

Effect of Polymerization Conditions on the Characteristics of Polyvinyl Acetate Emulsions

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ABSTRACT

Polyvinyl acetate emulsion has been widely used as adhesives for wood and paper, paint additives and binders for fiber, leather, and other materials because it is an excellent adhesive with many advantages including low in toxicity risks and manufacturing cost. It is expected the consumption of polyvinyl acetate emulsion as adhesives will increase in cigarette industry as well as in paperboard coating industry. Recently the operation speed of the cigarette tip wrapper increased so substantially that improvement of the emulsion properties is required including good wet tack development, narrow and controlled particle size distribution, low viscosity, etc.

In this study the effects of such polymerization conditions as the type and amount of emulsifier, internal or external plasticizing, and emulsification methods on the viscosity and particle size of polyvinyl acetate emulsions were examined.

Results showed that polyvinyl alcohol with a high degree of hydrolysis and low molecular weight and nonionic surfactants are superior to anionic surfactant in improving adhesion and emulsion stability. They also tend to produce emulsions with smaller particle size. External plasticization with dipropylene glycol dibenzoate was more effective in improving flexibility than internal plasticization with butyl acrylate. Monomer emulsification under high shear was more effective in decreasing the particle size.

1. Introduction

Polyvinyl acetate emulsion has widely been used as wood and paper adhesives not only because it has good adhesion characteristics but also it is a nontoxic and low odor product. In addition, it is one of the most cost-effective adhesives because of the simplicity of the polymerization process and availability of low cost monomers.¹⁾ Polyvinyl acetate emulsions are also being

used as binders for cigarette tip papers. When it is used as a binder for cigarette tip papers, rapid development of adhesion or tackiness in a few ms is required to reduce the production loss on a high-speed cigarette tip wrapper that wraps 6,000 cigarette tips/min. Furthermore, its viscosity and colloidal/mechanical stability are crucial in improving runnability.

The most widely used binder in paper coating industry is styrene/butadiene latex. It turns yellow, however, when heated and

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blisters when dried fast. To overcome these problems, in many countries, especially in Europe, significant amount of polyvinyl acetate is being used as a binder for board coating.²⁾

There are several domestic companies manufacturing polyvinyl acetate adhesives for wood and wallpaper. There is no domestic company, however, that produces polyvinyl acetate emulsions for bonding cigarette tip papers. Therefore, it is urgently required to develop polymerization technology for producing high quality polyvinyl acetate emulsions for this use.

In this study the effects of the type and amount of surfactants and colloidal stabilizers, plasticizing methods and monomer emulsification processes on the viscosity, particle size, and adhesion properties of polyvinyl acetate emulsions were examined.

2. Materials and Methods

2.1 Materials

Vinyl acetate and butyl acrylate were used as monomers, and 0.3% of ammonium persulfate was added as initiator. To control pH during the polymerization process sodium bicarbonate was used. Various grades of polyvinyl alcohol shown in Table 1 were used as steric stabilizer. To emulsify the monomers anionic sodium lauryl sulfate and nonionic nonyl phenol ethylate surfactants (NP40 and NP10) were used.

Various polyvinyl alcohols and dipropylene glycol dibenzoate (Benzoflex) were

added to the polymerized emulsions to evaluate their effects on adhesion strength and colloidal stability.

2.2 Methods

2.2.1 Emulsion Polymerization

The compositions of the raw materials used are shown in Table 2. In Table 2 the proportions of the components are shown as parts per hundred of total weight of monomers used.

Emulsion polymerization was carried out using a cylindrical glass reactor with three necks (Fig. 1). The polymerization step is depicted in Fig. 2. After adding the dissolved polyvinyl alcohol and surfactant in the reactor, it was heated to 80°C. Then emulsified monomer and initiator were added incrementally for three hours, while the reaction temperature was regulated at 80°C. To prepare the monomer emulsions either a glass stick or a high shear homogenizer was used. After all monomer emulsion had been fed into the reactor, the temperature was increased to 90°C and kept at this temperature for 30 minutes to strip off unreacted monomers. Then plasticizer and preservative were added. Finally the polymer emulsion was cooled and filtered.

2.2.2 Viscosity and Particle Size

Solids content of the polyvinyl acetate emulsion was determined after oven drying. Low shear viscosity of the emulsion was

Table 1. Properties of PVA

	C17	P17	P24	P05
Viscosity (cPs) ¹⁾	30.0±2.0	27.5±1.5	45.0±5.0	5.0±1.0
Degree of hydrolysis (mol %)	98.5±0.5	87.5±1.5	88.0±1.0	88.0±1.0

¹⁾ Brookfield viscosity of 4% aqueous solution at 20°C.

Table 2. Polymerization recipes

Poly- mer	Protective Colloid ^{*1}				Surfactant ^{*1}			Monomer ^{*1}		Post Addition ^{*2}				Emulsifi- cation method
	C17	P17	P24	P05	#6	NP40	NP10	VA	BA	PVA C17	PVA P24	PVA P05	BF	
P1	3.4					4.7		75	25					Homogenizer
P2	4.08					4.7		67	33					"
P3	3.4					4.7		75	25				5	"
P4	2.55	0.85				4.7		75	25				5	"
P5			3.4			4.7		75	25				5	"
P6	4.08					7.02		75	25					"
P7	4.08					4.14		75	25					"
P8	4.08				1.52	1.9		75	25					"
P9	3.4					4.7		71	29				5	"
P10	3.4					4.7		75	25	1				"
P11	4.08					4.7		67	33				5	"
P12	4.08				1.52	1.9		75	25				5	"
P13			1.94	4.86		6.19		75	25				3.26	"
P14			2.39	3.14		4.54	1.68	100	0				3	"
P15			2.25	3.25		5.9		100	0					"
P16					2.29	4.58		75	25				6	glass stick
P17	3.4			1.13	2.32	4.7		75	25		1.3	2.2	5	"

*1 wt pph based on monomer.

*2 wt % based on total amount.

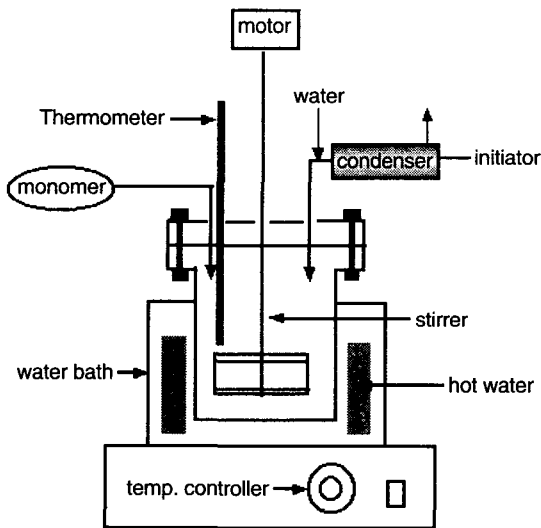


Fig. 1. Schematic diagram of the polymerization reactor.

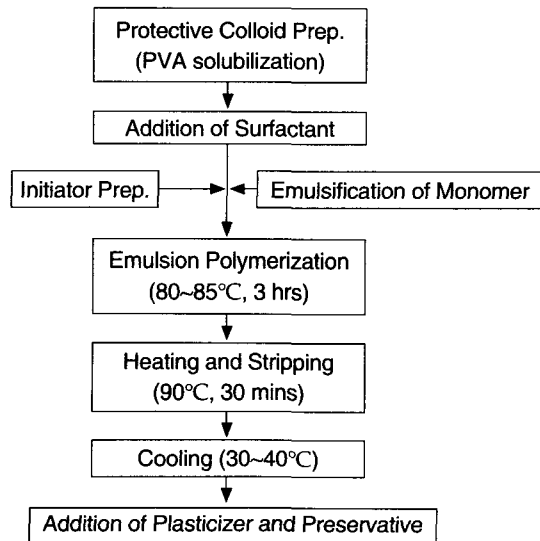


Fig. 2. Polymerization procedure of polyvinyl acetate emulsion.

measured with Brookfield viscometer at 60 rpm. Particle size and its distribution were determined with Master Sizer. The adhesion properties of the dried films on aluminum foils were evaluated.

3. Results and Discussion

General properties of polyvinyl acetate emulsions prepared according to the recipes described in Table 2 are shown in Table 3. Most of the dried films were transparent. They differ, however, in flexibility depending on the raw materials used.

3.1 Effect of Protective Colloids

Protective colloids improve emulsion stability by providing steric hindrance between

emulsion particles. Polyvinyl alcohol and HEC (hydroxyethyl cellulose) are commonly used as protective colloids in manufacturing polyvinyl acetate emulsions.³⁾ These provide adhesive power for the emulsions as well.

Effects of four polyvinyl alcohols with different degree of hydrolysis and molecular weights on emulsion properties were tested. The amount of nonionic surfactant was kept constant. Among the three polymers (P3, P4, and P5) produced with different polyvinyl alcohols as protective colloids, which are similar in molecular weights, polymer emulsion made using polyvinyl alcohol with the lowest hydrolysis degree, gave the lowest emulsion viscosity. And this agrees well with the finding by Lee.⁴⁾ Results also showed that the higher the molecular weight of polyvinyl alcohol, the greater the viscosity of polyvinyl acetate emulsions.

Table 3. Properties of polyvinyl acetate emulsions

Polymer	Solids Content (%)	Brookfield viscosity (cPs, 30°C)	Average particle size (μm)	Film character	Wet tack* ¹	Dry tack* ¹
P1	49.8	600	-	clear, ductile	△	○
P2	53.5	3900	-	clear	○	○
P3	53.0	800	-	clear	△	○
P4	53.3	650	-	clear	△	○
P5	51.0	4500	0.59	clear, slippery	○	○
P6	51.4	1300	-	clear	△	○
P7	50.0	500	-	clear	×	○
P8	54.0	1650	-	a little clear, ductile	×	△
P9	56.0	3500	-	clear	△	○
P10	49.6	1350	3.02	clear	△	○
P11	56.4	5000	1.13	clear	○	◎
P12	57.0	2000	-	clear	△	×
P13	43.0	2700	0.82	clear	○	○
P14	48.0	1500	0.64	clear	○	○
P15	46.0	1200	0.54	clear	○	○
P16	51.0	365	-	yellowish	△	△
P17	48.8	5960	3.29	yellowish	△	△

*1 ◎: excellent, ○: very good, △: good, ×: poor.

When the amount of protective colloid was increased, the emulsion viscosity increased.

Viscosity is one of the most critical variables affecting the runnability of polyvinyl acetate emulsions on a cigarette tip wrapper. In general, it is required the emulsions have around 1000 cPs of low shear viscosity for them to be used on a high-speed cigarette tip wrapper.⁵⁾ As shown in Table 3, when polyvinyl alcohol with high molecular weight was used, improvement of wet tack and reduction of colloidal stability were observed.

Degree of hydrolysis of the polyvinyl alcohol affects the colloidal stability of the emulsion. It is well-known that polyvinyl alcohol reduces the surface tension of the emulsion and improves colloidal stability. The lower the hydrolysis degree, the greater its effect as a colloidal stabilizer.⁶⁾ Therefore, polyvinyl alcohol with low degree of hydrolysis and viscosity is preferred.⁷⁾ When the degree of hydrolysis is lower than 80%, however, difficulties arise in the solubilization of polyvinyl alcohol.

3.1.2 Effect of Surfactant

Surfactant type did not show any significant effect on the viscosity of the polyvinyl acetate emulsions. When the ratio of colloidal stabilizer to surfactant decreased, however, viscosity and particle size of the emulsions were decreased. Depending on the amount of surfactant used the suspension polymerization or emulsion polymerization occurs. When the amount of surfactants increased above a critical point, micelles start to form that incurs emulsion polymerization. The number of micelles increases as the concentration of the surfactant is increased.

Although the effect of surfactant type on emulsion viscosity was insignificant, a sub-

stantial difference in adhesion property was observed depending on the surfactant type. When nonionic surfactants were used noticeable improvement in wet- and dry tack properties was achieved. On the other hand, when anionic surfactant was used as a sole surfactant, increase of emulsion viscosity and decrease of colloidal stability were resulted. This indicates that it is necessary to incorporate nonionic surfactant to improve adhesion property and colloidal stability of polyvinyl acetate emulsion.

Polymerization rate was appeared not to depend on surfactant concentration. It agrees well with the finding that the polymerization rate of vinyl acetate does not depend on the surfactant concentration since the solubility of vinyl acetate monomer is rather high.⁸⁾

Particle size of the polyvinyl acetate emulsion ranged from 0.5-3 μ m. While this particle size is appropriate for an adhesive for cigarette tip wrappers, it is considerably larger for being used as a coating binder which requires particle size of around 0.2 μ m.

3.2 Effect of Plasticizer

Plasticizer is used to reduce the hardness of dried polyvinyl acetate films. To increase the flexibility of polyvinyl acetate two different approaches are being used, i.e., external plasticizing and internal plasticizing. Post addition of low molecular weight additives is called external plasticizing and copolymerization of monomers with plasticizing effect with vinyl acetate monomer is called internal plasticizing. External plasticizing is a relatively simple and easy method to control plasticity. However, it has disadvantages including evaporation and migration of the additive which may cause variations in plasticizing effect.⁹⁾

3.2.1 Internal Plasticizing

Among various internal plasticizers butyl acrylate with glass transition temperature of -56°C is most widely employed.¹⁰⁾ In this study the addition rates of butyl acrylate monomer were adjusted to get polyvinyl acetate emulsions with glass transition temperatures ranging from $5\text{-}10^{\circ}\text{C}$. As the amount of butyl acrylate increased, wet tack of polyvinyl acetate emulsion and adhesion property onto cellulosic substrates were improved. However, incorporation of butyl acrylate increased the viscosity of the emulsion and slipperiness of the dried film.

3.2.2 External Plasticizing

External plasticizer also reduces the glass transition temperature of polyvinyl acetate and improves plasticity. When excess amount of external plasticizer is used, however, loss of tensile strength results.

Addition of Benzoflex improved plasticity and reduced slipperiness of the dried films as expected. Its addition, however, increased viscosity of the emulsion. It is appeared that external plasticizing with Benzoflex is more effective in increasing the plasticity of polyvinyl acetate emulsions than internal plasticizing. When excess amount of Benzoflex was added, however, the adhesion property decreased.

To improve the adhesion property polyvinyl alcohol was post added to the emulsion and its effect on the adhesion property of polyvinyl acetate emulsions was evaluated. Post addition of polyvinyl alcohol, however, did not show any significant effect in increasing adhesion property. Post addition of polyvinyl alcohol increased the emulsion viscosity.

3.3 Effect of Emulsifying Method

In emulsion polymerization many factors including polymerization temperature, reaction time, feeding rate of monomer and catalyst, stirring speed, etc., affect the polymerization process and quality of the polymer produced. Method of emulsification of monomers also plays an important role in emulsion polymerization.

Monomer emulsions were prepared with either a glass stick or a homogenizer to evaluate the influence of shear rate. These two methods of emulsification represent low and high shear rate conditions. Depending on the shear rate imposed the particle size of the monomer droplets was varied. Smaller monomer droplets with narrow distribution of the particle size were formed when a homogenizer was used. The particle size of the monomer droplets influenced the particle size distribution of the polymer emulsions. When a homogenizer was used, polymer emulsions with smaller diameter were obtained (Fig. 3). On the other hand, when emulsification was proceeded using a glass stick, the average particle size increased substantially and its distribution became wider (Fig. 4). Furthermore, polyvinyl

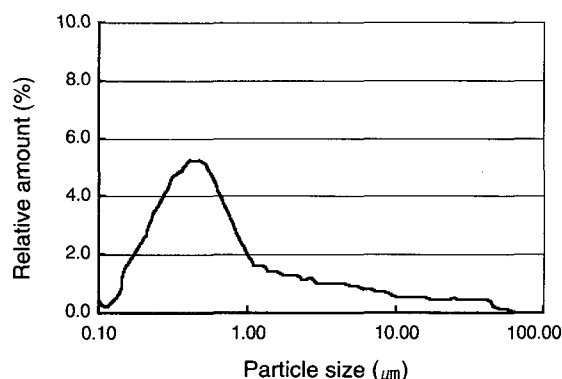


Fig. 3. Particle size distribution of polyvinyl acetate emulsion emulsified by a homogenizer.

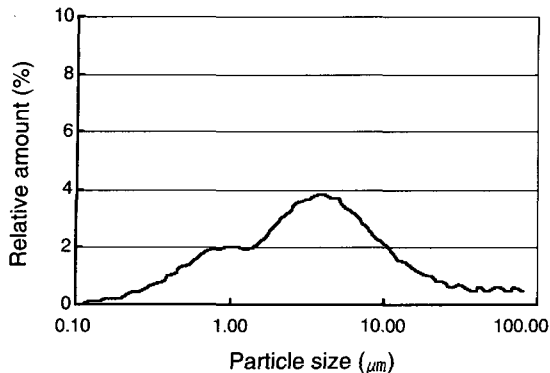


Fig. 4. Particle size distribution of polyvinyl acetate emulsion emulsified with a glass stick.

acetate emulsions made from the monomer droplets prepared using a glass stick were unstable and coagulated rather easily.

Therefore to produce polyvinyl acetate emulsion with suitable properties as an adhesive for high-speed cigarette tip wrappers, a high shear rate emulsification step should be employed.

4. Conclusions

The effects of the type and amount of surfactants and colloidal stabilizers, plasticizing methods, and monomer emulsification processes on the viscosity, particle size, and adhesion properties of polyvinyl acetate emulsions were examined. Results showed improvement in adhesion property, colloidal stability, and viscosity could be obtained when polyvinyl alcohol with a high degree of hydrolysis and low molecular weight was used as protective colloid. The stability of polyvinyl acetate emulsions increased when nonionic surfactant was used rather than anionic one. External plasticization with Benzoflex appeared to be more appropriate although internal plasticizing with butyl acrylate would provide more permanent plasticity to the product.

Monomer droplets prepared using a high shear homogenizer produced polymer emulsions with smaller diameter and good stability.

The polyvinyl acetate emulsion prepared in this experiment was found to have balanced properties for being used as a general adhesive for paper.

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