

PREPARATION AND CHARACTERIZATION OF A STABLE CORE-SHELL LATEX WITH VAE IN THE CORE

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ABSTRACT

A core-shell latex containing Butyl Acrylate (BA) and Styrene (St) in shell, and Vinyl Acetate-Ethylene (VAE) in core was successfully prepared by seeded emulsion polymerization with water as the reaction medium. Several key elements related to the polymerization, including core/shell ratio, BA/St ratio and Ammonium persulfate (APS) dosages were investigated in details. Accordingly, an optimal reaction condition was developed. The synthesized latex particles were characterized by Transmission electron microscopy (TEM) and Dynamic light scattering (DLS). The clear core-shell structure and chemical components of the core-shell latex particles were determined by TEM and Fourier transform infrared (FTIR) spectrometry, respectively. In addition, the comparisons between the core-shell latex and VAE latex were made. The experimental results indicated that the developed core-shell latex produced improved leather related properties for thermal stability, water resistance and adhesion.

RESUMEN

Un látex compuesto y modelado como núcleo-corteza, que contiene Acrilato de Butilo (BA) y Estireno (St) en la "cáscara" [exterior] y Acetato de Vinilo-Etileno (VAE) en el núcleo [interior], fue preparado con éxito por polimerización en emulsión utilizando agua como semilla, siendo así el medio de reacción. Varios elementos claves relacionados con la polimerización, incluyendo la relación de núcleo/corteza, la relación BA/St y la dosis de persulfato de amonio (APS), fueron investigados en detalle. Por consiguiente, una condición óptima de reacción fue desarrollada. Las partículas de látex sintetizadas se caracterizaron por microscopía electrónica de transmisión (TEM) y de dispersión de luz dinámica (DLS). La clara estructura de núcleo-corteza y componentes químicos de las partículas núcleo-corteza de látex se determinaron mediante TEM y espectrometría infrarroja con transformación de Fourier (FTIR), respectivamente. Además, las comparaciones entre el núcleo-corteza de látex y látex VAE fueron realizadas. Los resultados experimentales indican que el núcleo-corteza de látex desarrollado ha mejorado las propiedades del cuero relacionadas con la estabilidad térmica, la resistencia al agua y la adherencia.

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INTRODUCTION

Vinyl acetate-ethylene emulsion (VAE) is produced by copolymerization of vinyl acetate and ethylene under high pressure usually, the vinyl acetate content ranges from 60-95%, and ethylene from 5-40% of the total formulation. VAE can offer considerable performance advantages due to its lower glass transition temperature (T_g), which was obtained through the incorporation of the ethylene in the main chain.¹⁻³ As the ethylene content increases, the T_g of VAE decreases, allowing the molecular chain of VAE to be more flexible. VAE also exhibits a lower surface tension and higher temperature resistance. So VAE has more varied application in the leather industry, tobacco industry, wood machining, packing industry, weaving industry and so on. Especially in leather industry, VAE is important for adhesion and very good application of the finishes. However, VAE has some disadvantages, such as lack of depositing stability, poor water resistance, lower adhesion strength, etc. To improve the mentioned deficient properties, different methods, such as blend, graft and others⁴⁻⁶ have been applied for VAE modification. But the depositing stability of VAE is still in poor condition. In addition, the technique of seeded emulsion polymerization is not popular and very little information about this method has been reported.

The core-shell latex implies that some kinds of seed latex particles as core layer located at the center, and the second stage monomers are polymerized in the presence of the seed latex particles as shell layer.⁷ In recent years, core-shell latexes have attracted much attention due to their unique structure and excellent properties.⁸⁻¹¹ In this work, core-shell latex with VAE rich in core and poly(butyl acrylate and styrene) rich in shell was prepared by seeded emulsion polymerization without the addition of any emulsifier. The authors' know of no reporting of similar work. This technique could generate latexes with one or more of the following advantages:¹²⁻¹⁴ less emulsifier migration during film formation, excellent shear stability and monodisperse particle size distribution. The optimal polymerization condition was investigated in obtaining the emulsion with good stability. The morphology and composition of the latex particles were characterized by TEM and DLS, the surface properties were determined by the analysis of the water contact angle and Thermogravimetric (TG) analysis.

EXPERIMENTAL

Materials

VAE-600 was donated by Sinopec Sichuan Vinylon Works, China(60% of solid content, containing 17% of ethylene).The styrene(St) and butyl acrylate(BA) were purchased from Dongfang Chemical (China); ammonium persulfate(APS) was obtained from Kelong Chemical(China). These materials were used as received without any purification.

Seeded Emulsion Polymerization

The core-shell latexes with VAE as seed emulsion and distilled water as solvent, a series of polymerization under comparative conditions were conducted in a 250ml four-neck flask equipped with reflux condenser, nitrogen inlet, mechanical stirrer and dropping funnels. The four-neck flask was heated to 80°C using a water bath. After deaeration with nitrogen gas for 30min, all reagents including ammonium APS, St, BA and residual distilled water were gradually dropped into the 250ml four-neck flask within 1h at 80°C with an agitation speed of 250rpm, followed by an extension of polymerization time to 4h. After polymerization, the pH of the system was adjusted by adding of aqueous ammonia to pH7-8. The basic recipes were listed in Tables 1, 2 and 3.

Characterization

Solid Content and Conversion

The solid content and the polymerization conversion were measured by gravimetric analysis. A certain amount of latex was cast onto a petri dish and dried to a constant weight in an oven at 110–120°C. The solid content and the final conversion were calculated by the following formulas, respectively:

$$\text{Solid content (wt\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\%$$

where W_0 is the weight of the petri dish and W_1 and W_2 are the weight of latex before and after drying to the constant weight, respectively.

$$\text{Conversion (wt\%)} = \frac{\text{Solid content (wt\%)} \times W_3}{W_4} \times 100\%$$

where W_3 is the total weight of all the components added to the flask before polymerization, W_4 is the weight of materials

TABLE I
Recipes for the preparation of
core-shell (BA-St-VAE) by seeded
emulsion polymerization with
various core/shell ratio.

Ingredient	CS1	CS2	CS3	CS4
<i>core</i>				
VAE(g)	10	20	30	40
water(g)	60	56	52	48
<i>shell</i>				
BA(g)	18	13.5	9	4.5
St(g)	6	4.5	3	1.5
APS(g)	0.1	0.1	0.1	0.1
water(g)	6	6	6	6

BA/St ratio remains at 3/1; APS%, 0.1%
(by all the components); 80°C

TABLE II
Recipes for the preparation of core-shell(BA-St-VAE) by seeded emulsion polymerization with various BA/St ratio.

Ingredient	CS4	CS5	CS6	CS7
<i>core</i>				
VAE(g)	40	40	40	40
water(g)	48	48	48	48
<i>shell</i>				
BA(g)	4.5	4	3	1.5
St(g)	1.5	2	3	4.5
APS(g)	0.1	0.1	0.1	0.1
water(g)	6	6	6	6

core/shell ratio remains at 4/1; APS%, 0.1%
 (by all the components); 80°C

except water. Triplet experiments were conducted for getting the average value.

Stability of the Emulsion

The prepared latex was sealed and stored at room temperature for 12 months to evaluate the storage stability. The electrolyte-resistant stability of the prepared latex was determined by after adding electrolyte solution(5% CaCl₂ solution) for 48h. The ratio of coagulation,

$\sigma(\%)$, was calculated by the following formula:

$$\sigma(\%) = \frac{W_5}{W_6} \times 100\%$$

where W_5 is the weight of the dried coagulates and W_6 is the total weight of all the monomer. It showed that the larger the value of σ , the worse the latex stability was.

Water Absorption Ratio

A certain amount of emulsion was taken to make a film, then dried to a constant weight in an oven at 110–120 to create the film. The weighed latex films were dipped in distilled water for 24h. Then the water on film surface was removed quickly with water absorbing paper and the films were weighed again. The water absorption ratio of the films was calculated as follows:

$$\text{Water absorption ratio (wt\%)} = \frac{W_8 - W_7}{W_7} \times 100\%$$

where W_7 and W_8 are the weight of the films before and after the water absorbing step, respectively. Triplet experiments were conducted for obtaining the average value. The static contact angle was determined by an OCA 20/A contact angle system(DATAPHYSICS Germany)

TABLE III
Recipes for the preparation of core-shell(BA-St-VAE) by seeded emulsion polymerization with various content of APS

Ingredient	CS8	CS4	CS9	CS10
<i>core</i>				
VAE(g)	40	40	40	40
water(g)	48	48	48	48
<i>shell</i>				
BA(g)	4.5	4.5	4.5	4.5
St(g)	1.5	1.5	1.5	1.5
APS(g)	0.05	0.1	0.2	0.25
water(g)	6	6	6	6

core/shell ratio remains at 4/1; BA/St ratio remains at 3/1;
 80°C

Thermogravimetric Analysis

Thermogravimetric(TG) analysis was performed with a SDT Q600(NICOLET USA) thermogravimetric apparatus under the nitrogen atmosphere at a heating rate of 10°C/min from 35 to 700°C.

Adhesive Strength

The initial adhesive strength of emulsions were examined by BLD-200S Electronic Peeling Machine (China), and 180° peel strength test was performed in reference to GB2792-81.

Infrared Spectra

A certain amount of latex was dried to a constant weight and filmed at room temperature. Fourier transform infrared (FT-IR) spectra of latex films were recorded using a NICOLET MX-1E FT-IR spectrometer (USA) in the range from 4000 to 400cm⁻¹.

Particle Size and Morphology

Particles size was determined by dynamic light scattering (DLS) using a Malvern MS2000 particle size analyzer (UK) with a detection angle of 90°. The measurements were carried out at 23°C for highly diluted samples in order to rule out interaction of particles and multiple scattering effects. The intensity average diameter was computed from the intensity autocorrelation data using the statistic analysis method. The latex particle morphology was observed by TEM. First a certain amount of final emulsion was diluted properly with distilled water, and then dyed with phosphotungstic acid solution. After spreading on copper to make films, photos were taken to observe the particle morphology by a Hitachi H-600IV transmission electron microscope (Japan).

RESULTS AND DISCUSSION

Synthesis Conditions of the Core/shell

Core/shell Ratio

The experimental results of the effect of the core/shell ratio on the emulsion stability are shown in Table 4. As shown in Table 4, with increasing core/shell ratio, the emulsion stability increased accordingly. The seeded emulsion polymerization was carried in the absence of additive emulsifier, so the stability of the core/shell latex was dependent on the emulsifier in VAE itself. With the decrease of VAE, the emulsifier in the VAE decreased and the monomers (BA and St) increased accordingly. As a result, the stability of CS4 was optimal.

The relationship between the polymerization conversion and the core/shell ratio is illustrated in Fig. 1. As shown, the final conversion augmented with increasing core/shell ratio. It could be attributed to that with the increase of core/shell ratio where the concentration of the emulsifier in the VAE increased accordingly. This could provide additional possibility of the polymerization and then enhance the conversion. Similar experimental results have been reported elsewhere.¹⁴ where it was reported that the optimal core/shell ratio was about 4/1.

BA/St Ratio

The experimental results of the effect of the BA/St ratio on the latex stability are shown in Table 5. Comparison amongst CS4,

5, 6 and 7 have shown, when the BA/St ratio is decreased in the seeded emulsion polymerization, the value of σ increased accordingly. This supported the earlier claim that the stability of core/shell latex was obtained at higher BA/St ratio. This is in agreement with the results of storage stability and electrolyte-resistant stability. The reason could be due to the strong hydrophobicity of St. The emulsifier in the VAE could not fully emulsify St when the amount of St was high, resulting to an unstable core/shell latex product.

The relationship between the polymerization conversion and the BA/St ratio is presented in Fig. 2. We can see that the final conversion increased with the increase of the BA/St ratio, the optimal BA/St ratio is found to be about 3/1.

APS Dosage

APS is usually chosen as initiator in the seeded emulsion polymerization,¹⁵ it played an important roles in initiating the seeded emulsion polymerization and controlling the rate of the polymerization. The effects of APS dosage on the latex stability and polymerization conversion are shown in Table 6. The dose of APS should be neither too high nor too low; otherwise it could either affect the emulsion stability because of a fast rate of the polymerization (CS9 and CS10) or decrease the polymerization conversion for lack of free radical (CS8). Based on the results, the optimal amount of APS was found to be 0.1% of the total components amount.

FTIR Spectra

The IR spectrum of the latex films is shown in Fig.3(a) and (b). In Fig.3(a), we can see the characteristic absorption of the

TABLE IV
The latex stability with various core/shell ratio

	CS1	CS2	CS3	CS4
Appearance	PS	PS (a few)	NPS	NPS
Storage stability	poor	poor	fair	good
Electrolyte-resistant stability	poor	poor	poor	good
σ (%)	2.527	2.024	1.359	0.725

PS: phase separation; NPS: no phase separation

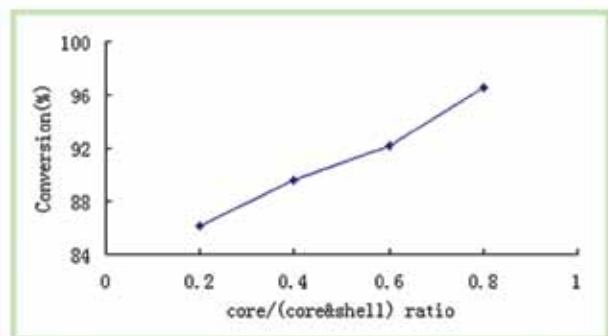


Figure 1. Polymerization conversion with various core/shell ratio.

TABLE V
The emulsion stability with various BA/St ratio.

	CS4	CS5	CS6	CS7
Storage stability	good	fair	poor	poor
Electrolyte-resistant stability	good	poor	poor	poor
σ (%)	0.725	1.136	1.568	2.214

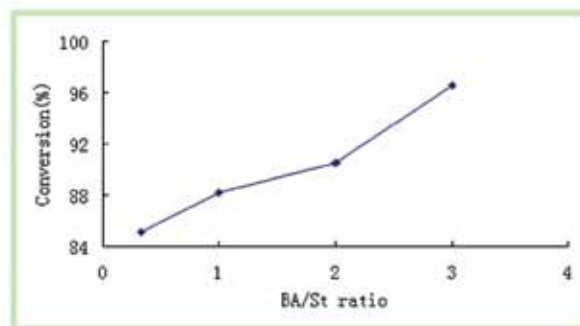


Figure 2. Polymerization conversion with various BA/St ratio.

TABLE VI
The latex stability and polymerization conversion with various APS dosage.

	CS8	CS4	CS9	CS10
Storage stability	good	good	poor	poor
Electrolyte-resistant stability	good	good	poor	poor
$\sigma(\%)$	0.581	0.725	2.025	3.374
Polymerization conversion(%)	83.76	96.56	95.05	92.70

C-H bond of vinyl acetate is at 2929cm^{-1} , the $-\text{COO}-$ group of vinyl acetate at 1240cm^{-1} , and the peaks at 1370cm^{-1} and 1020cm^{-1} also are the other characteristic absorption peaks of vinyl acetate. Comparing the IR spectrum of VAE latex, the core-shell latex containing BA and St in shell exhibit some new peaks shown in Fig.3(b), i.e. the characteristic absorption of acrylate at 1161cm^{-1} , and BA at 942cm^{-1} respectively. It is the evidence of the existence of BA. The peaks at 3006cm^{-1} , 759cm^{-1} and 698cm^{-1} are all assigned to the unsaturated bond of St, being the evidence of its existence.

Latex Particle Morphology of Core-shell Emulsion

Fig.4 shows the TEM micrographs of core-shell latex particles and VAE latex particles. The off-white region and the dark circles around it in Fig.4(a) are VAE core and BA/St shell respectively. In addition, as shown in Fig.5, the average diameter of core-shell latexes increased with the core/shell ratio decreasing. Namely, the particles size of the core-shell latex particles increased with the increase of the monomers in the shell dose. This is because that almost all the BA and St monomers grafts onto the surface of the VAE latex particles.

Thermal Stability Analysis

Fig.6 is showing the TG curves of VAE and core-shell latex films. It could be seen from Fig.6(a) that the weight loss of VAE began around 308°C , and the complete decomposition

occurred near 470°C . However, the starting decomposition temperature of the core-shell latex film containing VAE (CS4), presented in Fig.6(b), moved to be taking place at 350°C . It could be concluded that the thermal stability of the core-shell latex had been improved compared with VAE emulsion, which presumably was caused by the seeded emulsion polymerization, allowing St to be concentrated in the shell of the core-shell latex particles, and the phenyl group of St made the main chain difficult to break. Therefore, the thermal stability of core-shell latex was improved.

Water Absorption of Emulsion Films

As listed in Table 7, the water absorption ratio of VAE film was as high as 28%, implying its poor water resistance. However, the water absorption ratio of the core-shell latex was

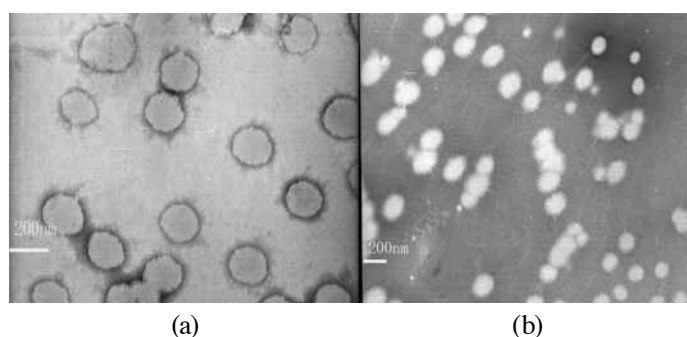


Figure 4. TEM micrographs of CS4 (a) and VAE emulsion (b).

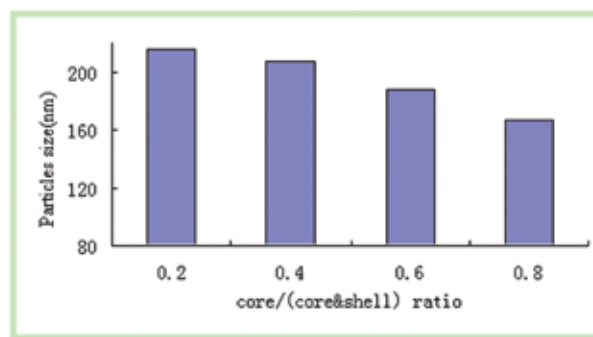


Figure 5. Particle size with various core/shell ratio.

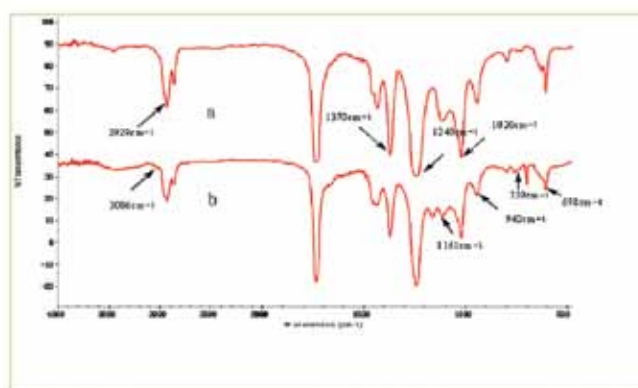


Figure 3. IR spectrum of VAE-600 (a) and CS4 (b).

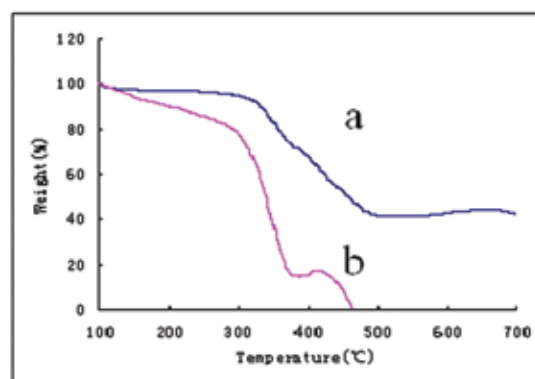


Figure 6. TG curves of VAE (a) and CS4 (b).

only 10.93%, which could be attributed to the excellent hydrophobicity of BA and St. These results are in accordance with the data of contact angle analysis.

Adhesion Performance of Emulsions

To test the adhesion performance of VAE and the core-shell latex we sprayed the VAE and the core-shell latex on the cow shoe upper leathers, then tested the initial adhesion and 180° peel strength of them as the method of 2.3.5. The adhesion performance of VAE and the core-shell latex are shown in Table 8. The initial adhesion and 180° peel strength of VAE emulsion are only 0.5 and 3.5N/25mm. Whereas the initial adhesion and 180° peel strength of the core-shell latex are 2.1 and 6.9N/25mm, indicating remarkable improvement of adhesion in comparison with the original VAE emulsion. It can be attributed to the introduction of BA.

CONCLUSION

Core-shell latex containing VAE in core was successfully prepared by seeded emulsion polymerization with water as the reaction medium. Based on this study of polymerization condition, the optimal condition of for preparing stable core-shell latex was established, i.e. the core/shell ratio was 4/1; the BA/St (in the shell) ratio was 3/1; APS' dosage was 0.33% of the total monomer amount. Clear core-shell structure and chemical components of the core-shell latex particles was investigated by TEM and FTIR, respectively. The particles size analysis indicated that the VAE/BA and St core-shell latex had been successfully prepared in our research. Meanwhile, the various stabilities of the core-shell latex, its adhesion performance on cow shoe upper leathers, water absorption and the thermal stability, were investigated and reported.

TABLE VII
The water absorption ratio and contact angle of latex films.

	VAE	Core-shell
Water absorption ratio(%)	27.86	10.93
Contact angle(°)	67.9	88.1

TABLE VIII
The adhesive strength of emulsions.

Types	VAE	Core-shell
Initial adhesion (N/25mm)	0.5	3.5
180° peel strength (N/25mm)	2.1	6.9

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