

Effects of Polymeric Emulsifiers on the Properties of Acrylic Emulsion Pressure-Sensitive Adhesives

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ABSTRACT: A series of polymeric emulsifiers was polymerized with 2-ethylhexyl acrylate, butyl acrylate, and acrylic acid. The polymeric emulsifiers were used to make emulsion copolymers of 2-ethylhexyl acrylate, butyl acrylate, and acrylic acid. The average particle size of the synthesized emulsions was around 145 nm and the size distribution was very narrow. Also, the emulsions showed good freeze-thaw stability and adhesion properties. The peel strength and holding power of the emulsions were investi-

gated by changing the composition and molecular weight of the polymeric emulsifier. The results show that the peel strength exhibits a maximum at particular molecular weight and acrylic acid content of the polymeric emulsifier, while the holding power increases with molecular weight. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1456–1460, 2004

Key words: pressure-sensitive adhesive; polymeric emulsifier; holding power; peel strength

INTRODUCTION

Most acrylic pressure-sensitive adhesives (PSA) are still solvent-borne systems, because of their superior adhesion properties, resistance to water, solvents, and plasticizer and aging performance compared to the water-borne PSA. Recently, the requirement for water-borne PSA, however, has been growing greatly due to environmental safety, ease of handling, and economical and process advantages. Therefore, solvent-borne PSA are more and more being replaced by water-borne PSA world-wide.¹

Conventional emulsion polymerization is by far the most important process for producing acrylic PSA. The process begins with a mixture of water, initiator, monomer, and emulsifier. Emulsifiers including anionic and nonionic emulsifiers play a very crucial role as stabilizers in the production and application of the dispersed polymer.² They are very important for the nucleation of the latex particles, emulsification of monomer droplets and/or preformed polymer, and stabilization of polymer particles during polymerization and longer shelf life of the products. However, conventional emulsifiers can also have many negative effects in the final application, such as poor water-resistance, poor adhesion, poor gloss, slow film formation, emulsifier migration, wastewater treatment, and altered polymer properties.³

Three methods have been studied recently to reduce these negative effects of the conventional emulsifiers. The first method is emulsifier-free emulsion polymerization. The second method uses reactive surfactants,^{3,4} which improve the performance of the latex, for example, increased stability of latices, decreased surfactant migration, improvement in the water resistance of the latex, and improved adhesive properties,^{5,6} because the use of a reactant surfactant can ensure that the surfactant moiety is chemically bound to the polymer particle, so that desorption from the latex particle surface or migration in the polymer film is prevented. This third method is to use a polymeric emulsifier in emulsion polymerization.^{7–9} Because the emulsifier moiety is bound covalently to the polymer material, both desorption from the polymer particles and migration through the polymer film are impeded.

In this study, acrylic emulsion PSA was prepared using polymeric emulsifiers instead of conventional emulsifiers. A series of polymeric emulsifiers was synthesized with solution polymerization by changing the monomer profile and molecular weight. These materials were used as emulsifiers for copolymerization of 2-ethylhexyl acrylate, *n*-butyl acrylate, and acrylic acid. Finally, the effects of polymeric emulsifier on the particle size, its distribution, adhesion property, and freeze-thaw stability of acrylic emulsion PSA were investigated.

EXPERIMENTAL

Materials

Monomers used in the synthesis of polymeric emulsifiers were 2-ethylhexyl acrylate (2-EHA, Aldrich), *n*-

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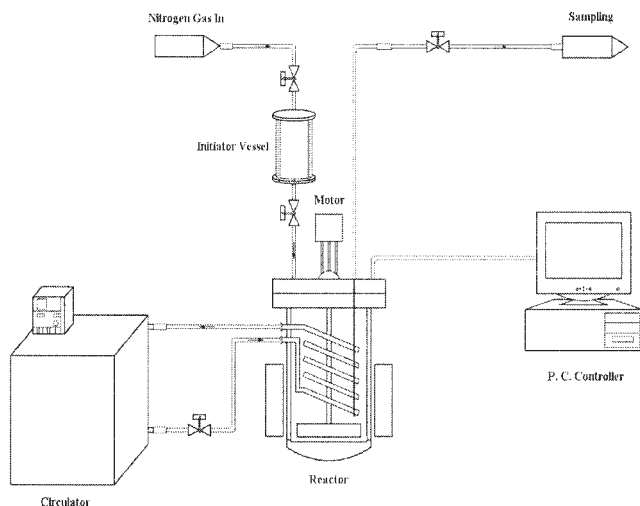


Figure 1 Schematic diagram of the experimental apparatus for synthesizing the polymeric emulsifier.

butyl acrylate (*n*-BA, Aldrich), and acrylic acid (AA, Aldrich). Toluene (Aldrich) as a solvent, *tert*-butyl peroxybenzoate (*t*-BPB, Aldrich) as an initiator, and 1-dodecanethiol (Fluka) as a chain transfer agent (CTA) were used throughout the work. Also, 2-ethylhexyl acrylate and *n*-butyl acrylate were used as monomers for emulsion polymerization. Potassium persulfate ($K_2S_2O_8$, Aldrich) and potassium peroxide (KOH, Junsei chemical) were used as initiator and pH controlling agent, respectively. All reagents were used as supplied without further purification. Deionized water was used throughout the experiments.

Synthesis of polymeric emulsifier [poly(2-EHA/*n*-BA/AA)]

A series of polymeric emulsifiers was synthesized using the reactor system shown in Figure 1. The reactor system consisted of a 500-mL stainless-steel reactor, a circulator, and a personal computer to control the reactor. The procedures were as follows. After the addition of 2-EHA, *n*-BA, AA, toluene, and 1-dodecanethiol at room temperature, the reactor was heated to 180°C by purging with nitrogen gas. The mechanical stirring rate was controlled at 500 rpm. The initia-

TABLE I
The Basic Recipe for Synthesizing Polymeric Emulsifiers

Ingredients	Amount (g)
2-EHA	Variable
<i>n</i> -BA	Variable
AA	Variable
<i>t</i> -BPB	5
Toluene	150
CTA	Variable

TABLE II
The Recipe for Emulsion Copolymerization

Reactant	Initial charge (g)	Pre-emulsion (g)
DDI water	60	90
Polymeric Emulsifier	—	Variable
KOH	Variable	Variable
$K_2S_2O_8$	—	1.5
<i>n</i> -BA	—	72
2-EHA	—	72

tor, *t*-BPB, was added into the reactor when the temperature of the system reached 180°C. After the initiator was added, the reaction was allowed to proceed for 20 min. The basic recipe of polymeric emulsifier is tabulated in Table I.

Emulsion copolymerization

The monomers 2-EHA and *n*-BA were polymerized in a 41/59 molar ratio. Using the recipes given in Table II, semicontinuous emulsion copolymerization was carried out in a 500-mL five-neck glass reactor with a mechanical stirrer (Teflon baffle stirrer), reflux condenser, pH electrode inlet, nitrogen inlet, and feed inlet tube. A circulating water bath was employed to control the reaction temperature at 75°C. The reactor was charged initially with potassium hydroxide and deionized water. The pre-emulsion was fed in two steps: in the first step, 10 wt % based on the total amount of the pre-emulsion containing monomers, polymeric emulsifier, initiator, and potassium hydroxide was added into the reactor followed by stirring for 30 min. Then, the residual pre-emulsions were fed into the reactor using the metering pump for 3 h. The pH

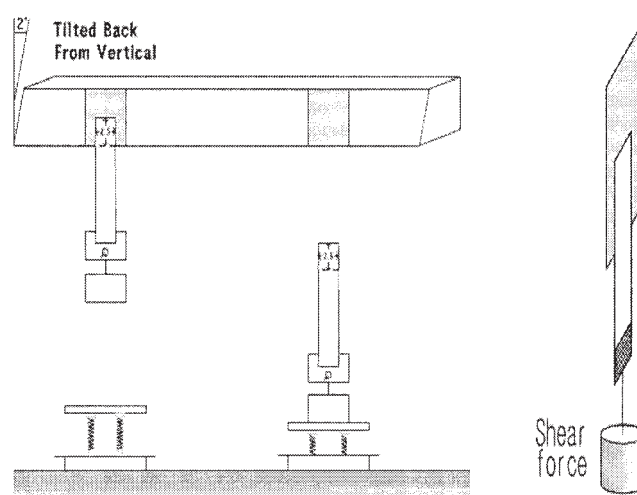


Figure 2 Principle of the holding power test.

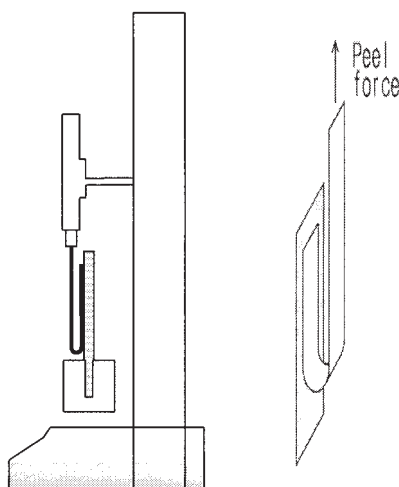


Figure 3 Schematic diagram of the resistance-to-peel test.

value was adjusted to 9.5 using 1.2 M potassium hydroxide aqueous solution during polymerization.

Characterization of the polymeric emulsifier

The acid number of polymeric emulsifiers was measured according to ASTM standards.¹⁰ The number-average molecular weight, weight-average molecular weight, and molecular weight distribution of polymeric emulsifiers were measured by Gel permeation

chromatography (GPC, Waters Instruments) with an Ultrahydrogel column preceded by a guard column. The mobile phase was a 0.1 M KOH solution. The glass transition temperature (T_g) of the polymeric emulsifier was determined by differential scanning calorimeter (DSC, TA Instrument).

Characterization of the PSA emulsion

The glass transition temperature of acrylic PSA was measured by DSC. The number-average particle size (D_n), weight-average particle size (D_w), and polydispersity (D_w/D_n) of the emulsion were determined by a BI-DCP instrument (Brookhaven Instruments Co.). To determine freeze–thaw stability, acrylic emulsion PSA was subjected to seven freeze–thaw cycles, where one cycle consisted of freezing at -12°C for 12 h and then allowing the emulsion to thaw at room temperature for 12 h.¹¹

Measuring adhesive properties

The backing material used to prepare the adhesive tapes was a kraft paper. The acrylic emulsion PSA was coated on the kraft paper with a spring bar that produced a $83.3\text{-}\mu\text{m}$ -thick coat and emulsions were dried in an oven heated at $50 \pm 1^\circ\text{C}$ for 30 min. The adhesive tape was then cooled for 30 min at room temperature and tested at room temperature. To determine the

TABLE III
Material Properties of Polymeric Emulsifiers

Sample	Composition profile (molar ratio)	Acid value ^d	T_g^e ($^\circ\text{C}$)	M_n^f (g/mol)	M_w^g (g/mol)	PDI (M_w/M_n)
	2-EHA ^a / <i>n</i> -BA ^b /AA ^c					
A30-0	13.9/40.2/45.9	198	-25.5	7,076	25,078	3.54
A30-1	13.9/40.2/45.9	193	-26.1	5,581	16,909	3.03
A30-2	13.9/40.2/45.9	196	-28.4	5,024	12,957	2.58
A30-3	13.9/40.2/45.9	196	-30.9	4,839	12,731	2.63
A30-4	13.9/40.2/45.9	190	-31.0	4,662	12,375	2.65
A40-0	11.2/32.0/56.7	239	-20.9	6,269	27,214	4.34
A40-1	11.2/32.0/56.7	230	-21.1	5,390	16,607	3.08
A40-2	11.2/32.0/56.7	240	-23.2	5,050	13,683	2.71
A40-3	11.2/32.0/56.7	231	-23.4	4,779	12,416	2.60
A40-4	11.2/32.0/56.7	235	-24.5	4,354	11,848	2.72
A50-0	8.7/24.9/66.4	284	-8.9	6,528	37,510	5.74
A50-1	8.7/24.9/66.4	279	-14.7	6,287	32,487	5.16
A50-2	8.7/24.9/66.4	279	-16.9	5,715	18,774	3.29
A50-3	8.7/24.9/66.4	270	-22.8	4,607	13,906	3.01
A50-4	8.7/24.9/66.4	280	-25.1	4,097	13,356	3.26

^a 2-EHA, 2-ethylhexyl acrylate, mol % based on monomer.

^b *n*-BA, *n*-butyl acrylate, mol % based on monomer.

^c AA, acrylic acid, mol % based on monomer.

^d Acid value is the number of milligrams of potassium hydroxide required to neutralize the alkali reactive groups in 1 g of material.

^e Glass transition temperature of polymeric emulsifier.

^f Number-average molecular weight of polymeric emulsifier.

^g Weight-average molecular weight of polymeric emulsifier.

TABLE IV
Material Properties of Acrylic Emulsion PSA

Run	Composition profile (molar ratio)	Emulsifier used	D_n^c (nm)	T_g (°C)	Stability
	2-EHA ^a / <i>n</i> -BA ^b				
PA30-0	41/59	A30-0	149	-51.5	Poor ^d
PA30-1	41/59	A30-1	155	-52.0	Good ^e
PA30-2	41/59	A30-2	150	-51.9	Good
PA30-3	41/59	A30-3	152	-52.1	Good
PA30-4	41/59	A30-4	148	-53.0	Good
PA40-0	41/59	A40-0	153	-51.8	Poor
PA40-1	41/59	A40-1	153	-51.9	Good
PA40-2	41/59	A40-2	146	-51.4	Good
PA40-3	41/59	A40-3	150	-52.3	Good
PA40-4	41/59	A40-4	146	-52.1	Good
PA50-0	41/59	A50-0	144	-53.1	Good
PA50-1	41/59	A50-1	144	-51.6	Good
PA50-2	41/59	A50-2	144	-53.4	Good
PA50-3	41/59	A50-3	146	-52.3	Good
PA50-4	41/59	A50-4	147	-53.0	Good

^a 2-EHA, 2-ethylhexyl acrylate, mol % based on monomer.

^b *n*-BA, *n*-butyl acrylate, mol % based on monomer.

^c Number-average particle size of acrylic emulsion PSA.

^d Coagulation after two cycles.

^e No coagulation after seven cycles.

adhesive properties, ASTM standard test methods for holding power¹³ and peel strength¹⁴ were used. Also, Figures 2 and 3 show schematics of the holding power tester (Chem Instruments) and the peel strength tester (VersaTester, Mecmesin Ltd., UK), respectively.

RESULTS AND DISCUSSION

Nine kinds of low-molecular-weight polymeric emulsifiers were synthesized by changing the acrylic acid content and molecular weight. The molecular weight was controlled by a CTA. Table III lists the various synthetic conditions, including the used monomer molar ratios and physical properties of these polymeric emulsifiers. DSC results show that the glass transition temperature increased with increasing acrylic acid content and molecular weight. The acid value was determined by the titration method: its range was from 190 to 280. Also, the acid value increased with the content of acrylic acid. The polydispersity index of molecular weight changed from 2.6 to 5.7, in which lower molecular weight emulsifiers showed a smaller index value.

A series of emulsion copolymerizations of 2-EHA and *n*-BA using the "A30, A40, A50" series polymeric emulsifier was carried out under the fixed molar ratio of 2-EHA/*n*-BA = 41/59. Table IV summarizes the particle size, freeze-thaw, and glass transition temperature data.

As can be seen in Table IV, all samples show nearly the same particle size, at around 150 nm, regardless of the molecular weight and acid content of their emul-

sifiers. This average size is smaller than the normal acrylic emulsion particles made using a conventional emulsifier. Also, all samples synthesized in this study were tested for freeze-thaw stability. Most of the samples show stability after seven cycles even though only two samples, PA30-0 and PA40-0, coagulate after two cycles.

Figure 4 shows that, in the optimum range of molecular weight of polymeric emulsifier, the peel strength has a maximum value: the optimum range is between 4500 and 5000 g/mol depending on the

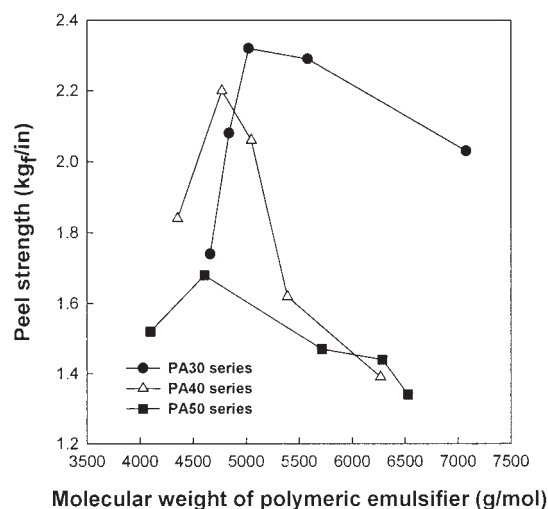


Figure 4 The change of the peel strength of acrylic emulsion PSA with number-average molecular weight and acrylic acid content of PEBA polymeric emulsifiers.

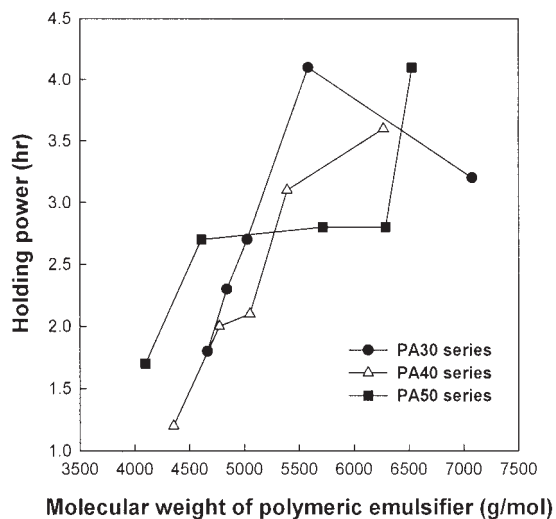


Figure 5 The change of the holding power of acrylic emulsion PSA with number-average molecular weight and acrylic acid content of PEBA polymeric emulsifiers.

acrylic acid contents. This means that too low or too high molecular weight of the polymeric emulsifier decreases the peel strength. It seems that too low a molecular weight polymeric emulsifier anchors stably on the surface of particle, while too high a molecular weight polymeric emulsifier inhibits monomer from entering the micelle. The maximum peel strength of PA50 is much lower than that of PA30 and PA40. It is known that higher contents of acrylic acid than the optimum value deteriorate the peel strength.

Figure 5 shows that the holding power increases as the molecular weight of polymeric emulsifier increases. This trend is predictable because holding power is highly dependent on the cohesion power, which is generally proportional to the molecular weight.

CONCLUSION

From this study, we found that low-molecular-weight 2-EHA/*n*-BA/AA copolymer can be used as a polymeric emulsifier in emulsion polymerization to prepare acrylic emulsion PSA. Most of the emulsions show excellent freeze-thaw stability. The results of adhesion tests showed that peel strength and holding power depend on the molecular weight and acrylic acid contents of the polymeric emulsifier. Good peel strength and holding power were found at optimum molecular weights and acrylic acid contents of the polymeric emulsifier.

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