

Hybrid Emulsifiers Enhancing Polymerization Stabilities and Properties of Pressure Sensitive Adhesives

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ABSTRACT: In this study, a series of (anionic and nonionic) emulsifiers were investigated to prepare acrylic pressure sensitive adhesives (PSA) with core-shell structure by semicontinuous emulsion polymerization. The cloud point of different emulsifiers was characterized to explain the emulsifier effects on the emulsification ability. It was interestingly found that the hybrid emulsifiers (anionic coupling with nonionic) with optimized compositions could enhance the stability of emulsion system and improve the properties of PSA compared with the mono-emulsifier. The stability of emulsion polymerization, the appearance of the emulsion system and the properties of PSA were studied in details by changing the proportion and the content of hybrid emulsi-

fiers. When the ratio of sodium dodecyl sulfate (SDS: anionic emulsifier) to polyoxyethylene alkyl phenyl ether (OP-10: nonionic emulsifier) reached 2 : 1, the content of hybrid emulsifiers reached 3 wt % and the reaction temperature was around 80°C, a better emulsion system was obtained in terms of comprehensive properties. At this condition, the synthesized PSA demonstrated the good holding power and 180° peel strength properties with fair tacky property, which was promising for industrial applications. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1125–1130, 2010

Key words: adhesives; emulsion polymerization; adhesion; hybrid emulsifier; acrylate polymer

INTRODUCTION

Pressure sensitive adhesives (PSA) are viscoelastic materials that can adhere to solid surfaces in a short time with an aid of light pressure. For PSA, the most common products are tapes, labels, and protective films.¹ Although PSA can be obtained by different polymerization processes such as solution, emulsion, and radiation curing, most of acrylic PSA are solvent-based PSA due to the desirable adhesion properties, resistance to water, solvents, and plasticizer, and aging performance.² Recently, acrylic emulsion pressure sensitive adhesives (EPSA) have been attracting more and more attentions due to the strict requirements of environmental safety (solvent-free), high solid content, low cost, ease of handling, economical and process advantages.^{3–6}

Commercially, EPSA are usually prepared with butyl acrylate (BA) and/or 2-ethylhexyl acrylate (2-EHA) as the main monomers.⁷ However, in most of cases, it is necessary to raise the glass transition temperatures (T_g) of homopolymers or copolymers of BA and EHA by copolymerization with other monomers to improve their room temperature resistance to shear and peel resistance at normal rates with the increase of EPSA cohesion energy.^{2,8} Such monomers typically include methyl methacrylate (MMA), vinyl acetate, styrene, and acrylic acid (AA). The copolymer composition of acrylic EPSA has been shown to affect its final performance. An advantage of AA monomer added in the EPSA formulation of emulsion polymerization is to provide additional colloid stability.⁹ The copolymerization of small levels of AA with acrylic ester monomers has also been demonstrated to increase peel strength^{10,11} and tackifying ability.¹² The increase of side chain length of acrylic ester used in copolymerization with MMA has been shown to increase peel strength.¹⁰ Besides, the emulsion copolymerization approach has a profound effect on the final properties of acrylic EPSA.

As the use of acrylic EPSA has increased significantly, various methods for fabricating acrylic EPSAs have been proposed. Conventional emulsion polymerization system includes water, initiator, monomer, and emulsifier, in which the emulsifiers including anionic or nonionic emulsifier play a crucial role

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as stabilizers although emulsifiers do not participate in the polymerization reaction directly.¹³ Emulsifiers are also very important for the nucleation of the latex particles, emulsification of monomer droplets, stabilization of polymer particles during polymerization, and maintaining product shelf life. Besides, emulsifiers can influence the initial reaction velocity and chain-growth reaction velocity, the molecular weight and the molecular weight distribution of products.¹⁴ As a result, the study of emulsifier effects on the properties of EPSA is of paramount importance.

In this study, acrylic EPSA latexes with core-shell structure were prepared by semicontinuous emulsion polymerization. A series of emulsifiers (anion, nonionic or hybrid) were used to copolymerize MMA, 2-EHA, BA, AA and dodecylmercaptan (DDM). The effects of the emulsifier types, the proportion of hybrid emulsifiers, and the content of emulsifiers on the emulsion polymerization and adhesion properties of final products were investigated in details.

EXPERIMENT

Materials

MMA and sodium dodecyl benzene sulfonate (SDBS) were purchased from Tianjing Bodi Chemical. BA and 2-EHA were purchased from Beijing Dongfang Chemical. Sodium dodecyl sulfate (SDS), polyoxyethylene alkyl phenyl ether (OP-10), AA and ammonium persulfate (APS) were purchased from Wuxi Jiani Chemical. Sodium alkane sulfonate (SAS) and *N*-hydroxymethyl acrylamide (NHMAA) were purchased from Tianjin Guangfu Chemical Institute. Other chemicals were of commercial grade and used as received.

Preparation of pre-emulsion and initiator solution

The 30 g deionized water (1/4 of total deionized water) and 0.75 g surfactant (1/4 of total surfactant) were added to a 250 mL four-neck glass reactor and were stirred rapidly to make the emulsifier dissolved sufficiently. The seed-stage MMA monomer (5 g equivalent to 5 wt % of total monomers) was added to the surfactant solution and stirred rapidly for 15 min. Then, the stirring rate was slow down and persisted for 1 h. The pre-emulsion solution of core component was ready for further reaction. At the same time, the emulsifier solution with 90 g of deionized water (3/4 of total deionized water) and 2.25 g of surfactant (3/4 of total surfactant) was prepared using a magnetic stirrer. Separately, monomer mixtures with 3 g of AA, 36 g of BA, 56 g of 2-EHA and 0.1 g of DDM (0.1 wt % of total monomers) were prepared. When the emulsifier was dissolved

sufficiently, the monomer mixture was slowly added into the water-surfactant mixture by pouring into the agitator blades over 20 min. The resulting monomer emulsion of shell component was milky in appearance and was ready for further reaction. Then, the initiator solution was prepared by adding 0.5 g of APS into 5 g of deionized water and continuously stirred to become homogenous solution. In this study, APS was mainly used as the initiator and NaHSO₃ is used as redox initiator accompanying APS. APS can produce the radicals and H⁺ and the H⁺ can be considered as catalysis to promote the decomposition of APS. As a result, the decomposing rate of APS would be self-accelerated. Therefore, at the initial stage of the reaction, NaHSO₃ is used to control the decomposing rate of APS. At the final stage of reaction, for making the reaction reach the maximum, NaHSO₃ was also applied as the redox initiator.

Polymerization procedure

The 2/5 initiator solution was added into the reactor with a stirrer, reflux condenser, thermometer and dropping funnel, in which the pre-emulsion of core component was ready for further reaction. The pre-emulsion of core component with a part of initiator was stirred and heated by circulating hot water. When the emulsion presented blue gloss, the reaction temperature was adjusted and maintained at 80°C. After holding for 30 min, the pre-emulsified shell monomer mixtures were slowly dropped into the reactor at a constant rate over 3 h. Another part of initiator solution was added to the reaction flask at 60, 120, and 180 min. After the completion of the addition of the growth-stage reactant mixture, the reaction was continued for 1 h to decrease the residual monomer. The ammonia (25% concentration) was added into the reactor to increase the pH and to enhance the latex shear and shelf stability. The latexes were cooled to room temperature and filtered to obtain the ready product latexes.

TEM characterization

The morphology of structural latex particles was observed by TEM (JEM-2010, 200 kV). The latexes were further diluted with distilled water, and then dilute droplets was transferred onto the copper grid (mesh 200) and dried in open air. Then, the samples were stained before the measurement to distinguish the core and shell regions.

Acrylic EPSA characterization

Acrylic EPSAs were applied using wire-rod coater directly onto 25 μm poly(ethylene terephthalate)

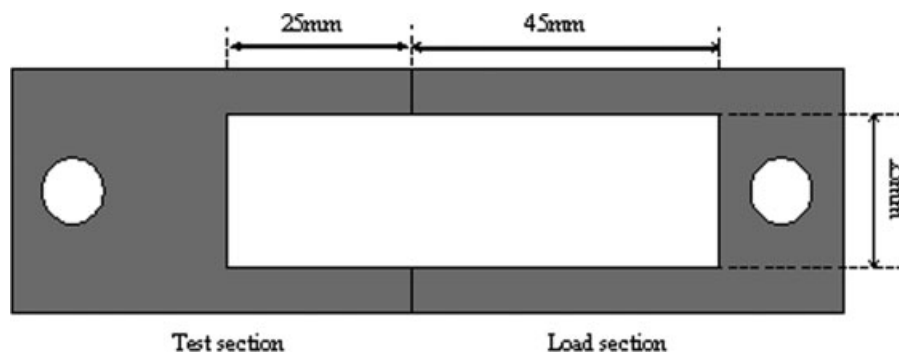


Figure 1 The schematic of the holding power test.

(PET) to give a 25 μm dry film thickness. A standard drying condition of 121°C and 10 min was used to dry acrylic EPSA film, unless it was otherwise indicated. Acrylic EPSA testing was done at 23°C and 65% relative humidity and the samples were conditioned for 24 h before testing.

For tack property tests, 30 \times 30 mm² strips were die cut from EPSA-coated PET film. The tack property was determined with a rolling ball tester. A steel ball with a particular weight and size was released from the top of an incline with an angle of 30°. Then the steel balls accelerated down and rolled onto adhesive tape. The tack was the maximum weight or size of the steel ball that could stop on the EPSA tape. For the holding power, 100 \times 25 mm² strips were die cut. The strips were laminated against stainless steel using 2 kg rubber roller to make contact areas of 25 \times 25 mm² (Fig. 1). After a dwelling time of 20 min, the sample was fixed in the tester vertically with a 1 kg load suspended in the other end. Automatic timers were placed below the weights to count the time of failure. The shear holding power was the time that elapsed between the application of the load and the completed separation of the strip from stainless steel. For the 180° peel test, 200 \times 25 mm² strips were die cut. The strips were laminated against the substrates using 2 kg rubber roller. After 6 h dwell, the 180° peel off the substrate was done at 250 mm/min. The average force for 25 mm wide tape was recorded as peel energy. The morphological characteristics of acrylic EPSA were tested with scanning electron microscopy (FEI Quanta 200). Both the surface and cross-section of EPSA were characterized.

RESULTS AND DISCUSSION

Effect of different emulsifiers

The effects of different kinds of emulsifier on the properties of emulsion latexes are investigated and the results are summarized in Table I. As shown in Table I, the hybrid emulsifier of SDS/OP-10 pro-

vides superior polymerization stability, fine emulsion, and good shelf stability. Compared with hybrid emulsifiers, the performance of other emulsifier species are not fully satisfied. If anionic emulsifiers or nonionic emulsifier are used separately, the polymerization system is unstable. Anionic emulsifiers are sensitive to the pH value and electrolyte ions so that it is difficult to control stability during the polymerization process. Meanwhile, when the mono emulsifier (anionic emulsifier) is applied, the surface of latexes will be charged. Therefore, the force between the surface of latexes and ion of emulsifier can be generated which result in the static tension.¹⁵ Therefore, the negative charge on the surface of emulsion latexes makes the free radicals enter into emulsion latexes with difficulties, which leads to a slower reaction velocity and a lower conversion. Although OP-10 can decrease the static tension by forming the hydrolyzed protective shield on the surface of latexes, the particle size of the nonionic emulsifier is so large that the emulsion latexes tend to sediment because of the gravity, which makes the shelf stability of emulsion latexes unsatisfied. When the temperature is higher than the cloud point (see next paragraph), the stability would be destroyed. Then, OP-10 separates from water, which leads to the de-emulsification during the later stage of polymerization reaction. When an anionic emulsifier is hybridized with a nonionic emulsifier, the two kinds

TABLE I
The Effect of Different Kinds of Emulsifiers on the Properties of Emulsion Latexes

Emulsifier	Emulsion appearance	Stabilities	
		Polymerization	Shelf
SDS	Fine blue	Good	Poor
SDBS	Visible particles	Poor	Poor
SAS	Visible particles	Poor	Poor
SDS/OP-10	Milk white	Good	Good
SDBS/OP-10	Visible particles	Poor	Poor
SAS/OP-10	Visible particles	Poor	Good
OP-10	–	Poor	–

TABLE II
Cloud Points of Different Emulsifiers^a

Emulsifier (proportion)	OP-10	SDBS/OP-10 (1 : 2)	SAS/OP-10 (1 : 2)	SDS/OP-10 (2 : 1)	SDS/OP-10 (1 : 5)
Cloud point (°C)	65	68	>90	>90	>90

^a The concentration of the emulsifier water solution is 3 wt %.

of emulsifier can be alternatively absorbed on the surface of emulsion latexes. The alternative effect decreases the static tension on the surface of emulsion latexes, enhances the adsorption of emulsifiers on the surface of emulsion latexes, and ultimately improves the stability of reaction system.

Cloud point can indicate the stability of emulsion solution and is defined as the temperature under which the clear solution becomes turbid (when increasing temperature). The cloud points of several hybrid emulsifiers are shown in Table II. The reaction temperature is about 80°C and is higher than the cloud point of OP-10 and SDBS/OP-10. As a result, the two (hybrid) emulsifiers can lead to demulsification under such conditions. The cloud point of SDS/OP-10 is higher than 90°C, regardless of the proportion. Hence, the emulsion latexes containing SDS/OP-10 show good stability. The cloud point of SAS/OP-10 is also higher than 90°C, but these hybrid emulsifiers are difficult to dissolve which may be due to the emergence of some flocculation.

Effect of SDS/OP-10 emulsifier ratio

As shown in Table III, if the SDS/OP-10 ratio is greater than 1, the polymerization process presents good stability. On the other hand, the polymerization stability decreases while the content of nonionic emulsifier in the composite emulsifiers increases, i.e. the SDS/OP-10 is less than 1. If the anionic emulsifier is combined with a small quantity of the non-

ionic emulsifier, the static tension on the surface of the emulsion latexes decreases and the adsorption of total emulsifiers on the surface of the emulsions is enhanced. Therefore, with the aid of the emulsification effect of the nonionic emulsifier, the polymerization stability of reaction system is improved. When the content of nonionic emulsifier increases to a certain degree (the proportion is less than 1), the emulsification effect of nonionic emulsifier will be the dominating effect. Compared with the effect of anionic emulsifiers, the emulsification effect of nonionic emulsifier is weaker and more sensitive to temperature. Hence, the polymerization stability decreases especially in the late period of the polymerization reaction because of the elevated temperature. The holding power increases with the increase of anionic emulsifier content, which should be due to the molecular weight (or cohesion power) increase of latexes with the anionic emulsifier content.¹⁶ From another point of view, the increase of OP-10 can result in the decrease of molecular weight of polymer. Therefore, the tack increase and holding power decrease as Table III shown. However, the effects of SDS/OP-10 ratio on the peel strength are more complicated and not very clear at the current stage.

In summary, SDS as anionic emulsifier is sensitive to pH value and electrolytes which results in the poor stability of latexes. OP-10 as nonionic emulsifier can stabilize the latex by forming the hydrolyzed shell around latexes. When the SDS and OP-10 are applied at the same time, they will be absorbed onto

TABLE III
The Effect of SDS to OP-10 Ratio on the Polymerization Reaction and Adhesive Properties of EPSA^a

Proportion of emulsifiers ^b	Tack ^c	Holding power (min)	180° peel strength (N/25 mm)	Coagulate content (%)	Emulsion appearance
1 : 5	10	700	6.49	6.01	Milk white
1 : 2	10	1180	6.51	1.52	White with slightly blue
1 : 1	9	>1440	6.66	Trifle	White with blue
2 : 1	7	>1440	7.42	None	White with blue
5 : 1	6	>1440	6.82	None	White with blue
3 : 0	6	>1440	6.31	None	White with blue

^a The emulsifier content is 3 wt % of total monomer.

^b The ratio is SDS/OP-10 ratio.

^c Tack is the number of a steel ball.

TABLE IV
The Effect of Emulsifier Content on Polymerization Stability and Viscosity of the Emulsion System^a

Content (wt %)	Result of emulsification	Emulsion appearance	Polymerization stability	Coagulate content (%)	Viscosity (mPa s)
2	Demixing	Milk white	Poor	5.51	2530
3	Mixing	White with blue	Good	None	3120
4	Mixing	White with blue	Good	Trifle	3400
5	Mixing	White with blue	Good	2.83	4800
6	Mixing	–	Poor	–	–

^a The emulsifier is SDS/OP-10 and the content is relative to the mass of total monomer.

the surface of latexes alternatively. The small amount of OP-10 in the system increase the distance among the ions of SDS and decrease the static tension, which results in the improved stability of latexes. However, when the OP-10 exceeds certain amount, the size of latexes in the reaction system will increase. Therefore, the large-size latexes intend to sediment driven by the gravity. Based on the experimental results, an optimized ratio obtained is 2 : 1 (SDS/OP-10) and the performance of EPSA prepared at this condition is generally superior except that the tack is a little unsatisfied.

Effect of emulsifier content on the polymerization stability of EPSA

As show in Table IV, when the emulsifier content is between 3–4 wt %, the general performance of the emulsified latexes is excellent. According to the emulsion polymerization theory, the particle size of emulsion latexes is continuously growing with the

polymerization process. Therefore, more emulsifier molecules are required to keep the polymerization stable. When the content of emulsifiers is little, the particle size of emulsion latexes is large and no blue gloss is observed because the amount of formatted latexes is small. As the polymerization reaction further processes, no more emulsifier molecules can be supplied to be absorbed on the surface of the latexes. As a result, the surface covering ratio of the emulsifier molecules decreases which leads to the unstable polymerization or even de-emulsification (as the case of 2% shown in Table IV). But if the emulsifiers are overused, the number (amount) of emulsion latexes increases significantly. The particle size of the latexes becomes very small, which means the surface area enlarges significantly. Then, the intermolecular interaction is so strong that the viscosity of reaction system increases rapidly, which makes the stirring difficult. During the later period of emulsion polymerization, the de-emulsification occurs and the blue gloss becomes weak or even disappears.

TEM characterization of latex

To examine the latex morphology, TEM is carried out and the result is demonstrated in Figure 2. According to Figure 2, the latex particles are spherical with a diameter range approximately from 40 to

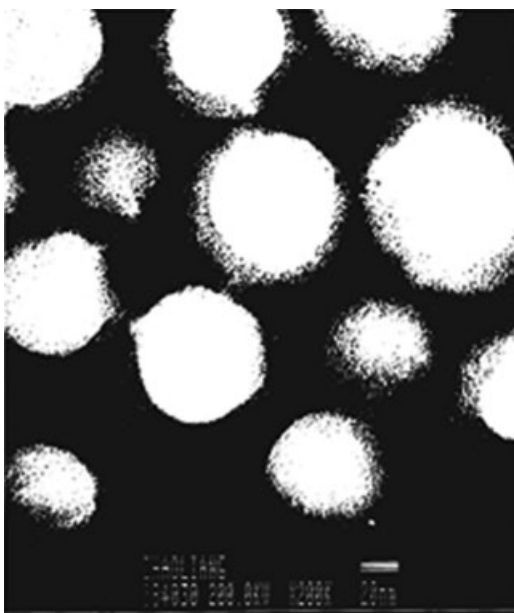


Figure 2 TEM result of the latex (The ratio of SDS to OP-10 = 2 : 1 and the emulsion content is 3 wt %).

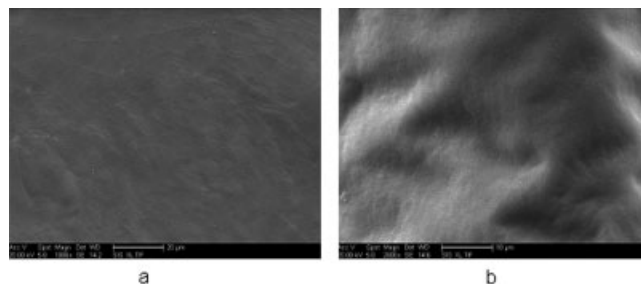


Figure 3 SEM morphology of (a) the surface and (b) the cross-section of acrylic EPSA (The ratio of SDS to OP-10 = 2 : 1 and the emulsion content is 3 wt %).

TABLE V
The Effect of Emulsifier Content on Adhesive Properties of EPSA^a

Content of the emulsifier (wt %)	Tack (no.)	Holding power (min)	180° peel strength (N/25 mm)
2	5	543	5.33
3	8	>1440	7.42
4	7	>1440	7.21
5	6	706	6.92
6	–	–	–

^a The emulsifier is SDS/OP-10 and the ratio is 2 : 1.

80 nm and the particles have a clear core-shell structure. Almost uniform spherical core-shell structure is presented due to the difference of electron penetration to the core and shell.

Effect of emulsifier content on adhesive properties of EPSA

From Table V, it can see that the ideal content of hybrid emulsifiers is 3–4 wt %. With the increment of emulsifier content, the molecular weight of EPSA increases which results in the enhanced adhesive properties of EPSA. However, if the emulsifier content is larger than a certain limit, a part of the emulsifier molecules will be at the free state. Therefore, when EPSA is coated to a film, those emulsifier molecules will induce a weak interface which has a negative effect on the final adhesive properties. In addition, too large molecular weight of EPSA makes it difficult to flow which induces the decline of EPSA tack. Lastly, excessive emulsifiers have also a negative effect on the core-shell structure because some core polymer particles will not become packed by the shell polymer.¹⁷ Therefore, the emulsion is a mixture of core polymer, shell polymer and core-shell structure polymer. The characteristic morphology of EPSA is examined by SEM and shown in Figure 3. Based on SEM result, the EPSA demonstrates homogenous structure indicating the homogenous properties. According to the above discussion, when the content of the hybrid emulsifiers is 3–4 wt %, EPSA demonstrates superior performances. Whereas, too much emulsifiers are disadvantageous

to water-resistance of EPSA and can induce a weak interface. As a result, the optimized content of hybrid emulsifiers is 3 wt %.

CONCLUSION

SDS/OP-10 hybrid emulsifiers show the good performance for stabilizing the reaction system of acrylic EPSA. The optimized ratio of SDS/OP-10 for the emulsion polymerization is 2 : 1. At this optimized condition, the fine emulsion latexes with little flocculation and visible blue gloss are obtained. The adhesion characterization shows that tack, holding power and 180° peel strength depend on the ratio and content of hybrid emulsifiers. When the content is 3 wt % coupling with the SDS/OP-10 ratio of 2 : 1, the performance of acrylic EPSA can meet the industrially strict requirements.

References

- Bendek, I. *Development and Manufacture of Pressure Sensitive Products*; Marcel Dekker: New York, 1999; p 262.
- Tobing, S.; Klein, A. *J Appl Polym Sci* 2001, 79, 2230.
- Staicu, T.; Micutz, M.; Leca, M. *Prog Org Coat* 2005, 53, 56.
- Jovanovic, R.; Dube, M. A. *J Macromol Sci Part C: Polym Rev* 2004, 44, 1.
- Wei, S. Q.; Bai, Y. P.; Shao, L. *Eur Polym J* 2008, 44, 2728.
- Urban, D.; Takamura, K. *Polymer Dispersions and their Industrial Applications*; Wiley-VCH: Weinheim, 2002; p 408.
- Garrett, J.; Lovell, P. A.; Shea, A. J.; Viney, R. D. *Macromol Symp* 2000, 151, 487.
- Satas, D. *Handbook of Pressure Sensitive Adhesive Technology*; 2nd ed.; Van Nostrand Reinhold: New York, 1989; p 400.
- Vorweg, L.; Gilbert, R. G. *Macromolecules* 2000, 33, 6693.
- Mao, T. J.; Reegen, S. L. In *Proceedings of the Symposium on Adhesion and Cohesion*, Weiss, P., Ed. Elsevier: Amsterdam, 1962; p 209.
- Aubrey, D. W.; Ginosatis, S. J. *Adhesion* 1981, 12, 1989.
- Chan, H. K.; Howard, G. J. *J Adhes* 1978, 9, 279.
- Piirma, I. *Emulsion Polymerization*; Academic Press: New York, 1982; p 319.
- Wang, X.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci A Polym Chem* 2001, 39, 3093.
- Cao, T.; Liu, Q.; Hu, J. *Synthesis, Properties and Application of Polymer Emulsion*; Chemical Industry Press: Beijing, 2002; p 170.
- Park, M. C.; Lee, M. C. *J App Polym Sci* 2004, 94, 1456.
- Liang, J.; He, L.; Zheng, Y. S. *J App Polym Sci* 2009, 112, 1615.