

Modification Research on the Peel Strength of the Acrylate Emulsion Pressure-Sensitive Adhesives

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ABSTRACT: Pressure-sensitive adhesives (PSAs) were produced with latexes synthesized via starved semibatch emulsion polymerization processes with butyl acrylate, three different kinds of hard monomers [styrene (St), methyl methacrylate, and 2-phenoxy ethyl methacrylate (SR340)], acrylic acid, and 2-hydroxy ethyl acrylate. The management of both the copolymer composition and the polymerization process allowed us to control the behavior of the PSAs. For the acrylate latexes, the types of hard monomers and their contents, the concentration of buffer [bicarbonate (NaHCO_3)], and three kinds of semibatch processes were manipulated to modify the polymer properties. The performance of the PSA films cast from these latexes was evaluated by the peel strength. The results show that the PSA prepared with St exhibited the highest peel strength among the three hard monomers, and the latex synthesized by SR340 showed the largest gel content compared with the other two hard monomers. With increasing buffer, the latex particle size increased, and the peel strength initially increased to a maximum and then decreased. Nevertheless, the stability of the latexes decreased with increasing buffer concentration. In addition, the effects of the three kinds of semibatch processes on the peel strength of the PSA were also evaluated. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40095.

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic materials with permanent stickiness and can adhere strongly to solid surfaces upon the application of slight contact pressure under a relatively short contact time.¹ PSAs can be classified into five categories: natural rubber, thermoplastic elastomer, silicon, polyurethane, and acrylate PSAs. Acrylate PSAs have wide applications in fields such as tapes, labels, and protective films² because of their excellent adhesive properties, resistance to light and water, and aging performance.³ Although acrylate PSAs can be obtained by different polymerization processes (i.e., emulsion, solution, hot melting, and radiation curing), much attention has recently been devoted to the use of more environmentally friendly processes, such as emulsion polymerization.^{4–6} Commercially, acrylate monomers prepared for use in PSA formulations usually include butyl acrylate (BA) and/or 2-ethyl hexyl acrylate as the principal building-block monomers.⁷ BA and 2-ethyl hexyl acrylate as homopolymers or copolymers provide tacky dried polymer films with low glass-transition temperatures (T_g 's). However, to improve the room-temperature performance of PSA, it is necessary to increase their T_g 's;⁸ this can be achieved by copolymerization with high- T_g monomers such as methyl methacrylate (MMA), vinyl acetate, styrene (St), and acrylic acid (AA).

The adhesion properties of PSAs are characterized by three basic applicative properties: *tack* (the property that enables an adhesive to form a bond of measurable strength with a surface of another material upon brief contact under light pressure), *peel strength* [the force required to remove a standard PSA strip from a specified test surface under a standard test angle (90 or 180°) under standard conditions], and *shear strength* (the length of time it takes for a standard strip of PSA to fall from a test panel after the application of a load).⁹ From the basic research point of view, the peel properties of PSA are very interesting behavior. Recently, many researchers have undertaken a lot of work from every aspect to modify the peel strength of PSAs. Qu et al.¹⁰ reported the synthesis of a series of poly[(*n*-butyl acrylate)-*co*-(acrylic acid)] latexes with different particle sizes with changing levels of surfactant at the seed stage. They found that small latex particles gave adhesive films with a higher peel force at short adhesion times, whereas adhesive films from larger particles required more time to achieve their ultimate peel force. Xu et al.¹¹ discussed the effect of the hard monomer (MMA) content on the adhesive properties of poly(butyl acrylate-*co*-methyl methacrylate-*co*-acrylic acid) latexes. They found that the peel adhesion decreased with the MMA content; this was attributed to a reduction in the ability of the adhesive to wet the substrate. Shen et al.⁵ researched the effect of the

chain-transfer agent content on the PSA; they found an increase in the level of CTA at the growth stage from 0.0 to 0.15 wt % of the monomer caused the shear resistance to decrease and the peel force and loop tack to increase. They also examined a series of peel tests conducted at peel rates that were varied from 5 to 500 nm/min; at low peel rates, the PSAs exhibited cohesive failure, whereas at high rates, the PSA polymers failed adhesively. This was attributed to the viscous response to the rubbery one. Qie and Dubé¹² noted an increase in the peel strength of acrylic PSAs by their copolymerization with small levels of AA. Semibatch polymerizations have always been used in these syntheses of acrylate emulsions.^{13,14} They can generally be divided into several categories: unseeded semibatch,¹⁵ monomer-seeded semibatch,¹² and pre-emulsion-seeded semibatch¹⁶ polymerizations. However, no study to date has examined the effect of different semibatch processes on the peel strength of PSAs. Meanwhile, sodium bicarbonate (NaHCO_3) is usually used as a buffer in the emulsion polymerization to adjust the pH value of the system.^{17,18} However, few researchers have paid attention to the effect of NaHCO_3 on the peel strength of the PSAs.

In this study, acrylate PSA latexes were prepared by a semibatch emulsion polymerization. We compared the effects of three hard monomers [St, MMA, and 2-phenoxy ethyl methacrylate (SR340)] on the gel content, T_g , and peel strength of the PSAs. The influence of NaHCO_3 on the particle size, ζ potential, and peel strength was also studied. Finally, we examined the effects of different semibatch processes on the peel strength of the PSA.

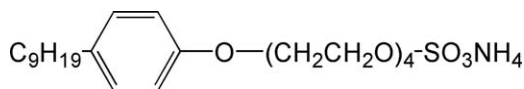
EXPERIMENTAL

Materials

Our materials included BA (technical grade, Shanghai Huayi Acrylic, China), methyl methacrylate (MMA; reagent grade, Shanghai Lingfeng Chemical, China), St (reagent grade, Shanghai Lingfeng Chemical, China), SR340 (technical grade, Sartomer Chemical, USA), AA (reagent grade, Shanghai Lingfeng Chemical, China), and 2-hydroxy ethyl acrylate (HEA; technical grade, Shanghai Huayi Acrylic, China). Ammonium persulfate (APS; technical grade, Shanghai Aijian Modern Reagent Factory, China) and NaHCO_3 (reagent grade, Shanghai Lingfeng Chemical, China) were used as the initiator and the buffer agent, respectively. All of these materials were used without further purification. The emulsifier used in this study was CO-458 (58–60%), which was supplied by Shanghai Honesty Fine Chemical (China), and it was used as received. Deionized water was used in all of the experiments. The structure of CO-458 is shown in Scheme 1.

Preparation of the Pre-Emulsion and Initiator Solutions

Amounts of 25 g of deionized water and 2.0 g of surfactant were added to a 500-mL, four-necked, round-bottomed flask and were stirred rapidly to make the emulsifier dissolve suffi-



Scheme 1. Structure of CO-458.

Table I. Emulsion Polymerization PSA Recipe

Component	Amount
Monomers (g) ^a	100
AA (mol %) ^b	2
HEA (mol %) ^b	2
CO-458 (g)	2.1
APS (g)	0.5
NaHCO_3 (g)	0–0.7
Deionized water (g)	105

^a Indicates the total weight of soft monomer (BA) and hard monomer (MMA or St or SR340).

^b On the basis of the total monomer weight.

ciently. Then, the monomer mixture listed in Table I was slowly added to the water–surfactant mixture through a constant-pressure funnel over 20 min. After that, the pre-emulsion was stirred for further 30 min.

Then, the initiator stock solution was prepared by the addition of 0.35 g of APS into 25 g of deionized water and continuously stirred until it was a homogeneous solution.

Polymerization Procedure

The emulsion polymerization was carried out in a four-necked, round-bottomed flask equipped with an electromotive stirrer, a thermometer, two separated addition funnels, and a reflux condenser. The basic recipe can be found in Table I. The theoretical solid content in the formulation was 50%. The concentrations of hard monomers in the polymer were varied from 2 to 10 wt % on the basis of the total amount of monomers. The content of NaHCO_3 in the polymer were varied from 0 to 0.7 g. In this study, acrylate latexes were prepared by three distinct semibatch technologies.

Unseeded Semibatch Emulsion Polymerization Process

A homogeneous aqueous solution containing 50 g of deionized water, 0.1 g of CO-458, and 0.1 g of NaHCO_3 was charged into a 500-mL, four-necked, round-bottomed flask. The stirring speed was maintained at 270 rpm throughout the experiments. When the temperature reached 70°C, an initiator solution containing 0.15 g of APS and 5 g of water was charged into the flask. Then, when the temperature reached $83 \pm 2^\circ\text{C}$, 130.76 g of pre-emulsion and 25.35 g of the initiator stock solution were added slowly to the flask with two separate constant-pressure funnels. The feeding times for the pre-emulsion and the initiator solution were 3.5 and 4.0 h, respectively. After the feed was completed, the reaction was allowed to proceed for an additional 1 h to increase the monomer conversion. The latex was then cooled to room temperature and poured into a glass bottle to be used for further characterization.

Monomer-Seeded Semibatch Emulsion Polymerization Process

A homogeneous aqueous solution containing 50 g of deionized water, 0.1 g of CO-458, and 0.1 g of NaHCO_3 was charged into a 500-mL, four-necked, round-bottomed flask. The stirring speed was maintained at 270 rpm throughout the experiments. When

the temperature reached 70°C, an initiator solution containing 0.15 g of APS and 5 g of water and a monomer mixture containing 5.7 g of BA and 0.3 g of MMA were charged into the flask to form the seed latex. Then, when the temperature reached 83 ± 2°C, 124.76 g of pre-emulsion and 25.35 g of the initiator stock solution were added slowly to the flask with two separate constant-pressure funnels. The feeding times for the pre-emulsion and the initiator solution were 3.5 and 4.0 h, respectively. After the feed was complete, the reaction was allowed to proceed for an additional 1 h to increase the monomer conversion. The latex was then cooled to room temperature and poured into a glass bottle to be used for further characterization.

Pre-Emulsion-Seeded Semibatch Emulsion Polymerization Process

A homogeneous aqueous solution containing 50 g of deionized water, 0.1 g of CO-458, and 0.1 g of NaHCO₃ was charged into a 500-mL, four-necked, round-bottomed flask. The stirring speed was maintained at 270 rpm throughout the experiments. When the temperature reached 70°C, 6 g of pre-emulsion and an initiator solution containing 0.15 g of APS and 5 g of water were charged to the flask to form the seed latex. Then, when the temperature reached 83 ± 2°C, 124.76 g of pre-emulsion and 25.35 g of the initiator stock solution were added slowly to the flask with two separate constant-pressure funnels. The feeding times for the pre-emulsion and the initiator solution were 3.5 and 4.0 h, respectively. After the feed was complete, the reaction was allowed to proceed for an additional 1 h to increase the monomer conversion. The latex was then cooled to room temperature and poured into a glass bottle to be used for further characterization.

Characterization

Particle Size and ζ Potential. The particle sizes and ζ potential values of the latexes were measured with a dynamic light scattering instrument (Malvern NanoS Zetasizer). The analyses were carried out at 25°C, and every result was an average of three parallel measurements. The latex was diluted until the solid content was about 1%. The reported diameter is an intensity-weighted average particle size. The polydispersity index (PDI) values given by the instrument reflected a narrower distribution, with PDI values closer to 0.01. Latexes having a PDI smaller than 0.1 were considered to have a narrow particle size distribution (PSD). The detection range of the instrument was 0.6 nm to 6 μ m. On the basis of the principles of electrophoretic light scattering, quantitative measures of the charge on colloidal particles in a liquid suspension were performed.

T_g . Differential scanning calorimetry (DSC) was used to test the T_g values. A model 204 F1 DSC instrument from Netzsch Instruments was used. Amounts of 5–15 mg of dry polymer were weighed into standard DSC hermetic alumina crucibles. High-purity nitrogen was used as a purge gas with a gas flow rate 20 mL/min. The sample was first cooled to -70°C and then raised from -70 to 50°C at a heating rate of 10°C/min. T_g was calculated from the inflection point in the reversed heat flow curve with the software provided.

Gel Content. The gel was separated from the soluble polymer by exhaustive Soxhlet extraction for 24 h with a thimble with tetra-

hydrofuran as the solvent. The gel polymers left in the thimble were dried in a vacuum oven at 70°C until they reached a constant weight. The weights of the remaining dry gels were taken, and the gel contents were calculated with the following equation:

$$\text{Gel content} = \frac{\text{Mass of the dry gel}}{\text{Mass of the initial dry polymer}}$$

PSA Testing. The prepared latexes were adjusted to pH 7 with a 25 wt % ammonia solution. After that, they were coated with an RK KHC.10.5 wire-rod coater (Manchester, United Kingdom) onto a poly(ethylene terephthalate) (PET) strip with a thickness of 30 μ m, a width of 25 mm strip to give a film with a dry thickness of 20 μ m and dried in a vacuum oven at 105°C for 3 min. The PET strips with adhesive coated on its one side were stuck on release paper for further tests. Before tests, the PET strips were conditioned for 24 h at standard conditions of temperature and humidity (23 ± 2°C and 50 ± 5% relative humidity). A universal BLD-100S electronic stripping tester was used to evaluate the peel strength. For the 180° peel test, strips of the adhesive-coated films were laminated onto a stainless steel substrate with the help of a 2000 ± 50 g press roll. The press roll was passed through the PET strip front to back three times. Placed 0.5 h later, the substrate and the strip were inserted into the both grips, respectively, and then, the upper grip was set to move upward at a speed of 300 mm/min. The average force per 25 millimeters required to peel the strip from the substrate was recorded and reported as the 180° peel strength, and every result was an average of five parallel measurements.

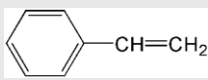
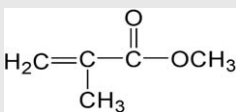
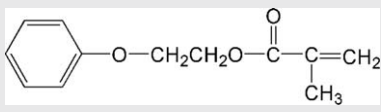
RESULTS AND DISCUSSION

Influence of the Hard Monomers on the Gel Content and T_g Values of the Latexes

In this experiment, PSA latexes with different hard monomers were synthesized by unseeded semibatch emulsion polymerization technology. The content of NaHCO₃ was 0.1 g and was kept constant. Table II gives some of the physicochemical properties for the hard monomers used in this study.

The gel content is an important parameter, which contributes to the adhesion performance of PSAs and has been shown to be strongly influenced by the hard monomers. As we know, when a BA-rich monomer mixture is polymerized in the absence of a crosslinker, a gel is formed by a chain-transfer mechanism, and it involves two steps: (1) branch radical formation via either intramolecular chain transfer by back-biting or intermolecular chain transfer to polymer due to the presence of labile hydrogen in the BA unit of the polymer chains^{19–21} and (2) gel formation through combination termination between the branched polymer radicals.²² As shown in Table III, as the structure in both MMA and SR340 did not contain tertiary carbon atoms, the higher contents of both monomers were, the lower the gel contents were. The result was consistent with the work of Araujo et al.,²³ who found that increasing the level of copolymerized MMA served to lower the gel content. On the other hand, the gel content of the PSA decreased with the St content, and the results can be interpreted in terms of the reactivity of propagating radicals with St end units compared to those with BA end units. The St radicals had a much lower reactivity and longer lifetimes than the BA radicals and had a very much lower

Table II. Physicochemical Properties of the Hard Monomers

Property	St	MMA	SR340
Molecular structure			
Molecular formula	C ₈ H ₈	C ₅ H ₈ O ₂	C ₁₂ H ₁₄ O ₃
Molecular weight	104	100	206
T _g (°C)	100	105	54

tendency to abstract hydrogen atoms from acrylic repeat units. This combination of effects led to a reduction in chain transfer to the polymer and branching.²⁴ For the latex prepared with St, the gel content was lower than that of its MMA counterpart. The reason was that as the nonacrylic monomer (St) was added, the intermolecular chain transfer to the polymer decreased, so the gel content decreased.²⁵

T_g is one of the most important factors affecting PSA performance. Thus, in this study, T_g was determined for each final polymer latex. When the amounts of all of the other components in the polymerization recipe were kept constant, the final value observed should have been dependent only on the ratio of monomers in the recipe. Only one transition was observed in the temperature range from -70 to 50°C for all of the final latexes; this indicated that the copolymers had a homogeneous composition. The T_g's of the polymers with different hard monomers in the growth stage are given in Table III. It was obvious that T_g increased with the hard monomers content as expected. In fact, the T_g values of the respective polymers increased linearly with increasing amount of hard monomers, as shown in Figure 1. Moreover, we observed that the T_g curves of the PSAs prepared with three kinds of hard monomers were nearly parallel to each other. This similarity in T_g was likely caused by the similar polymer microstructures of these PSAs. In the meantime, the latex prepared with St had a similar T_g value compared with MMA counterpart because of their equivalent T_g (MMA T_g = 105°C and St T_g = 100°C). The latex prepared with SR340 showed the lowest T_g value among the three hard monomers; this was caused by its own lowest T_g (SR340 = 54°C).

Influence of the Hard Monomers on the Peel Strength of the PSAs

Surface force interactions play a significant role in PSA bonds. The adsorption of the adhesive molecules onto the adherent

surfaces occurs mainly by physical adsorption. In physical adsorption, the attractive forces for the adhesive molecule to the adherent surface are secondary to van der Waal's forces. Yang²⁶ found that for polyacrylic samples, the surface tensions were in the range between 31 and 37 dyn/cm. Because the surface tension of the stainless steel was 44 dyn/cm, we can expect good wetting to be achieved for all samples. Thus, the PSAs need the polymers to be soft, capable of wetting the adherent surface, and capable of sufficient cold flow to fill the surface irregularities.

The peel testing results are shown in Figure 2. We observed that the peel strength increased up to a maximum with increasing St content; beyond this maximum, the adhesive became too stiff and did not wet the surface appropriately. This reduced the peel strength. The result was consistent with the works of Benedek and Heymans¹ and Roberge and Dubé.⁹ On the other hand, the peel strength decreased with increasing proportion of MMA and SR340 contents; this was mainly because that as the levels of these two hard monomers increased, the interfacial adhesion became lower. This may have been due to the incomplete wetting of the substrate as a consequence of a lower polymer mobility, which was caused by the rigid structure of these two hard monomers. In the meantime, we found that when St was used as the hard monomer, adhesive failure was observed during the process of the peeling test (except when the dosage of St was 10 wt %). On the contrary, there were no residues on the stainless steel panel when the other were two used as the hard monomers.

The effect of the gel content on the adhesion properties in this range may have been correlated with the bonding of the adhesive. The lower the amount of gel in the adhesive was; the more efficient the bonding process of the adhesive to the substrate was. The high amount of gel negatively influenced the adhesion properties, and a minimal amount of soluble sol fraction was

Table III. Influence of the Hard Monomers on the Gel Content and T_g

Hard monomers (g)	Gel content (%)			T _g (°C)		
	MMA	St	SR340	MMA	St	SR340
2	58.7	56.5	67.4	-36.80	-37.32	-38.15
5	54.6	52.8	65.3	-34.79	-35.21	-36.25
8	50.8	47.3	61.4	-32.02	-32.41	-33.46
10	48.9	45.2	58.8	-30.31	-30.56	-31.68

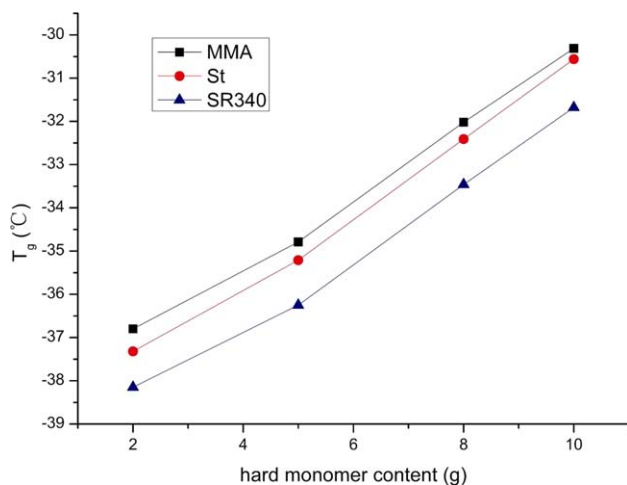


Figure 1. Relationship between the T_g and hard monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

needed for the successful wetting of the adhesive with the substrate. These could be used to explain why the peel strength of the PSA obtained by SR340 was smaller than the PSA prepared with St or MMA.

In conclusion, the peel strength was significantly affected by the types and concentration of the hard monomers used, as shown in Figure 2. The peel strength of the final latex PSAs prepared with different kinds of hard monomers under the same amounts in decreasing order was $St > MMA > SR340$.

Influence of $NaHCO_3$ on the Particle Size and ζ Potential of the Latexes

In this experiment, PSA latexes with different amounts of $NaHCO_3$ were prepared by a monomer-seeded semibatch emulsion polymerization process. MMA was used as the hard monomer, and its content was kept constant at 5 g.

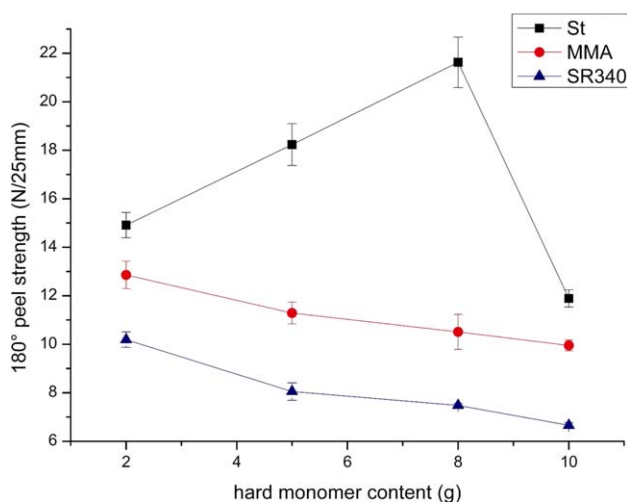


Figure 2. Relationship between the 180° peel strength and hard monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

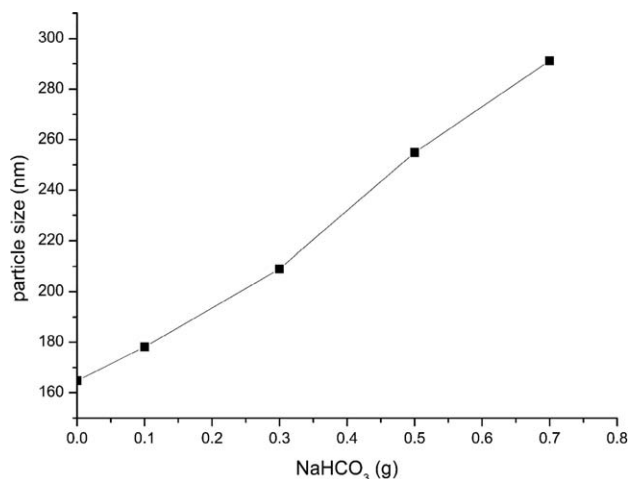


Figure 3. Relationship between the particle size and amount of $NaHCO_3$.

The particle size increased with increasing amount of $NaHCO_3$, and a good linear relationship between the particle size and amount of $NaHCO_3$ is shown in Figure 3. The result was consistent with the work of Chern and Hsu,²⁷ who found that the resulting latex particle size increased with increasing electrolyte concentration in the initial reactor charge. There may have been two reasons for this:

1. The experiment showed that the pH value of the latex was less than 3 in the absence of $NaHCO_3$. When $NaHCO_3$ was introduced, the thermal decomposition rate of APS and the concentration of the free radicals decreased because of the increased pH value, and the nucleation rate in the aqueous phase decreased. This resulted in a decrease in the number of polymerization loci,²⁸ so the latex particle size increased.
2. $NaHCO_3$ was not only a buffer but also an electrolyte. When it was introduced, the more mobile cationic ions (Na^+) derived from the hydrolysis of $NaHCO_3$ rather than the less mobile quaternary amino ions derived from the hydrolysis of APS were considered to be preferentially located in the Stern layer surrounding the polymer particles, and they effectively neutralized the anionic charge on the surface²⁹ and compressed the electrical double layer surrounding the polymer particles. This resulted in the coalescence of the particles to increase the particle size.

The PDI values reflected the PSD. The smaller the PDI value was, the better the monodispersity of the particle was. We observed that the PSD of these latexes was very narrow with a PDI of less than 0.1 when the concentration of $NaHCO_3$ was below 0.7 g; this suggested that the monodispersity was comparatively good. This was also consistent with the assumption that neither secondary particle nucleation nor coagulation occurred during the semicontinuous polymerization process.³⁰ The appearance of these latexes was translucent. Nevertheless, when the amount of $NaHCO_3$ was 0.7 g or above, the PSD of the latex was very broad, with a PDI of greater than 0.1. This was caused by the coalescence of latex particles. The appearance of the latex at this moment was milk white and opaque.

Table IV. Some Parameters of the Final Data for the Latexes with Different NaHCO_3 Contents

NaHCO_3 content (g)	Final particle size (nm)	PDI of the final latex	ζ potential (mV)	180° peel strength (N/25 mm)
0	164.8	0.018	-61.5	8.83
0.1	178.1	0.018	-55.4	10.62
0.3	209.0	0.019	-46.9	12.05
0.5	254.9	0.033	-29.0	8.36
0.7	291.2	0.194	-24.4	8.43

The ζ potential value, as an important measurement standard for the stability of the latex, indicated the thickness of the electrical double layer, which plays a decisive role in repellency between particles. If all of the particles have a large negative or positive ζ potential, they would repel each other, and there would be no tendency for them to aggregate together. Generally, particles with ζ potential values more positive than 30 mV or more negative than -30 mV are regarded as stable, and their latexes would have a long-term good stability when the absolute value of ζ potential is higher than 40 mV.³¹ The absolute value of the ζ potential of the final latex showed a decreasing trend with the amount of NaHCO_3 , as shown in Table IV. This was, to some extent, because of the counter ions generated from the dissociation of NaHCO_3 in the aqueous phase, which weakened the anionic charge distribution on the surface of latex particles. Meanwhile, we found that when the amount of NaHCO_3 was greater than 0.5 g, the stability of the latex became worse, and coarse particles appeared during the polymerization process.

Influence of NaHCO_3 on the Peel Strength of the PSAs

The distribution of carboxyl groups in the latex was obviously influenced by the amount of NaHCO_3 . With increasing amount of NaHCO_3 , the amount of surface carboxyl increased.²⁸ As we know, the peel strength increased with increasing amount of surface carboxyl because of the formation of hydrogen bonds.¹² On the other hand, the larger the particle size was, the smaller the peel strength was. This was thought to be because large particles could not quickly conform to nanometer-scale roughness on the surface of the stainless steel plate and thus reduce the area of contact between the adhesive and the adherent, so during the drying process, perhaps the large particle sizes imparted some inherent weaknesses to the peel strength property at their lowest packing density. The effect of NaHCO_3 on the 180° peel strength in this study may have been a combination of these two aspects. From Table IV and Figure 4, we can see that when the amount of NaHCO_3 was below 0.3 g, the peel strength increased with increasing in the NaHCO_3 concentration; this may have been due to the increasing amount of surface carboxyls. The effect of the surface carboxyls on the peel strength was predominant here. Nevertheless, when the amount of NaHCO_3 was above 0.3 g, the peel strength decreased with increasing NaHCO_3 concentration; this was mainly at a larger particle size, the effect of the particle size on the peel strength was predominant at this moment. In conclusion, the buffer NaHCO_3 had a significant effect on the particle size, ζ potential, and peel

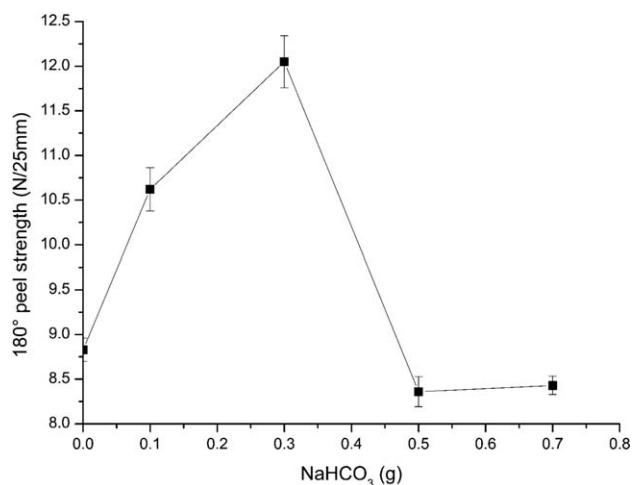


Figure 4. Relationship between the 180° peel strength and amount of NaHCO_3 .

strength of the latexes. The peel strength reached a maximum when the concentration of NaHCO_3 was 0.3 wt %.

Influence of Different Semibatch Processes on the Particle Size and ζ Potential Values of the Latexes

Table V clearly shows that the latex particle size in decreasing order was as follows: Monomer-seeded semibatch > Unseeded semibatch > Pre-emulsion-seeded semibatch. When we adopted the monomer-seeded semibatch process, the concentration of the emulsifier in the initial stage was lowest among the three methods and produced the least number of micelles; this resulted in the biggest latex particle size.^{32,33} However, when we used the pre-emulsion-seeded semibatch technology, the concentration of the emulsifier in the initial stage was highest compared with the other two methods; therefore, the number of polymerization loci was largest, and this led to the smallest latex particle size. The unseeded semibatch emulsion polymerization showed intermediate particle size behavior. In addition, the PSD values of the latexes synthesized by these processes were all very narrow, with PDI values of less than 0.1. As shown in Table V, all of the ζ potential values were below -60 mV; this indicated excellent stabilities in the latexes.

Influence of Different Semibatch Processes on the Peel Strength of the PSAs

The peel strength testing results are shown in Table V and Figure 5. The latex PSA prepared with the pre-emulsion-seeded semibatch process showed the largest peel strength because of its smallest particle size¹⁰ among the three methods. This could

Table V. Some Parameters of the Final Data for the Latexes with Different Semibatch Processes

Semibatch process	Particle size (nm)	PDI of the final latex	ζ potential (mV)	180° peel strength (N/25 mm)
Unseeded	148.3	0.023	-64.9	13.23
Pre-emulsion-seeded	141.4	0.008	-63.7	15.07
Monomer-seeded	172.7	0.013	-61.3	11.29

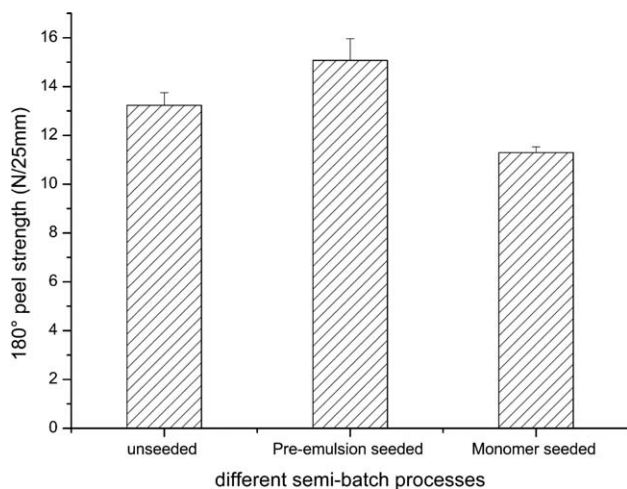


Figure 5. Relationship between the 180° peel strength and different semi-batch processes.

be explained by the fact that the latex PSA with a small particle size exhibited a good ability to flow uniformly and wet the substrate surfaces; this resulted in continuous adhesion between the adhesive and the substrate and led to a large peel strength. However, with a similar particle size, the latex PSA synthesized by unseeded semibatch technology showed a smaller peel strength than its pre-emulsion-seeded semibatch counterpart. This may have been caused by its broader PSD.¹⁷ As discussed previously, different kinds of semibatch polymerization processes had significant effects on the properties of latex PSA. The 180° peel strength in decreasing order was Pre-emulsion-seeded semibatch > Unseeded semibatch > Monomer-seeded semibatch.

CONCLUSIONS

In this study, PSAs were produced with latexes synthesized via starved semibatch emulsion polymerization processes with BA, three different kinds of hard monomers (St, MMA, and SR340), AA, and HEA. The main conclusions derived were as follows:

1. The type and content of hard monomers had significant effects on the properties of latex PSAs. When the hard monomer content increased, the gel content of the latexes decreased, and T_g increased, as expected. Moreover, the T_g curves of the PSAs prepared with three kinds of hard monomers were nearly parallel to each other because of the similar polymer microstructures of these PSAs. The peel strength increased up to a maximum with increasing St content; beyond this maximum, the adhesive became too stiff and did not wet the surface appropriately. Hence, the peel strength decreased. On the other hand, the peel strength decreased with increasing proportion of MMA and SR340 content. This was mainly caused by the rigid structure of these two hard monomers. PSA prepared with SR340 showed the lowest peel strength among the three kinds of hard monomers because of the highest gel content of the latex. The peel strength of the final latex PSAs prepared with different kinds of hard monomers in decreasing order was St > MMA > SR340.
2. The buffer (NaHCO_3) used in the emulsion polymerization had great effects on the properties of the latex PSA. The particle size increased with increasing amount of NaHCO_3 , and a good linear relationship between the particle size and the amount of NaHCO_3 was observed. The PSD of the latex became broader with the NaHCO_3 content because of particle coalescence. However, the stability of the latex decreased when the concentration of NaHCO_3 increased because of the counter ions generated from the dissociation of NaHCO_3 in the aqueous phase. This weakened the anionic charge distribution on the surface of the latex particles. The peel strength increased with increasing NaHCO_3 concentration when the amount of NaHCO_3 was below 0.3 g, and above 0.3 g, the peel strength decreased.
3. Different semibatch polymerization technologies play significant roles in the modification of the properties of latex PSAs.

The latex particle size in decreasing order was as follows: Monomer-seeded semibatch > Unseeded semibatch > Pre-emulsion-seeded semibatch. The 180° peel strength in decreasing order was as follows: Pre-emulsion-seeded semibatch > Unseeded semibatch > Monomer-seeded semibatch.

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