Properties of PHMS-g-P [butylacrylate (BA)-*N*-hydroxylmethyl acrylamide (NMA)] Graft Copolymer Emulsions

HUANG SHIQIANG, XU ZUSHUN, PENG HUI, CHENG SHIYUAN

Institute of Chemistry and Material Science, Hubei University, Wuhan, 430062, People's Republic of China

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ABSTRACT: Emulsion graft copolymerization of poly(hydrogenmethylsiloxane) (PHMS) and butyl acrylate (BA) in the presence of functional comonomer N-hydroxyl-methyl acrylamide (NMA) was conducted by batch emulsion copolymerization to modify the properties of polysiloxane. Morphology of graft copolymer particles was characterized by transmission electron microscopy. The effect of polymerization method, PHMS content, initiator concentration, and NMA content on stability of emulsion, morphology, size of particle, and rheological properties were investigated. It has been found that stability of emulsion is better by semicontinuous emulsion polymerization than that of batch emulsion polymerization and it increased with increasing PHMS-NMA concentration. Increasing PHMS concentration and NMA concentration, the particle size and the viscosities increase. The property of resistance to electrolytes of graft copolymer emulsions and swelling property of film were also discussed. Results showed PHMS-g-P [butylacrylate (BA)-N-hydroxyl-methyl acrylamide (NMA)] graft copolymer emulsion has good resistance to electrolytes and the water absorption of its film increases with increasing BA-NMA content grafted onto PHMS. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2209-2217, 1999

Key words: copolymer emulsion; emulsion polymerization; property of emulsion

INTRODUCTION

Copolymers of functional polysiloxane derivatives have been known for some years¹ and are of use in such diverse applications as release coating,² adhesives, and as release agents.³ These copolymers present interesting combinations of physical properties, such as physical strength, and gaseous permeability. Acrylate copolymers, such as coatings, adhesives, and handling agents of spinning and weaving are produced and used widely.^{4,5} As a matter of fact, it has already been shown to be an artful means of associating the binding ability; and the water permeability properties in the same material.⁶ The former property

Journal of Applied Polymer Science, Vol. 71, 2209–2217 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/132209-09 is classically brought about by a film-forming vinylacrylic copolymer emulsion, whereas the latter arises from silicone polymer emulsion.

Blending polymer has been proven to be a versatile way for combining preferential properties of the materials and compensating nonadapted features of one component. However, most polymer pairs have been found to be immiscible, and give rise to phase separation, the extent to which it depends on various parameters and, more generally, the thermal treatment of the sample. In the case of polymer emulsions, the situation seems to be more complicated, due to the crucial problem of colloidal stability of the resulting dispersion, Richard and colleagues⁷ have studied the stability and compatibility in blends of silicone and vinylacrylic polymer emulsion.

Graft polymerization is a convenient and wellknown method to modify the chemical and phys-

Correspondence to: H. Shiqiang.

Table I	Recipe for	Preparation
of Graft	Copolymer	Emulsion
by Batch	n Emulsion	Polymerization

Ingradient	Amount (parts by weight)
	(8)
PHMS	25.0
BA	25.6
NMA	1.5
Polyglycol octyl phenyl ether	3
(OP-10)	
Ammonium persulfate (APS)	0.4
H_2O	100

ical properties of polymeric materials. The technique of emulsion graft polymerization has been widely used.^{8,9} Under appropriate experimental conditions, the modification of polymer can be accomplished not only at the surface, but also throughout the internal phase of a polymer matrix, forming homogeneous polymeric materials. The hydrosilation reaction is an especially attractive route for preparation of siloxanes bearing functional groups for several reasons, the most important of which is that the hydrosilation reaction leads directly to the formation of thermally and hydrolytically stable carbon-silicon bonds. By the hydrosilation reaction, polyacrylate grafting onto polysiloxane is prepared to modify polysiloxane.

Our goal was to obtain stable PHMS-g-P [butyl acrylate (BA)-*N*-hydroxyl-methyl acrylamide (NMA)] graft copolymer emulsion; the properties of emulsion and copolymer film were also interesting. In this article, we report the stability of emulsion polymerization and the properties of emulsion and copolymer film of PHMS-g-P (BA-NMA). The effect of polymerization method, PHMS concentration, NMA concentration on the stability of emulsion polymerization, particle size, rheology property, property of resistance to electrolytes and resistance of swelling of copolymer film have been studied.

EXPERIMENTAL

Materials

Poly(hydrogenmethylsiloxane) (PHMS), which M_w is 21,200 and content of H is 0.5% (by weight), was purchased from Chemical Factory of Xinhuo,

Jiangsu Province, and was used without any further purification. BA was distilled in a stream of inert gas at a reduced pressure and stored in a refrigerator. NMA and ammonium persulfate were recrystallized. Nonionic emulsifier OP-10 was of analytical grade and was used without purification.

Preparation of Graft Copolymer Emulsion

Polymerizations were conducted in a 0.5 L reactor equipped with stirred, reflux condenser, sampling device, and inert system for nitrogen. Copolymer emulsions were prepared by a batch process using the recipes given in Table I, and the polymerizations were conducted at 78°C for 5 h. Copolymer emulsions were prepared by semicontinuous emulsion polymerization using the recipes given in Table II. First-stage polymerization was conducted at 78°C, after 30 min; second-stage polymerization was conducted by dripping the mixture of ingredients to the seed emulsion (first stage) at 78°C; this temperature was maintained for 2 h after completing the addition of ingredients.

Particle Size and Its Distribution

Particle size [i.e., particle average diameter (D_w)] was determined by dynamic light scattering. A polydispersity index value was obtained using a Malvern Autosizer Loc.

Morphology of Emulsion Particles

Emulsion particle morphology was observed by transmission electron microscopy using a 100-SX transmission electron microscope. Internal parti-

Table IIRecipes for Preparation of GraftCopolymer Emulsion by SemicontinuousEmulsion Polymerization

	Amount (parts by weight) (g)	
Ingredient	First Stage	Second Stage
PHMS	8.0	17.0
BA	8.5	17.1
NMA	0.5	1.0
Polyglycol octyl phenyl ether (OP-10)	1.0	2.0
$\begin{array}{l} \mbox{Ammonium persulfate (APS)} \\ \mbox{H}_2\mbox{O} \end{array}$	0.2 20	0.2 80



Figure 1 IR spectrum of PHMS.

cle morphologies were examined by staining emulsion with phosphotungstic acid aqueous solution.

Stability of Emulsion

Stability of Emulsion Polymerization

After emulsion polymerization, the gel polymer was filtered from the emulsion and washed, then dried in an oven to constant weight. Stabilities were calculated from the following equation:

$$\sigma = \frac{W_1}{W_0} * \ 100\% \tag{1}$$

where W_1 and W_0 are the weight of gel and monomers, respectively; and σ is the stability of emulsion polymerization.

Stability of Emulsion Storage

Emulsion was rested at room temperature; store stability was determined by the time that demixing or caking phenomena appeared.

Rheology Property

The viscosity of composite emulsion was tested by NDJ-I type viscosimeter for the cylinder torsion method at room temperature. The relation of viscosity *vs.* spin rate was obtained.

Property of Resistance to Electrolytes

Measurements of the resistance to electrolytes were performed by uniform mixing 1% (wt) graft

copolymer emulsion and K_2SO_4 , NaCl solution of different concentrations (0.025–1.000 mol L⁻¹) with the same volume, respectively, then measuring absorbance (*E*) in the maximum absorption wavelength (λ_{max}) immediately and 24 h later *via* a 721 ultraviolet-visible spectrophotometer. The degree of relative stability was determined as E_0/E_{24h} . Criticle condensation concentration (CCC) was obtained from the logarithmic diagram of relative stability to inonic concentration. At the same time, particle size of the emulsion was measured, which mixed with electrolytes 24 h later.

Swelling Property of Graft Copolymer Film

PHMS-g-P (BA-NMA) films were immersed in a swelling agent for 48 h at 25°C. Specimens were weighed immediately after the solvents attached to the surface were wiped off.

Swelling (%) =
$$\frac{W_s - W_g}{W_g} * 100\%$$
 (2)

where W_s and W_g are the weight of film and swollen film respectively.

Molecular Structure

Polymer molecular structure was studied by infrared (IR) spectroscopy using a Daojin Japan IR-440 Spectrometer (KBr preforming).

RESULTS AND DISCUSSION

Polymer Molecule Structure

Figure 1 was the IR spectrum of PHMS; from the



Figure 2 IR spectrum of PHMS-g-P (BA-NMA).

spectrum, it can be observed that a strong Si-H characteristic spectrum in 2100 cm⁻¹, Si-CH₃ characteristic spectrum in 1260 cm⁻¹. After emulsion copolymerization, the emulsion was demulsified and separated, then the copolymer was extracted 48 h at Sorbite abstraction using ketone as extracting agent to remove small molecules and oligomers. The IR spectrum of the graft copolymer, that had been purified, was shown in Figure 2. The strong Si-CH₃ characteristic spectrum was still existing, but the Si-H characteristic spectrum was weakened; moreover, a strong C=O characteristic spectrum (1734 cm⁻¹) obviously appeared. The C=C characteristic spectrum (1640 cm⁻¹) was not observed. These results indicated that there existed hydrosilication between PHMS, BA-NMA, and the graft copolymer was obtained.

Stability of Emulsion

To understand the effect of polymerization conditions, such as the preparation method, and PHMS and NMA concentration on the stability of emulsion, a series of polymerization experiments were conducted varying one parameter at a time.

Effect of Preparation Method

Table III shows the effect of the preparation method on the stability of emulsion. The result indicates that the σ values of emulsion prepared by batch polymerization is greater than that of semicontinuous polymerization. Attention was paid to the polymerization process, polymerization sites. Conversions are focuses on clarifying the difference between the two polymerization processes (i.e., at the surface or in the interior of the particles). In batch emulsion polymerization, the monomer and initiator enters the interior of the particles, the polymerization took place mainly in the interior of the particles. The number of monomer molecules in the particles was larger, but the number of monomer molecules in different particles was almost the same; also, the rate and degree of polymerization in different particles were almost the same. Thus, the diameter of the emulsion particles was bigger, and size distribution was narrower [Fig. 3(A)], the hydrophilic ingredients (BA-NMA) are mainly in the interior of the particles, and the minority are on the surface of the particles. In semicontinuous polymerization, it is, contrarily, that polymerization at the surface of the particles was faster than that in the interior of the particles. Polymerization at the surface was affected by surface phenomena, such as radical adsorption and desorption: the monomer concentration at the surface of the particles was different for the diffusiveness of the monomer. There was generation of a new crop of secondary particles. Therefore, the diameter of

Table IIIEffect of Preparation Method on theStability of Emulsion

Preparation Method	σ (%)	Time (day)
Batch Semicontinuous emulsion	$\begin{array}{c} 8.88\\ 4.75\end{array}$	180 210



Figure 3 Size distribution of graft copolymer emulsion particles. (A) Prepared by batch emulsion polymerization. (B) Prepared by semicontinuous emulsion polymerization.

the emulsion particles was smaller, and size distribution was wider [Fig. 3(B)]. The hydrophilic ingredients (BA-NMA) are mainly in the surface of the particles. Thus, semicontinuous polymerization has better stability of emulsion than batch polymerization.

Effect of PHMS Concentration

Table IV indicates that the stability of emulsion increases with increasing PHMS content. This result is related to the properties of PHMS. Because PHMS can be emulsified in water,¹⁰ emulsification leads to decreasing the surface tension of water, which improves the stability of emulsion. Moreover, with increasing PHMS content, the components of BA-NMA-grafted onto PHMS may increase, which improves the stability of emulsion as well.

Table I	V Effect	of PHMS	Concentration
on the	Stability -	of Emulsic	on

BA/Si—H (mol/mol)	σ (%)	Time (day)
0.2/0.075	17.2	60
0.2/0.090	9.6	90
0.2/0.100	3.4	105
0.2/0.125	1.8	150
0.2/0.150	0.6	180
0.2/0.175	0.2	210

Effect of NMA Concentration

With increasing NMA concentration, the content of NMA in graft copolymer is increased, the solvation of NMA prevents the particles from being too close to aggregate. Therefore, the stability of emulsion increases. Results are shown in Table V.

Morphology and Size of Copolymer Emulsion Particle

Effect of Preparation Methods

The morphology and size of the emulsion particle have close relations with emulsion properties. Figure 4(A,B) shows the particles prepared by batch and semicontinuous emulsion polymerization, respectively. Comparison of the two micrographs has led to the following conclusions: (1) the morphology of the composite particles was of a spherical structure, (2) the size of the particles that were prepared by batch emulsion polymer-

Table V	Effect	of NMA	Concentration
on the St	ability	of Emul	sion

Amount (g)	σ (%)	Time (day)
1.0	23.95	75
1.5	14.30	120
2.0	3.02	180
2.5	2.82	195



A(*10000)

B(*40000)

Figure 4 Transmission electron micrograph of graft copolymer emulsion particles. (A) Prepared by batch emulsion polymerization. $10,000 \times$. (B) Prepared by semicontinuous emulsion polymerization. $40,000 \times$.

ization was bigger than that prepared by semicontinuous emulsion polymerization, and (3) the size distribution of the particles that was prepared by batch emulsion polymerization was more uniform than that prepared by semicontinuous emulsion polymerization.

Effect of PHMS Concentration

Table VI shows change of the particle size with increasing PHMS concentration. The result indicates that higher PHMS concentration results in bigger particle size. Because not only does the extent of reaction between Si—H and C=C bond increase, but also the crosslinking reaction between PHMS, copolymer, and NMA increases with increasing PHMS concentration.

Effect of NMA Concentration

With increasing NMA concentration, the solvation and crosslinking reactions increase, which

Table VIEffect of PHMS Concentrationon Particle Size

BA/Si—H	Particle Size
(mol/mol)	(nm)
$\begin{array}{c} 0.2/0.075\\ 0.2/0.090\\ 0.2/0.100\\ 0.2/0.125\\ 0.2/0.150\\ 0.2/0.175\end{array}$	$157.2 \\183.3 \\220.6 \\242.6 \\263.8 \\318.4$

leads to a particle size increase (as shown in Table VII).

Effect of Initiator Concentration

Table VIII shows the size of the copolymer emulsion particles prepared by different initiator concentration. The particle size decreases with increasing APS concentration when the APS amount was < 0.6 g; when the amount was > 0.6 g, it was anomalously large. With increasing initiator concentration, the polymerization rate was faster and the number of emulsion particles was bigger, which resulted in a decrease of particle size. But, early nucleation, condensation, and crosslinking reactions took place when the initiator amount was too high.

Rheology Property

In rheology property studies, a polymerization series was performed, varying one ingredient and maintaining a constant of other ingredients.

Table VII	Effect	of NMA	Concentration
on Particle	Size		

Amount	Particle Size
(g)	(nm)
$1.0 \\ 1.5 \\ 2.0 \\ 2.5$	$171.0 \\188.5 \\267.2 \\512.3$

Amount	Particle Size
(g)	(nm)
$0.25 \\ 0.30 \\ 0.40 \\ 0.60$	267.2 251.3 231.1 460.6

Table VIIIEffect of Initiator Concentrationon Particle Size

Effect of PHMS Concentration

From Figure 5, we can draw the following conclusions: (1) the PHMS-g-P (BA-NMA) graft copolymer emulsion was a pseudoplastic fluid (i.e., with increasing rate of shear, the viscosities decrease); and (2) the viscosities increase with increasing PHMS concentration because not only does the extent of reaction between Si—H and C=C bond increase, but also the crosslinking reaction between PHMS, copolymer, and NMA increase with increasing PHMS concentration. The size of the particle became bigger (Table VI), thus resulting in viscosity increase.

Effect of NMA Concentration

Key factors that NMA affect the rheology properties of graft copolymer emulsions was solvation. With increasing NMA concentration, solvation between copolymer particles and water became stronger, thus resulting in the viscosities increase. The result was shown in Figure 6.



Figure 5 Effect of PHMS concentration on rheology property (1.15 g; 2.20 g; 3.25 g; 4.30).



Figure 6 Effect of NMA concentration on rheology property (1, 1.0 g; 2, 1.5 g; 3, 2.0 g; 4, 2.5 g).

Effect of APS Concentration

With increasing APS concentration, the rate of polymerization was increased, the number of particles was greater, and the size of the particle became smaller (Table VII). These result in the viscosity decrease, as shown in Figure 7.

Property of Resistance to Electrolytes

Figure 8 was the logarithmic diagram of relative stability to ionic concentration of PHMS-g-P (BA-NMA) graft copolymer emulsions. Results showed the CCC of Cl^- and SO_4^{2-} were 0.327 mol L^{-1} and 0.200 mol L^{-1} , respectively. We know the corresponding CCC of dimethylpolysiloxane anionic



Figure 7 Effect of initiator concentration on rheology property (1, 0.2 g; 2, 0.3 g; 3, 0.4 g; 4, 0.6 g).



Figure 8 Resistance to electrolytes $(1M = \text{NaCl}; 2M = \text{K}_2\text{SO}_4)$.

emulsion were 0.158 mol L^{-1} and 0.007 mol L^{-1} , and dimethypolysiloxane cationic emulsions were 0.300 mol L^{-1} and 0.006 mol L^{-1} from ref. 11. Thus, the resistance to electrolytes of graft copolymer emulsions were much better than that of dimethylpolysiloxane anionic emulsions and cationic emulsions. By hydrosilication, the BA-NMA monomer was graft onto PHMS; the graft chain forms steric hindrance, which makes it difficult for the emulsion particle to get together. So, the graft copolymer has better resistance to electrolytes. In addition, the CCC value decrease with the increasing heteropolar valence. Thus, dimethylpolysiloxane emulsions have resistance to SO_4^{2-}



Figure 9 Resistance to electrolytes $(1M = \text{NaCl}; 2M = \text{K}_2\text{SO}_4)$.

Table IXSwelling Property of GraftCopolymer Film

Amount of BA (g)	Amount of NMA (g)	Swelling (%)
18.3	1.5	14.47
21.3	1.5	23.83
25.6	1.5	30.09
29.0	1.5	40.45
32.0	1.5	56.26
25.6	1.0	23.11
25.6	1.5	28.63
25.6	2.0	32.33
25.6	2.5	41.38

inferior to Cl⁻, but the CCC value of PHMS-g-P (BA-NMA) emulsion nearly do not decrease for steric hindrance. Therefore, the PHMS-g-P (BA-NMA) emulsion has better resistance to electrolytes than dimethylpolysiloxane emulsions, especially to SO_4^{2-} . It shows that the particle size nearly keep constant with increasing Cl⁻ concentration, and increases slightly with increasing SO_4^{2-} concentration in Figure 9.

Swelling Property of Graft Copolymer Film

The hydrophobic silicone film shows a higher swelling behavior in chloroform and toluene, because they are good solvents for silicone, but cannot be swelled by water, ethanol, or glycerol. Graft polymerization is a better way to modify the properties of silicone rubber. The graft of BA-NMA onto PHMS would improve the water absorption of the PHMS-g-P (BA-NMA) film to some degree. The BA-NMA graft PHMS film gives a linear relationship between swelling capacity and BA-NMA concentration (as shown in Table IX). Water absorption increases with increasing BA-NMA concentration.

CONCLUSIONS

- 1. A kind of PHMS-g-P (BA-NMA) graft copolymer emulsion was prepared. The properties of graft copolymer emulsion were better than that of polysiloxane emulsion.
- 2. The stability of emulsion prepared by semicontinuous emulsion polymerization was better than that of batch emulsion polymerization, and the stability increased with increasing PHMS and NMA concentrations.

- 3. Increasing PHMS and NMA concentrations, particle size and viscosities increased.
- 4. PHMS-g-P (BA-NMA) graft copolymer emulsion had good resistance to electrolytes, the water absorption of its film increased with increasing BA-NMA concentration grafted onto PHMS.

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