0.15	0.16	0.18

examined the optimum condition for the agglomeration process. The agglomerating latex synthesized (B-7 sample in Table I) was added to the NBR base latex and the stirred for 5 min at room temperature and the mixture was stood still for a certain period of time. Figure 5 shows that the particle size of agglomerated NBR latex becomes constant after about 120 min of settling time. Next, we investigated the optimum amount of agglomerating agent. The plots of particle size of agglomerated NBR latex vs. the amount of agglomerating agent are shown in Figure 6. Here we measured the particle size of NBR latex twice, that is, after mixing with the agglomerating agent and after settling for 2 h. As for the amount of agglomerating agent, we chose about 4 wt % of agglomerating agent based on NBR latex solid as optimum. The particle size of agglomerated NBR latex could be further increased with the increasing amount of agglomerating agent, but it was found that too large an amount of agglomerating agent caused unstability of latex mixture in the concentration process.

The effects of the particle size of agglomerating agent on the stability and particle size of agglomerated NBR latex are shown in Figure 7 and Table IV. The agglomerating lattices used in this experiment are the ones synthesized under the reaction conditions in Table I. As shown in Figure 7, the particle sizes of agglomerated NBR latex became large as the size of the agglomerating latex increased. However, the data in Table IV on the amount of coagulum after the agglomerating and concentration (up to about 57 wt %) indicated that large size (above 200 nm) agglomerating agent caused an unstability problem in the concentration step.

To optimize the amount of hydrophilic monomer for the better process during the agglomeration and concentration of the NBR latex, new agglomerating lattices were synthesized by changing the amount of hydrophilic monomer in the second stage of emulsion polymerization. For these samples we chose methacrylamide (MAAm) as the hydrophilic monomer as discussed in Table III. The synthetic condition and the results of the agglomeration and concentration of NBR latex are shown in Table V. As the amount of hydrophilic monomer (MAAm) was varied from 2 to 8 g in the second stage of emulsion polymerization, the change in particle size of the resulting agglomerating latex was not large (from 119.2 to 111.5 nm). However, the agglomerating lattices made with more than 5 g of MAAm caused unsta-

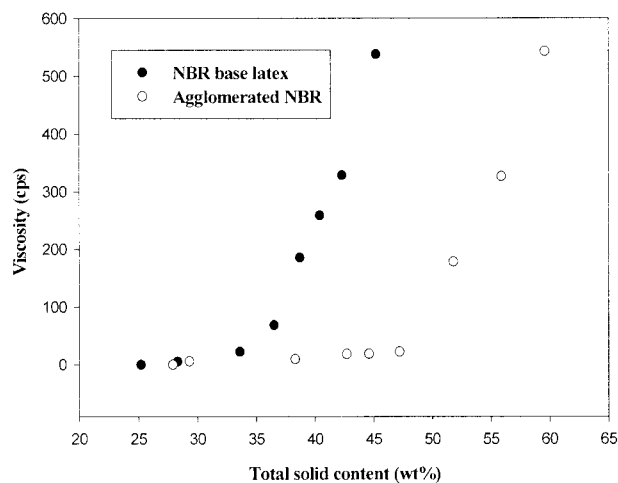


Figure 8 Plot of viscosity of NBR latex untreated (●) and treated (○) with agglomerating agent vs. total solid content during the concentration step.

bility problems in the concentration process as shown in Table V. The change of viscosities of the agglomerated NBR latex during the concentration step is shown in Figure 8. The agglomerating latex B-7 was used in these experiments. The NBR base latex that was not treated with the agglomerating agent showed a rapid increase of viscosity from the solid content of 45.0 wt % in the concentration process. The NBR latex agglomerated with the B-7 latex, however, could be concentrated up to 60.5 wt % solid with a relatively low increase of viscosity. This may be explained by the viscosity equation of suspensions derived by Einstein in which the viscosity is directly proportional to the number of particles.

CONCLUSIONS

The agglomerating agents were synthesized by the seeded emulsion polymerization method for the application to high solid content NBR latices. The agglomerating latices of the different average particle sizes made with different hydrophilic monomers were mixed into the NBR latex, settled, and then concentrated to increase the solid contents while maintaining proper viscosity and stability of the NBR latex. Some important results were as follows: (1) in the synthesis of agglomerating agents, sodium octadecyl sulfate (ODS-Na) emulsifier was found to give both high conversion and stable latices; (2) among the hydrophilic monomers used in the seed stage of emulsion polymerization, the conversion decreased in the order of increasing water solubility, i.e., MMAM > Aam > MAAC > AAC; (3) in the

concentration of the NBR latex, the NBR latex treated with large particle size agglomerating agents became unstable, resulting in gelation or large amounts of coagulum; (4) NBR latex treated with a proper amount of agglomerating agent could be concentrated up to 60 wt % solid, while the untreated NBR latex exhibited high viscosity and could only be concentrated to about 45 wt % solid.

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