

SEED SEMICONTINUOUS EMULSION MULTI-COPOLYMERIZATION OF (METH)ACRYLATES WITH HIGH- SOLID CONTENT: EFFECT OF THE OPERATION CONDITIONS*

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ABSTRACT

The seeded semicontinuous emulsion multi-copolymerization of butyl acrylate (BA), 2-ethylhexyl acrylate (2EHA), methyl methacrylate (MMA), 2-hydroxyl propyl acrylate (HOPA) and acrylic acid (AA) was used to prepare the acrylic latexes with high-solid content. The effects of monomer emulsion feed rates (R_a) and $(R/E)_E$ values, the ratio of emulsifier amount between the initial charge (R) and the addition monomer emulsion (E), on the polymerization reaction features, the viscosities, surface tensions, particle sizes and particle sizes distributions of latexes, T_g and the insoluble fractions of films, the 180° peel strength, tack and holding power of pressure-sensitive adhesive (PSA) tapes, prepared from the latexes, were studied. Experimental study shows that the grafting and cross-linking fraction in the PSA tapes must be controlled within a suitable range to keep the balance of the 180° peel strength, tack and holding power.

INTRODUCTION

As high-solid content latexes reduce shipping and storage costs due to their lower water content, allow increased productivity of plant equipment, have a short drying time and an adjustable film thickness in fewer passes, they have been widely used as pressure-sensitive adhesives (PSA),

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coatings, adhesives, sealants et al. . Much attention has been paid to the study of their preparation in recent years. But most reports were published with the limits of patents^[1-7]. No study dealt with the emulsion multi-copolymerization with high-solid content in the open literature, except some limited reports on the emulsion terpolymerization^[8-10]. However, most syntheses of latex adhesives and coatings, and preparation of high-solid content latexes adopt the semicontinuous emulsion multi-copolymerization, so the study on the polymerization reaction features of semicontinuous emulsion multi-copolymerization with high-solid content is important, meaningful and practical.

On the research of emulsion terpolymerization with high-solid content, Masa^[8] reported the effects of the type and amount of surfactant on the overall polymerization features and the product properties for the seeded semicontinuous emulsion terpolymerization of styrene (St), 2-ethylhexyl acrylate (2EHA) and methacrylic acid (MAA). Arbina^[9] studied the effects of the type and amount of surfactant, amount of cosurfactant and sonication time on both the amounts of coagulum and the final latex properties in the batch miniemulsion terpolymerization of St, 2EHA and MAA also. Unzue^[10] investigated the effects of the solid content, initiator concentration, feed rate and amount of surfactant on the kinetics of high-solid content semicontinuous miniemulsion terpolymerization of butyl acrylate (BA), methyl methacrylate (MMA) and vinyl acetate (VAc), in addition, the effect of the operation variables on the feasibility of obtaining 65 wt% solid content latex with low amount of coagulum was studied.

In the present work, the seeded semicontinuous emulsion multi-copolymerization of BA, 2EHA, MMA, acrylic acid (AA) and 2-hydroxyl propyl acrylate (HOPA) was used to prepare the high-solid content acrylic latexes, the effects of the semicontinuous operation condition on the polymerization features, properties of the latexes and the PSA tapes, prepared from the latexes, were investigated.

EXPERIMENTAL

Materials

BA (CP), 2EHA (polymeric grade), HOPA (polymeric grade) and AA (CP) were distilled under the vacuum. MMA (CP) was rectified at the

atmospheric pressure. The fractions of distillation were stored in a refrigerator before use. Ammonium persulfate (AR), sodium lauryl sulfate (SLS, AR) and octylphenol ethylene oxide adduct (OP, prepared by ourselves) were used as received. Distilled and deionized (DDI) water was used throughout the work.

Seeded semicontinuous emulsion copolymerization

The recipes used in making latexes are given in Table 1. The polymerization reactor was a 500-milliliter four-neck jacketed glass tank equipped with a stirrer, thermometer, reflux condenser, nitrogen inlet, dropping funnel and sampling hatch. The entire polymerization system was swept with N_2 and the temperature was controlled within $\pm 0.5^\circ\text{C}$. For the seeded semicontinuous emulsion multi-copolymerization, the seed formation was first completed and the remaining monomer emulsion was fed into the reactor at a constant feed rate using a metering reciprocation pump. The seed latex was prepared batchwise at 70°C using the recipe given in Table 1. In the addition stage, the monomer emulsion, which contained the remaining monomer mixture, emulsifier, initiator, and DDI water and was emulsified for about 30 min in advance, was fed into the reactor at a constant feed rate and reacted at 70°C . When the monomer emulsion addition was completed, the polymerization was continued for an additional one hour at 70°C and 1.5 hour at 75°C to reach the high conversions.

Table 1 Recipes of (meth)acrylates seeded semicontinuous emulsion multi-copolymerization

Ingredients		Run	
Monomer mixture:	165.00g	Coemulsifier in seed:	Seed:
BA	82.50g	E1:0.00g(0%)*	Monomer mixture: 16.50g(10%)*
2EHA	49.50g	E2:0.33g(10%)*	$(\text{NH}_4)_2\text{S}_2\text{O}_8$: 0.10g(30%)*
MMA	24.75g	E3:0.99g(30%)*	DDI Water: 92.31g(70%)*
AA	1.65g	E4:1.65g(50%)*	Feed rate of emulsion:
HOPA	6.60g	E5:2.31g(70%)*	1.34g/min
Coemulsifier	3.30g	Feed rate of emulsion:	
SLS	1.65g	V1:0.33g/min	Monomer mixture: 16.50g(10%)*
OP	1.65g	V2:0.61g/min	Coemulsifier: 0.99g(30%)*
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.33g	V3:1.02g/min	$(\text{NH}_4)_2\text{S}_2\text{O}_8$: 0.10g(30%)*
DDI Water	131.87g	V4:1.34g/min	DDI Water: 92.31g(70%)*
		V6:2.30g/min	
		V7:3.01g/min	

* Based on total amount wt%

Conversion measurement

Conversions were determined gravimetrically. The samples of reactant taken at various intervals were kept below 0.5 wt% of contents in the reactor to avoid making significant changes in the total amount (about 1 g). Once a sample was removed, it was short stopped with about 0.01 g of hydroquinone and mixed with 0.2 ml of alcohol (AR), then dried at $100 \pm 5^\circ\text{C}$ to constant weight under the atmospheric pressure and vacuum, respectively. The percentage solid and percentage conversion of each sample were calculated from the dried sample weight based on the total amount of monomer mixture in the recipe.

Particle size measurement

The particle sizes and particle sizes distributions were determined by the light scattering using a Malvern Autosizer 2c. The weight-, number-, Z-average diameters and sizes distributions can be obtained.

Viscosity and surface tension of latex

The viscosities were determined by a rotational viscometer. Using the power model defined as equation (1) to calculate the shear forces (τ , N/m^2) at different shear rates ($\dot{\gamma}$, $1/\text{s}$), the consistency coefficient (K_{psu} , $\text{N} \cdot \text{s}^n/\text{m}^2$) and flow behavior index (n) would be gotten.

$$\tau = K_{\text{psu}} \cdot \dot{\gamma}^n \quad (1)$$

The surface tensions were measured by the ring method.

Film properties

The films were obtained by drying latexes at 85°C under the atmospheric pressure and vacuum respectively. The glass transition temperatures (T_g) of films were determined using a PE DSC-7. The amounts of the soluble polymer were established gravimetrically to calculate the fractions of insoluble polymer after films were subjected to successive extractions in acetone (AR) at boiling for 48 h.

PSA tape's properties

The PSA tapes were prepared by manual spreading the latexes on general 80g Kraft papers with $50 \pm 2 \text{ g/m}^2$ of dry spread, dried at 120°C for 15 min and tested for the 180° peel strength, tack and holding power.

RESULTS AND DISCUSSION

Influence of feed rate

Fig. 1 shows the overall conversion versus time curves of run V1 to V7. In all runs, the rates of polymerization reaction (R_p) increased with increasing the feed rates (R_a). Specifically in run V1 and V2 (0.33 g/min, 0.61g/min), conversions had a linear relationship to times, indicating that the polymerization of run V1 and V2 occurred under the monomer starved conditions. However, for run V3 to V7, in the initial stage, in which the monomer emulsion was continuously added, the polymer concentration was lower and R_p was low, too, so that the concentration of unreacted monomer increased. In this case, the system was like the flooded systems. With the increase in the amount of polymer, the surface offered by the particles increased, so the R_p increased and exhibited a linear relationship in time

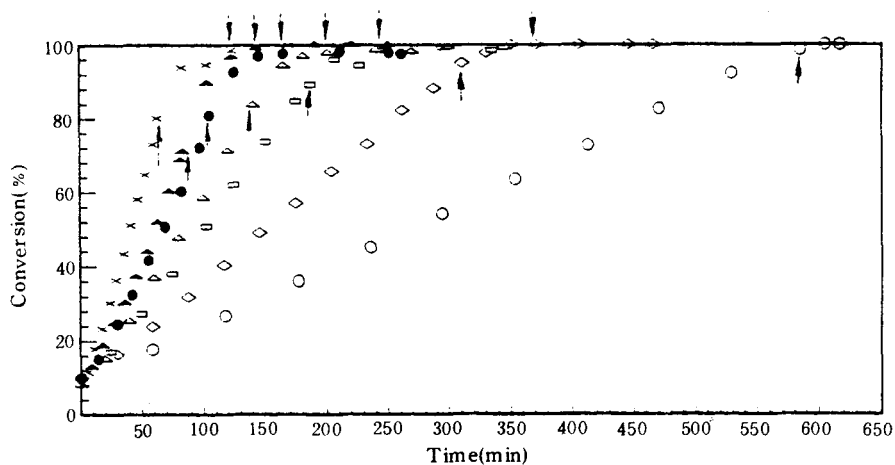


Fig. 1 The overall conversion versus time on the condition of different feed rate

- ↑ end point of emulsion addition
- ↓ start point of increasing temperature from 70°C to 75°C
- V1 ◇ V2 □ V3 △ V4 ● V5 ▲ V6 × V7

under the condition of an unchangeable R_a . It means that the reactant system varied from the flooded state to the starved. This was similar to the results of VAc, VAc and di-2-ethylhexyl maleate semicontinuous emulsion polymerization^[11-13]. Calculating the R_p of run V1 and V2 as well as the linear sections in run V3 to V7, the linear relationship of R_p to R_a was found

as equation (2).

$$\frac{1}{R_p} = \frac{1}{R_a} + 2341 \quad (2)$$

Where, R_p is the polymerization reaction rate per unit molar of monomer ($\text{mol/s} \cdot \text{mol}$), R_a is the monomer feed rate per unit molar of monomer ($\text{mol/s} \cdot \text{mol}$).

All runs gave stable latexes of almost 100% conversion with negligible coagulum. Table 2 shows the particle sizes and particle sizes distributions of latexes made at different R_a . Fig. 2 exhibits the viscosities and surface tensions of latexes. With the increment of R_a , the particle sizes, viscosities and surface tensions of latexes decreased and the particle sizes distributions were nearly constant. At a lower R_a , the slight aggregation of particles occurred and more particle numbers existed in polymerization system. In such a case, the amount of emulsifier added from the monomer emulsion to the polymerization system was insufficient to cover the great interface between particle and water. Consequently, this led to the system with high surface tension and viscosity. With the increase in R_a , the aggregation of particles increased. The amount of emulsifier continuously added to the system was sufficient to cover the relatively small particle-water interface. Then the surface tension decreased and remained low, the viscosity was low, too. As the aggregation of particles occurred during the polymerization process, the particle sizes distributions of all runs varied insignificantly and were almost constant.

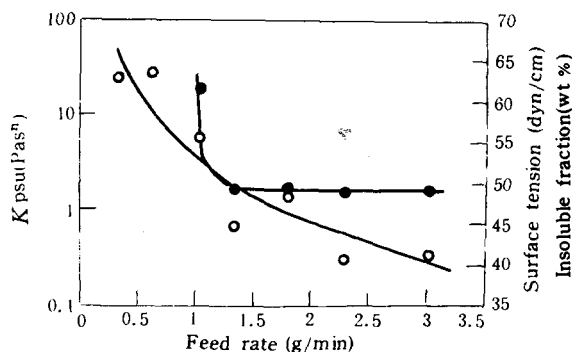


Fig. 2 The viscosity and surface tension of latexes versus different feed rate
● surface tension; ○ K_{psu}

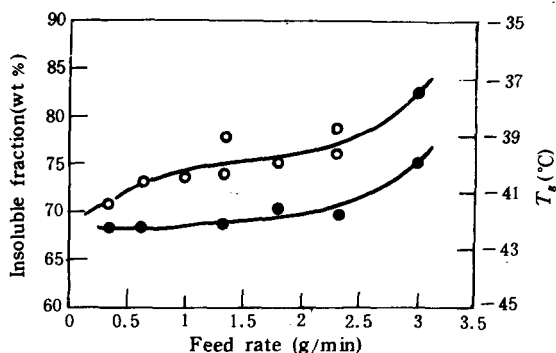


Fig. 3 Influence of feed rate on the glass transition temperature (T_g) and the insoluble fraction of the films
● T_g ; ○ insoluble fraction

Table 2 The particle sizes and particle sizes distributions at different feed rates

Run	Feed rate(g/min)	d_n (nm)	d_w (nm)	d_z (nm)	d_w/d_n
V1	0.33	147.2	169.6	178.0	1.152
V2	0.61	161.7	180.8	186.9	1.118
V3	1.02	171.1	187.1	193.2	1.094
V4	1.34	180.1	223.9	220.0	1.243
V5	1.81	206.8	239.8	234.3	1.160
V6	2.30	223.0	386.5	258.3	1.733
V7	3.01	218.8	241.3	239.2	1.103

As AA and HOPA were used in the present work, there existed the hydroxyl groups and carboxylic groups in the polymer, so they will cross-link themselves when heated to form the film. The cross-linking reaction is shown as follows.

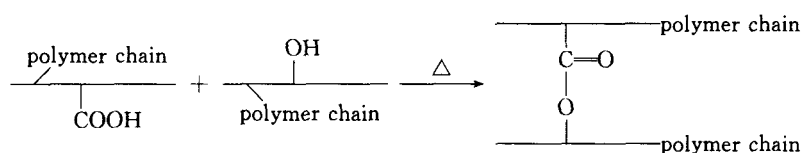


Fig. 3 shows that T_g and the insoluble fractions of films increased with the increment of R_a . The insoluble fractions are the grafting and cross-linking section in the polymer films. This result may be explained that a higher R_a results in higher ratios of monomer to particles and monomer to active centers, when the monomer mixture contains the cross-linking type monomers, HOPA and AA, the extent of grafting and cross-linking reaction will increase with increasing R_a . In addition, cross-linking reaction will continue further during film forming. Due to the higher grafting and cross-linking structure, the film had higher T_g .

The properties of PSA tapes, prepared from the latexes, are shown in Table 3. The PSA tapes produced at the higher R_a had the lower peel strength and tack, and the higher holding power. It indicated that the higher grafting and cross-linking contents as well as T_g would increase the peel strength and tack, but reduce holding power. This is opposite to the conclusion that the high branching frequencies are always preferred for PSA applications^[14]. For run V1, the higher holding power may be due to the more homogeneous copolymer composition at lower R_a .

Table 3 The properties of PSA tapes for different feed rates at $28 \pm 2^\circ\text{C}$, humidity $58 \pm 5\%$

Run	Feed rate (g/min)	Peel strength (N/25mm)	Holding power (min)	Tack (No.)
V1	0.33	5.92	107	10#
V3	1.02	7.33	3	10#
V4	1.34	4.84	55	9#
V5	1.81	6.67	>240	8#
V7	3.01	3.19	>240	8#

Effect of distribution of emulsifier

The ratio of emulsifier amount between the initial charge (R) and the continuously introduced monomer emulsion (E), $(R/E)_E$, is another important factor affecting the semicontinuous emulsion multi-copolymerization. Fig. 4 shows that R_p for run E2 to E5 were almost the same and increased slightly with the increase in $(R/E)_E$. It seems that R_p is mainly controlled by R_a although the larger particle numbers exist in seed latex for higher $(R/E)_E$. From Fig. 4, the phenomena, in which R_p varied from the flooded state to the starved, for all runs can also be seen.

Table 4 shows the particle sizes and particle sizes distributions of

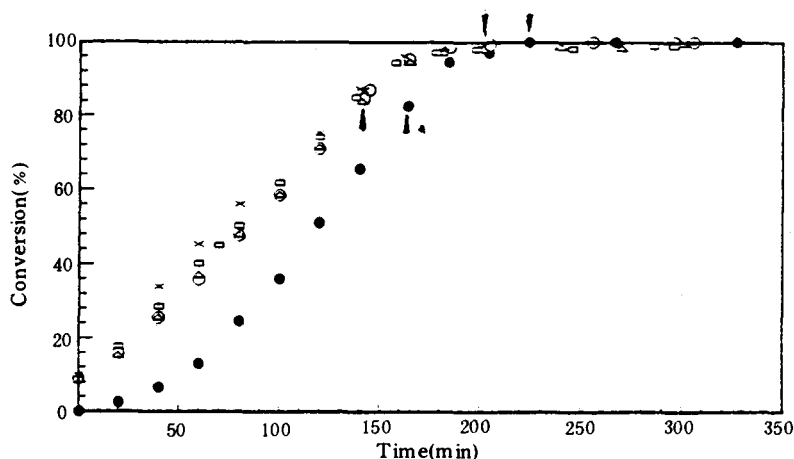


Fig. 4 The overall conversion versus time on the condition of different $(R/E)_E$

- ↑ end point of emulsion addition
 ↓ start point of increasing temperature from 70°C to 75°C
 ● E1 ○ E2 △ E3 × E4 □ E5

latexes for run E1 to E5 and Fig. 5 gives the viscosities and surface tensions of latexes simultaneously. All the latexes were almost 100% conversion with slight coagulum. As $(R/E)_E$ increased, the particle sizes decreased and the particle sizes distributions broadened slightly. This result was also given by Donescu^{[15][16]} for VAc and Snuparek^{[17][18]} for acrylates semicontinuous emulsion polymerization. The viscosities decreased and tended to be a constant, the surface tensions increased slightly with increasing $(R/E)_E$ as shown in Fig. 5. The increment of $(R/E)_E$ produced more particle numbers and led the particle sizes to decrease, meanwhile, it reduced the amount of emulsifier in the addition monomer emulsion and induced insufficient emulsifier to cover the great interface between particle and water phase, thus, increased the possibility of aggregation of particles. Consequently, this led to the surface tensions and particle sizes distributions increased. For run E2 to E5, two factors, the decrease in particle sizes and the increase in particle sizes distributions, compensated each other to keep the viscosities of latexes almost constant. Due to larger particle size and smaller particle sizes distribution, the latex of run E1 had a higher viscosity.

Table 4 The particle sizes and particle sizes distributions at different $(R/E)_E$

Run	$(R/E)_E$ wt	d_n (nm)	d_w (nm)	d_z (nm)	d_w/d_n
E1	0/100	280.9	366.3	283.8	1.304
E2	10/90	185.8	261.5	229.1	1.407
E3	30/70	180.1	223.9	220.0	1.243
E4	50/50	162.2	236.5	213.6	1.458
E5	70/30	164.4	219.9	212.6	1.338

The insoluble fractions and T_g of latex films versus $(R/E)_E$ are shown in Fig. 6. The larger the values of $(R/E)_E$, the higher the T_g and the more the insoluble fractions are. This result may be explained that the particle numbers in the polymerization system increased and produced the more active centers as the $(R/E)_E$ increased, thus led the grafting and cross-linking reaction increased.

The peel strength and tack decreased, and the holding power increased with the increase in the value of $(R/E)_E$ as shown in Table 5. It shows also that the higher grafting and cross-linking fraction as well as T_g are not benefit to the peel strength and tack though the holding power is high. So

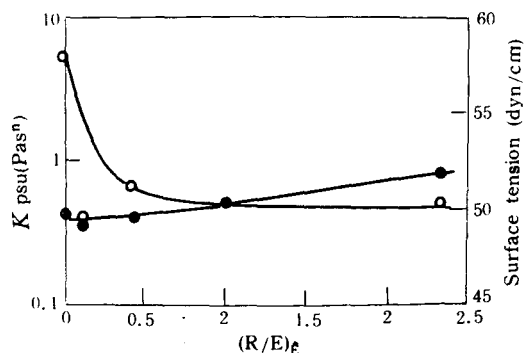


Fig. 5 The viscosity and surface tension of latexes versus different $(R/E)_E$

● surface tension; ○ K_{pas}

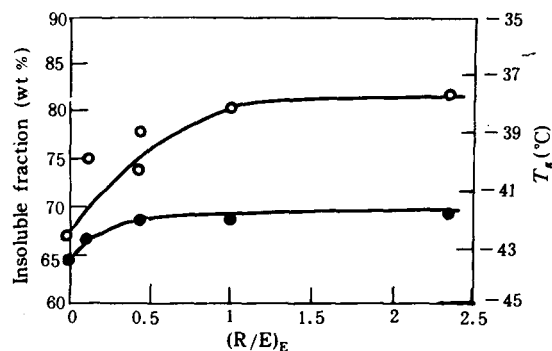


Fig. 6 Influence of $(R/E)_E$ on the glass transition temperature (T_g) and the insoluble fraction of the films

● T_g ; ○ insoluble fraction

the grafting and cross-linking section in the polymer film must be controlled within a suitable range to keep the balance of the peel strength, tack and holding power, leading the PSA tapes with good performance.

CONCLUSIONS

At the lower R_a (0.33g/min, 0.61g/min), conversions had a linear relationship to times. However, for the higher R_a , the polymerization systems existed the flooded state in the initial stage and varied from the flooded to the starved with the reaction continued. Meanwhile, the linear relationship of R_p to R_a existed in the starved state for all runs.

Table 5 The properties of PSA tapes for different $(R/E)_E$ at $28 \pm 2^\circ\text{C}$, humidity $58 \pm 5\%$

Run	$(R/E)_E$ wt	Peel strength (N/25mm)	Holding power (min)	Tack (No.)
E1	0/100	5.50	3	10 #
E2	10/90	5.54	3	8 #
E3	30/70	4.84	55	9 #
E4	50/50	4.40	60	8 #
E5	70/30	3.70		8 #

Although the same recipe, the different operation conditions can lead the high-solid content latexes to different properties. The viscosities and

surface tensions of latexes decreased, the particle sizes of latexes increased with the increment of R_a . Varying $(R/E)_E$ from 0/100 to 70/30(wt), the viscosities and particle sizes of latexes decreased, the surface tensions and particle sizes distributions increased.

The different operation conditions had an influence on the properties of films also. The larger the R_a and $(R/E)_E$, the higher the T_g and insoluble fractions were. Meanwhile, the properties of PSA tapes were affected by the operation conditions. The larger R_a and $(R/E)_E$ gave the PSA tapes with the lower peel strength, tack and the higher holding power. This was due to the effect of the grafting and cross-linking fraction in the polymer film. It means that the higher grafting and cross-linking fraction as well as T_g are not beneficial to the peel strength and tack though the holding power is high, they must be controlled within a suitable range for keeping the balance of the three types of strength to produce the PSA tapes with good performance.

Keywords:

Emulsion polymerization; Seeded semicontinuous polymerization; Latex; High-solid content; Acrylate; Pressure sensitive adhesives

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