Preparation and Characterization of the Latexes with Different Particle Sizes by Semibatch Emulsion Polymerization and the Influence on Properties of Waterborne Pressure-Sensitive Adhesives

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ABSTRACT: Increasing environmental concerns and regulations are the major driving forces for the development of waterborne pressure-sensitive adhesives. This article reported the synthesis of a series of poly[(*n*-butyl acrylate)-*co*-(acrylic acid)] latexes with different particle sizes using a semibatch emulsion polymerization process. By changing the levels of surfactant (Aerosol Series) at the seed stage, the *z*-average particle diameters (d_zs) measured with dynamic light scattering varied from 124 to 366 nm. The polymerizations proceeded under monomer-starved conditions, and the values of d_z measured for samples removed during the polymerizations were consistent with theoretical prediction for particle growth spherically without the secondary nucleation. The gel contents of the polymers were determined by Soxhlet extraction, and the molecular parameters were characterized by gel permeation chromatography and dynamic mechanical thermal analysis. The adhesive properties, loop tack, peel force, and shear resistance were measured according to the Fédération Internationale des Fabricants et Transformateurs d'Adhésifs et Thermocollants sur Papiers et Autres Supports (FINAT) test methods. The results were reported and correlated with the latex particle size and molecular parameters. The spatial architecture of gel domains in the dry film and the molecular connectivity between those gel domains play an important role in controlling its adhesive properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3030–3040, 2009

Key words: adhesion; dynamic light scattering; emulsion polymerization; structure–property relations

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are characterized by instantaneous adhesion upon the application of light pressure. The most common products are tapes, labels, and protective films. Although PSAs can be obtained by different manufacturing processes (i.e., emulsion, solution, hot-melt, and radiation curing), much attention has recently been devoted to the utilization of more environmentally friendly processes such as emulsion polymerization.[1–3] Emulsion polymerization not only offers better environmental compliance but also advantages such as a wide selection of raw materials, better control of final product properties, and a low possibility of runaway reactions because of the utilization of water as the dispersion medium.

The process used in an emulsion polymerization affects the composition of the copolymer formed. The batch process is carried out by adding all the reactants at the beginning and allowing the reaction to proceed to completion with agitation.[1,2] The higher quantity of monomer droplets associated with batch processes can also give a decrease in colloid stability, with excessive amounts of coagulum formed during the reaction, whereas the semicontinuous batch process can be used as a seeding technique, i.e., a small particle size seed latex is charged to the reactor as a preformed latex or is formed *in situ* in the first stage of a two-stage polymerization. This is the so-called core-shell emulsion copolymerizations, which have long been used in industry to combine the desirable

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properties of the core and the shell polymers. For example, core and shell polymers differing in T_gs may be used to modify the properties of latex-based paints and adhesives. Effects of components and their miscibility upon waterborne PSAs have been previously studied.[4–10] Despite the common knowledge that the particle size of a polymer aqueous dispersion can influence the final properties of this film cast, less work has been dedicated to systematically cover the influence of particle size on the adhesive properties of PSAs.

This work involved the preparation and characterization of waterborne PSAs from the latexes with different particle sizes. Sequential emulsion polymerization was used to form different particle sizes of poly(*n*-butyl acrylate) [Poly(BA)] seed particles, which were then to be grown by the formation of poly[(*n*-butyl acrylate)-*co*-(acrylic acid)] [Poly(BA-*co*-AA)]. PSAs were, therefore, designed to consist of poly(BA) core with outer shell of poly(BA-*co*-AA). They were used to study the effects of particle size and molecular parameters on adhesive properties.

EXPERIMENTAL

Materials

Potassium persulfate (KPS, 99%; Aldrich, Lancaster, UK), *tert*-dodecylmercaptan (TDM; Fluka, Gillingham, UK) were used as supplied. The anionic surfactant used in the study was Aerosol Series obtained from Cytec (Hevens City, The Netherlands). *n*-Butyl acrylate (BA) monomer (98%; Aldrich) was freed of inhibitor by washing it with a 2% NaOH solution using the same volume of monomer for three times, followed by repeated washing with water for several times. The monomer was then dried with $CaCl_2$ overnight. The inhibitor was removed from acrylic acid (AA, 99%; Aldrich) just before use by passing through a column of activated aluminum oxide. Hydroquinone (99%; Aldrich) was used as an inhibitor of the latexes taken from the emulsion polymerization procedure. Deionized water was used in all the preparations.

Latex preparation

PSAs were prepared as 50% solid latexes by semicontinuous emulsion polymerization involving two sequential stages, seed stage and growth stage.[4] The weighed surfactant (1.0, 2.5, 5.0, and 7.5 g) and water (700 g) were added to a 3-L flanged reaction flask. The flow of nitrogen was started, and the water batch temperature was attained at 75°C. During the following 30 min, the seed-stage BA monomer (50.0 g, 5 wt % of total monomer) was added to the surfactant solution and stirred for 10 min before KPS (2.15 g) dissolved in water (100 g), which was added to start the reaction. The seed stage was 60 min. In the growth stage, the preemulsified monomer mixture of BA (922.64 g) and AA (27.36 g; 95 mol % BA : 5 mol % AA) with surfactant (11.88 g) and TDM (0.333 g) were pumped using a Watson-Marlow peristaltic pump (Model 505S) at a rate of ~ 5.34 g/min in 3 h. KPS (0.215 g) dissolved in distilled water (50.0 g) was added to the reaction flask at 115, 175, and 235 min. After the completion of the addition of the growth-stage reactant mixture, a further 60 min was allowed before the latex was cooled to room temperature and filtered through a 53-μm sieve to obtain the coagulate content. For the latex sample of 20.0 g of surfactant, the lack of control of the growth particles would appear if we used the same feeding procedure as described earlier. The changes to the procedure were as follows. The surfactant (20 g) and water (700 g) were added to a 3-L flanged reaction flask. The flow of nitrogen was started, and the water batch temperature was attained at 75°C. During the following 30 min, the seed-stage BA monomer (50 g) was added to the surfactant solution and stirred for 10 min before KPS (2.15 g) dissolved in water (100 g) was added to start the reaction. After 60 min, the addition of BA (92.26 g) and AA (2.74 g) was fed over 30 min by syringe pump at a rate of 3.167 g/min, and then allowed a further 30-min reaction. The total time at the seed stage for this latex was 120 min. In the growth stage, the preemulsified monomer mixture of BA (830.38 g) and AA (24.62 g) with surfactant (11.88 g) and TDM (0.333 g) were pumped using a Watson-Marlow peristaltic pump (Model 505S) at a rate of ~ 4.818 g/min in 3 h. KPS (0.215 g) dissolved in distilled water (50 g) was added to the reaction flask at 115, 175, and 235 min. After the completion of the addition of the growth-stage reactant mixture, a further 60 min was allowed before the latex was cooled to room temperature and filtered through a 53-μm sieve to obtain the coagulate content. Residual monomer was measured using gas chromatograph/mass spectrometer (GC/MS) and was less than 0.1% on the basis of the wet latex weight.

Characterizations

Conversion and particle size measurement of the latexes

At 30-min intervals, samples of the latex (10 mL) were removed into preweighed vials containing 1 mL hydroquinone solution to prevent the further polymerization; these were surrounded by ice to quench the polymerization and then analyzed gravimetrically to determine the instantaneous conversion (on the basis of the monomer fed until the sampling time) and overall conversion (on the basis of the monomer fed in the full emulsion polymerization process). A

Brookhaven BI-9000AT dynamic light scattering (DLS) was used to determine the particle size of the latex samples with cumulants analysis of 90° scattering data. Analyses were carried out at 25°C ± 0.1°C.

Solvent extraction and molecular weight measurement

The soluble polymer fractions were separated from poly(BA-*co*-AA) polymers by the extraction of the dried latexes with boiling tetrahydrofuran (THF) for 2 days by means of Soxhlet extraction. The addition of the dried latex was about 0.5 g, which was put into a thimble. The insoluble polymers left in the thimble were dried in the breezy cupboard overnight, and finally dried in a vacuum oven at 60°C for 48 h to obtain the gel content, which was considered the ratio of the insoluble polymer content to the initial polymer content by weight. The soluble polymers were subjected to molecular weight measurements with a Knauer Type 64 HPLC pump equipped with refractive-index detector (Knauer Type 98 differential refractometer) and data system (PL Caliber® Version 6.0). THF was used as the flow phase. A calibration curve was constructed using polystyrene standards.

Zeta potential

The latex was diluted with deionized water to 5 wt % colloid concentration under mechanical stirring. The value of zeta potential was determined by ESA 9800 (Metac Applied Sciences) at 25°C.

Transitional behavior

The analysis was carried out using a Rheometrics Mechanical Spectrometer (RMS-800). The plate sample with typical dimensions of $40 \times 10 \times 2$ mm^3 was prepared through cast molding. Analysis was carried out in the temperature, ranging from −120 to +50°C at a heating rate of 5°C/min and a frequency of 1 Hz. Glass transition temperatures (T_gs) were located from the peaks in the loss tangent.

Latex coating and PSA testing

The latexes prepared were adjusted to pH 5.5 with a 25 wt % ammonia solution and filtered again. After that, they were coated with a Elcometer (Manchester, UK) 4360/15 bar onto 36-μm-thick poly(ethylene terephthalate) to give a film with a dry thickness of 30 μm and dried at 105°C for 4 min. Adhesive bonds were formed by the application of a standard 2-kg roller passing over twice. All adhesive testing was performed at 23 and 50% relative humidity, and the samples were climatized into this condition 24 h before testing. Loop tack and 180° peel were done with a stainless steel substrate. Test methods were in accordance with the Fédération Internationale des Fabricants et Transformateurs d'Adhésifs et Thermocollants sur Papiers et Autres Supports (FINAT) test methods Nos. 9 and 1 at 300 mm/min. Shear resistance was done using a glass plate substrate with a 25×25 mm^2 poly(ethylene terephthalate)-coated strip and a 1000 g hanging weight according to FINAT test method No. 8. The average values were from five trials.

RESULTS AND DISCUSSION

Latex preparations with different particle sizes

Emulsion polymerizations were carried out on a 3-L scale at a temperature of 75°C. The overall reaction time was 5 or 6 h. This consisted of a 1- or 2-h seed stage, followed by 3 h of monomer addition at the growth stage and finally a further 1 h of reaction to ensure complete polymerization. Samples were taken at 30-min intervals during the polymerization to monitor the conversion and particle growth.

The samples removed from polymerization contained volatile materials (unreacted monomer and water) and nonvolatile materials (polymer, surfactant, and initiator). The conversion of volatile monomer into nonvolatile polymer, therefore, can be monitored by measuring the latex solid content. The instantaneous and overall conversions are calculated for each of the aliquots taken using a mass balance approach from the solid content measured at each sampling time.

$$\text{Instantaneous conversion \%} = \left(\frac{\text{Mass of polymer formed}}{\text{Mass of monomer added}}\right) \times 100 \quad (1)$$

where the mass of monomer added is the sum of the monomer at the seed stage and any monomer that has been added at each sampling time during the growth stage.

$$\text{Overall conversion (\%)} = \left(\frac{\text{Mass of polymer formed}}{\text{Total mass of monomer}}\right) \times 100 \quad (2)$$

where the total mass of monomer is the sum of the monomer at the seed stage and all of the monomer in the growth stage.

Figures 1(a)–5(a) plot conversion–time data for each of the latex preparations with different contents of surfactant at the seed stage. Table I lists the results of final percentage conversion and percentage coagulum for the latexes prepared. For each of the preparation from Table I, we could see that the levels of coagulum were less than 0.85 wt %, hence making valid the use

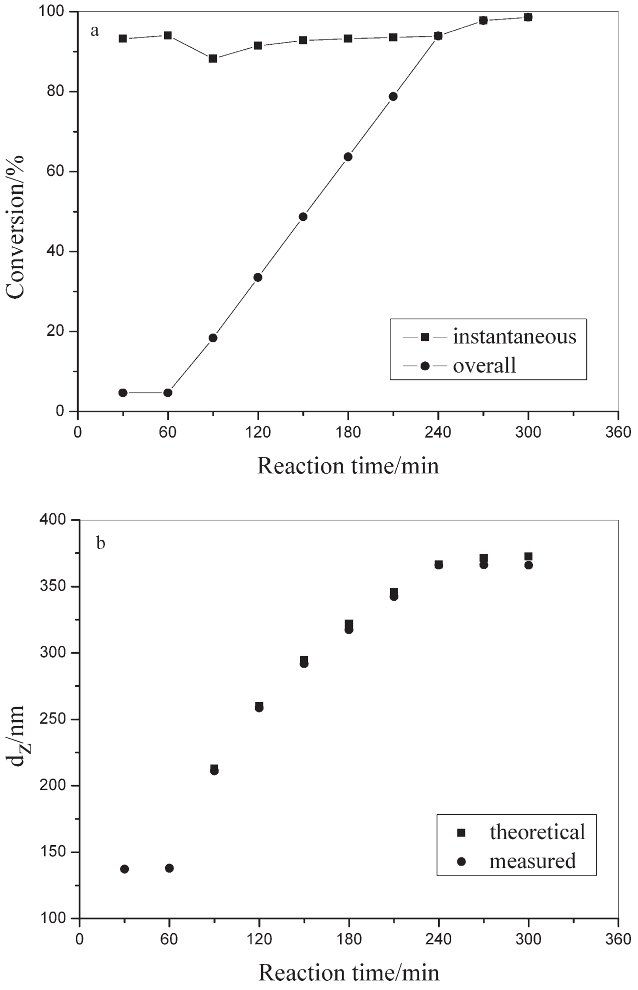

Figure 1 Preparation of a PSA latex using 1.0 g surfactant at the seed stage. Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical z-average particle diameter, d_z.

of solid contents to evaluate monomer conversion. The majority of the coagulum (80–90%) was deposited on the stirrer, with some on the reaction vessel and the sieve.

For all these samples, instantaneous conversion was more than 90 wt % at the end of the seed stage. This high conversion represented the formation of the seed particles, prior to the addition of the growth-stage monomer. For reaction times at the start of the growth stage, the instantaneous conversion decreased, coinciding with the start of the monomer addition stage. The decrease in instantaneous conversion might be due to the time required for the monomer to absorb on the surface of the particles before polymerization occurred. As the reaction proceeded in the growth stage, the instantaneous conversion was more than 90 wt %. This showed that during the growth stages, the particles grew under monomer-starved conditions. Under these conditions, the copolymer composition would be uniform and approximately equal to the composition of the BA/AA comonomer feed mixture. Monomer addition was completed after 240 or 300 min (for 20-g surfactant latex system). The samples taken at 270 or 330 min showed that the instantaneous conversions increased, indicating that the residual monomer had been polymerized. The high final conversions meant that only small amounts of residual monomer were present in the final latexes. This was an important factor because any residual monomer could behave as a plasticizer, which would affect the adhesive properties. Final overall conversions were found to be high (> 98 wt %) for all of the latex procedures with different surfactant levels at the seed stage.

In the semicontinuous batch process, the initially charged surfactant can be used to control the number and the particle size of the seed particles. Increasing the surfactant concentration at the seed stage generally leads to an increase in the number of particles formed. In this study, DLS technique was used to provide a rapid means of monitoring the

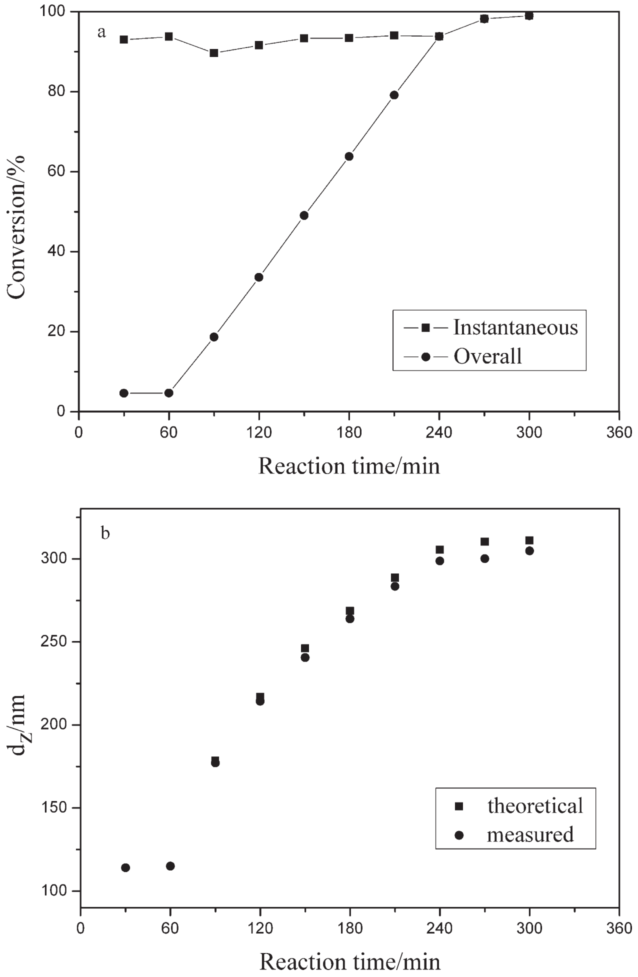

Figure 2 Preparation of a PSA latex using 2.5 g surfactant at the seed stage. Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical z-average particle diameter, d_z.

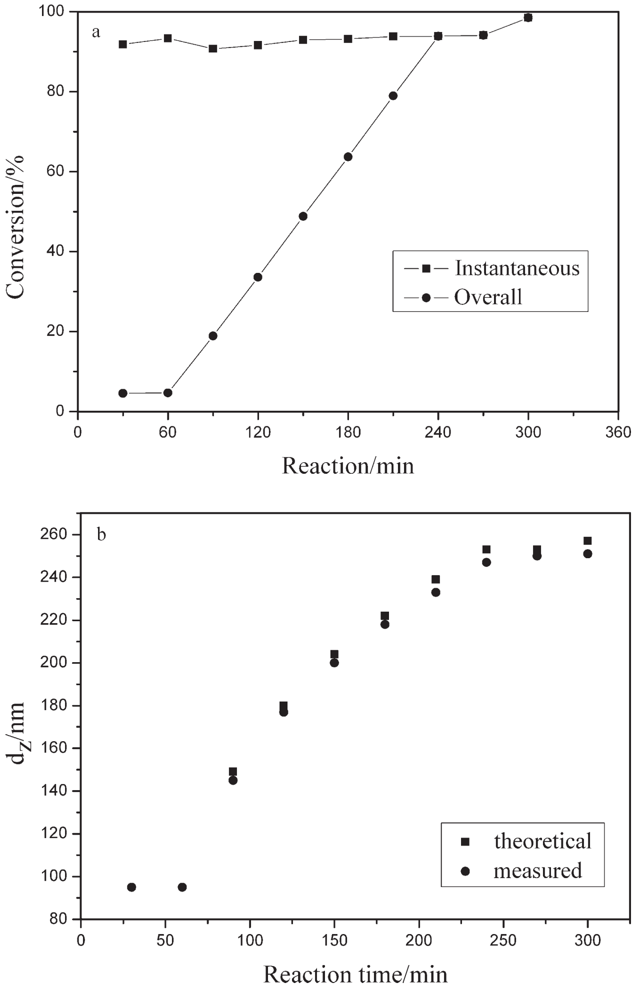

Figure 3 Preparation of a PSA latex using 5.0 g surfactant at the seed stage. Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical *z*-average particle diameter, d_z.

particle size of the latex during both the seed and growth stages of emulsion polymerization. With this information, it was not only possible to establish and reproduce a latex system of known particle diameter but also determine whether, during the growth stage of polymerization, the latex particles grew sequentially or secondary nucleation occurred.

Theoretical values of *z*-average particle diameter, d_z, for particles during the growth stage were calculated from the measured value of d_s at the end of the seed stage measured by DLS and the instantaneous conversion, I, assuming that the particles grew without secondary nucleation and were not swollen by unreacted monomer.[11] The calculation equation is as follows:

$$d_t = \left(\frac{M_t I}{M_s}\right)^{1/3} \times d_s \tag{3}$$

where d_t is the diameter of the particle at time t, M_t is the total mass of the monomer added at time t, and M_s is the mass of the monomer added in the seed stage. The density of poly(BA-*co*-AA) is assumed to be the same as that of poly(BA).

Figures 1(b)–5(b) show the variation of particle size with the reaction time. The good agreement shown between the experimental and theoretical particle diameters throughout the polymerization for the latexes with 1.0–7.5 g of surfactants at the seed stage provided strong evidence that the observed particles grew without significant secondary nucleation and that all of the polymer particles formed were spherical. When the seed-stage surfactant level was 20 g, the measured particle size was much smaller than the theoretical prediction during the growth stage, which was thought to be caused by second nucleation arising from unused surfactant from the seed stage. Using the new procedure described in the "Experimental" section, this might enable nucleation to be completed before feeding the growth-stage monomer. Therefore, the particle diameter measured at the end of this 120-min period was

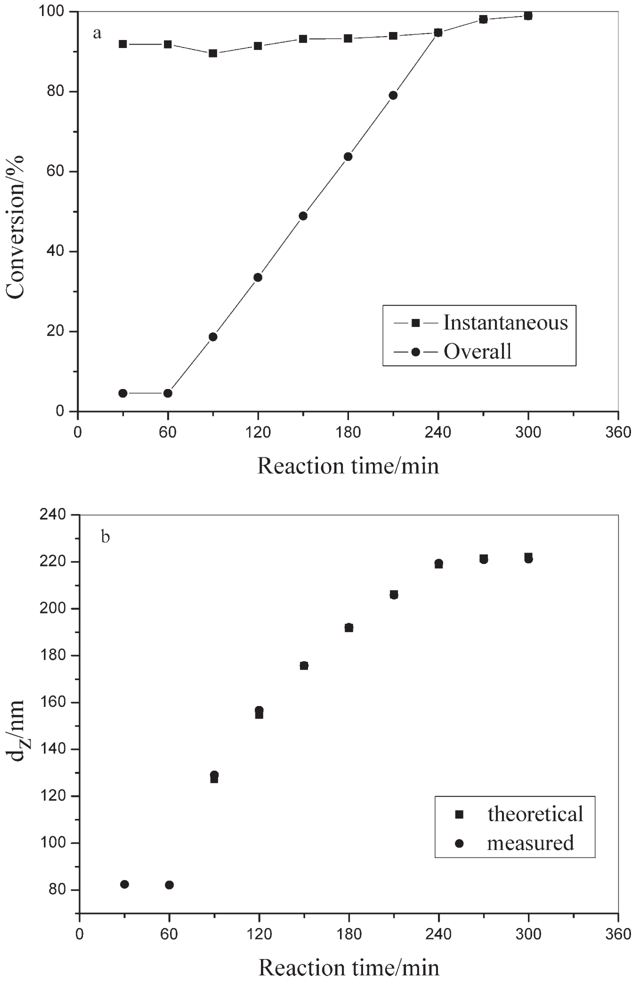

Figure 4 Preparation of a PSA latex using 7.5 g surfactant at the seed stage. Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical *z*-average particle diameter, d_z.

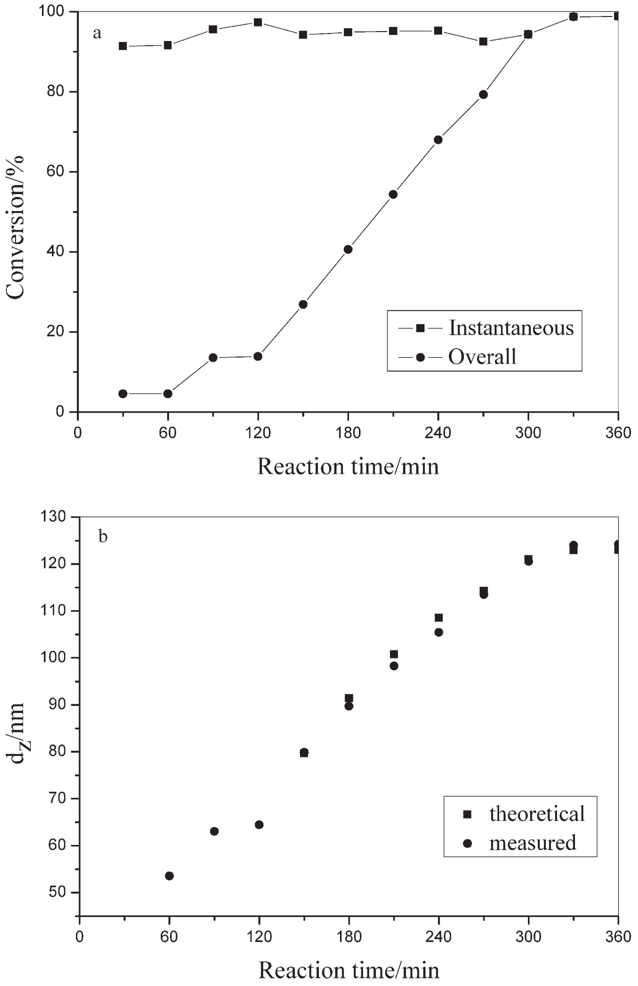

Figure 5 Preparation of a PSA latex using 20.0 g surfactant at the seed stage. Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical *z*-average particle diameter, d_z.

used as the seed particle diameter (d_s) to calculate the theoretical diameters during the growth stage. The result was the same as those in Figures 1(b)–4(b), shown in Figure 5(b). The final values of d_z were 124, 221, 251, 305, and 366 nm for the latexes with 20.0, 7.5, 5.0, 2.5, and 1.0 g, respectively, of surfactant at the seed stage. Table I summarizes the results of the emulsion polymerization procedure with different surfactant levels. By the comparison of the final monomer conversions and the theoretical latex diameters with the measured latex ones, we could see that the latex preparations of different particle sizes, i.e., different surfactant levels at the seed stage, had no significant effect on the final monomer conversion and the particles′ formation in the emulsion polymerization procedures of poly(BA-*co*-AA).

TABLE I
Summary of the Final Data for the Poly(BA-*co*-AA) Latexes

Surfactant content at the seed stage (g)	The final conversion (wt %)	The final particle size (nm)	Coagulum content (wt %)
20.0	98.83	124	0.80
7.5	98.96	221	0.30
5.0	98.46	251	0.34
2.5	99.01	305	0.24
1.0	98.60	366	0.48

Molecular parameters

Gel content

After the latex was dialyzed for 7 days to remove the surfactant, coagulated samples were obtained by freeze–thaw cycling and washed with deionized water several times. After drying the samples, the gel contents of the copolymers were determined by Soxhlet extraction. The gel arose from termination by coupling of propagating long-chain branches formed by intermolecular chain transfer to polymer.[12] Figure 6 shows that the gel contents is nearly the same for all five latexes within the experimental error, as may be expected because all the reactions proceed at the same temperature under monomer-starved conditions, and use the same level of chain transfer agent and the same monomers′ composition at the seed stage and the growth stage.

ξ-Potential

The ξ-potential is a useful practical quantity as it can be related to colloid stability. According to the theory of DLVO, the colloid system is stable if the ξ-potential value is less than −30 mV. Figure 7 presents the change of the ξ-potential with particle size for the poly(BA-*co*-AA) latex. It indicated that the ξ-potential decreased as the particle size increased (i.e., as the surfactant level reduced). Meanwhile, these results

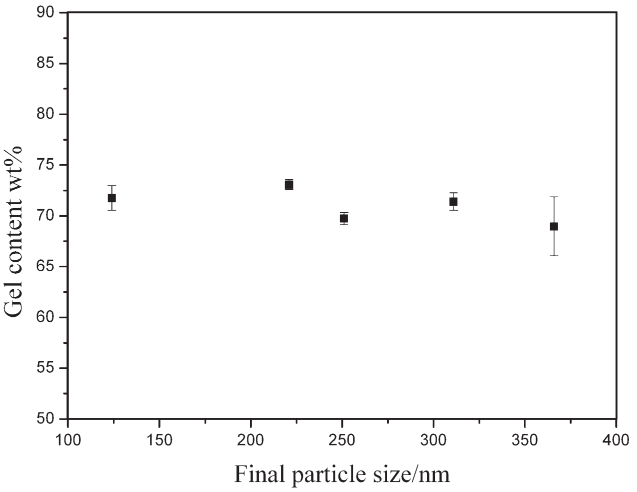

Figure 6 Gel content of the copolymers from latexes with different particle sizes.

also showed that all the latexes were very stable even when the surfactant was only 1 g at the seed stage.

Transitional behavior

Dynamic mechanical thermal analysis (DMTA) is a sensitive thermal analytical technique for detecting the transitions associated with the molecular motions within the polymers in the bulk state. In Figure 8, the dynamic mechanical spectrum of the film cast from the latex shows only one transition, indicating that the transitions are not resolved by the instrument and are superimposed upon the poly(BA) and poly(BA-*co*-AA) phases. Therefore, the overall T_gs of the systems were predicted theoretically by assuming that the glass transitions of the separation phases were superimposed upon each other. Figure 9 presents the copolymer glass transition temperatures obtained from the peak in loss tangent for films with different particle sizes. The T_gs measured by DMTA were −28°C ± 1°C, and no significant decrease in T_g was observed with the increase of the latex particle size. This was because the polymer produced during the emulsion polymerization was of the same initial monomer feed composition.

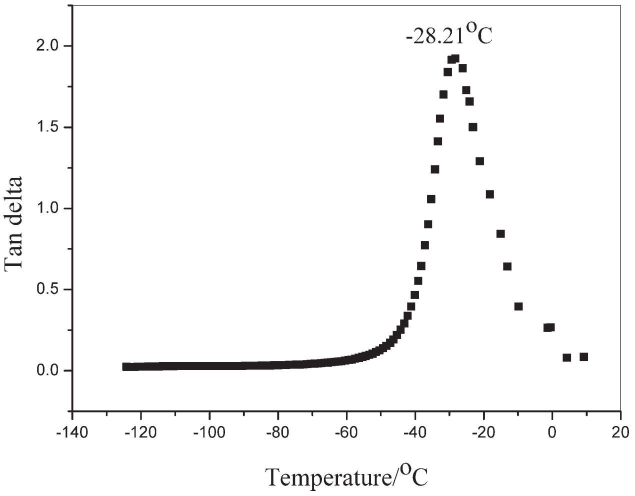

Figure 8 The variation of tan δ with the temperature of poly(BA-*co*-AA) (the final particle size: 305 nm).

Effect of the latex particle size on the adhesive properties of PSAs formed

PSAs need the polymers to be soft, capable of wetting the adherent surface, and capable of sufficient cold flow to fill the surface irregularities. Such properties are found in polymers of low T_g. To possess the necessary tack, a PSA must have a T_g well below the room temperature. This allows the adhesive to flow (i.e., to spread). Poly(BA) with T_g, about −28°C as determined by DMTA, has sufficient tack and flow to serve as a PSA, but has a low shear resistance.[11] Copolymerization of acrylic ester with other monomers is used to change the chemical and physical properties of the adhesives. When BA was copolymerized with AA, there was an increase in the shear resistance, peel adhesion, and tack, which was believed to be due to the molecular interactions of —COOH groups within the bulk polymer.[13] As described earlier, the latexes prepared with different levels of surfactant at the seed stage have the same chemical composition, gel content, and T_g, exception of the particle size. Therefore, we would just consider the effect of the latex particle size on the pressure-sensitive properties in the following section.

Peel force

Surface force interactions play an important role in PSA bonds. The adsorption of the adhesive molecules onto the adherent surfaces occurs mainly by

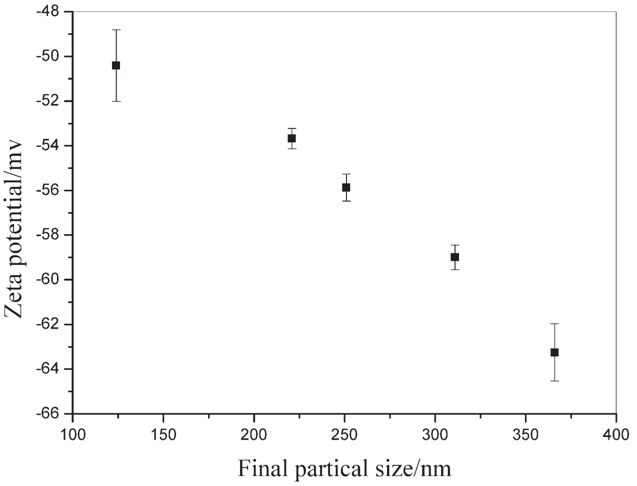

Figure 7 Variation of ξ-potential of the latexes with different particle sizes.

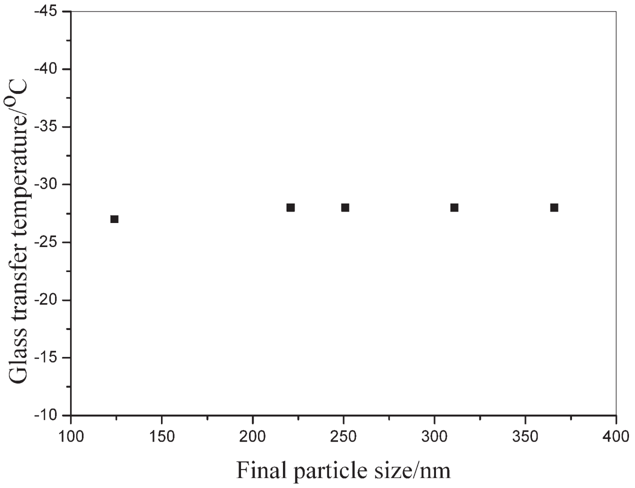

Figure 9 Glass transition temperatures of the copolymers from latexes with different particle sizes.

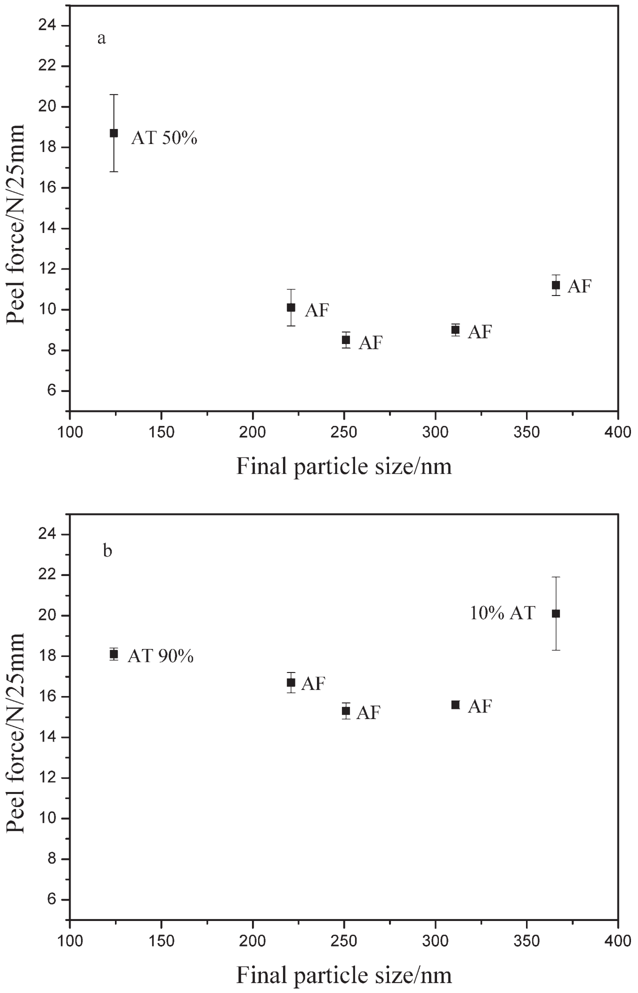

Figure 10 Variation of PSA peel force with latex particle size after (a) 20 min and (b) 24 h. The mode of failure is indicated as follows: AF, adhesive failure; AT, adhesive transfer.

physical adsorption. In physical adsorption, the attractive forces for the adhesive molecule to the adherent surface are secondary or Van der Waal's force. Yang[7] found that for polyacrylic samples, the surface tensions were in the range between 31 and 37 dyne/cm. Because the surface tension of the stainless steel is at 44 dyne/cm, we can expect good wetting to be achieved for all samples.

Figure 10(a) shows that at the short adhesion time of 20 min, the latex with the smallest particle size gives the highest peel force. This is thought to be due to small particles being able to quickly conform to nanometer-scale roughness on the surface of the stainless steel plate, and thus increase the area of contact between the adhesive and the adherend. The larger particles require more time to accommodate to the surface roughness by polymer relaxation processes. During the drying process, perhaps the largest particle sizes impart some inherent weaknesses to the peel strength property as their lowest parking density. Once contact is established, free molecular chain ends and soluble polymer chains start to diffuse. Ultimately, the peel force achieved can be seen by the large increase after 24 h for the PSAs with large particle size latexes as shown in Figure 10(b). Prior to any bond formation through thermodynamic interactions, two materials (adhesive and adherend) must be brought into intimate contact. At the longer adhesion time of 24 h, the peel force is slightly higher for the latex with the largest particle size.

Tack force

Figure 11 is the variation of the tack force with the particle size, which shows a similar dependence of the peel force on the particle size. The strength of an adhesive bond is determined by the thermodynamic contributions to the interfacial energy (van der Waals interactions, electrostatic forces, and hydrogen bonding) and the rheological contributions due to the viscoelastic dissipation during deformation of the polymer chains in the adhesive layer itself. In a tack test, the work of adhesion is dominated by this viscoelastic contribution.[11] The monomer composition was the same and so was the gel content. This discrepancy in tack suggests that the interfaces between the particles might play an important role in determining the linear viscoelastic properties of the drying film. The DMA data (Fig. 9) show identically low T_gs, which indicate that the homogeneous films are easily formed because of the fast diffusing species from soluble fraction of the polymers. For the high molecular weights from the soluble polymers, fibrillation increased the work of adhesion above that because of the contributions of good initial wetting and initial resistance to flow. When the particle size is large, high-average molecular weight (M_w), especially when the contacting time is short,

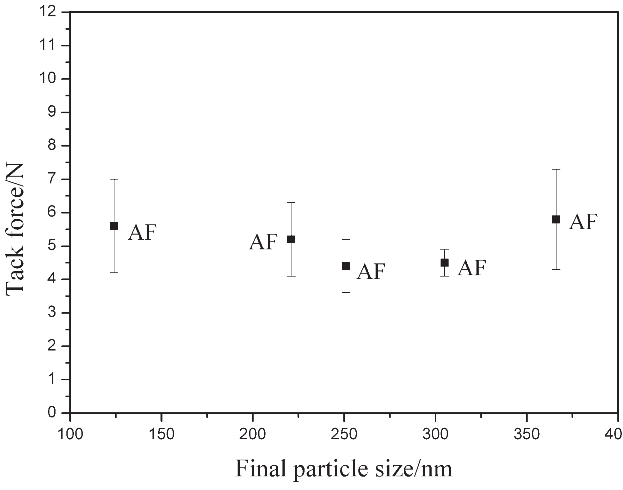

Figure 11 The variation of PSA tack force with latex particle size (AF, adhesive failure).

TABLE II
Summary of the Molecular Weights and Their Distributions of the Soluble Poly(BA-*co*-AA) Polymers

The final latex particle size (nm)	124	221	251	305	366
M_n (g/mol) × 10^{-4}	4.44	5.48	6.22	6.77	6.58
M_w (g/mol) × 10^{-4}	10.6	12.8	15.0	18.4	16.2
MWD	2.39	2.33	2.41	2.72	2.46

gives less viscous flow during debonding. Hence, high viscoelastic energy dissipation can be obtained when there is good anchorage of the adhesive onto the substrate and low modulus–high elongation fibrils that are deformed during the debonding process as the high debonding rate in the tack measurement. This is likely due to the strong correlation exhibited between the particle size and molecular weight. The data in Table II demonstrate how an increase in the particle size is often associated with an increase in the molecular weight, while the final molecular weight distribution (MWD) obtained is similar to those commonly obtained in emulsion polymerization for all the latexes.[11]

Shear resistance

Emulsion polymerization of low-T_g polyacrylics carried out to complete conversion produced a significant amount of microgels inside the particles because of the chain transfer to the polymer via the hydrogen abstraction of tertiary vinyl carbons.[12] The monomer composition was the same and so was the gel content. As the mode of failure in shear testing was cohesive for all PSAs, this suggested that the interfaces between the particles might play an important role in determining the shear resistance of the dry film. It is well known that controlling the degree of interdiffusion across interfaces is crucial to the mechanical properties of polymer blends. The T_g values (−28°C) of all the latexes were well below the ambient temperature, and that the interdiffusion of polymer chains across the interfaces should be complete. Recent experiments on particles containing a significant amount of gel fraction had shown, however, that only the mobile chains could diffuse across the interface, whereas the gel remained essentially immobile.[14] The original structure of the latex, i.e., the particle size, would then be retained, and it was conceivable that the interfaces, enriched in the soluble molecular weight species, would play a significant role in influencing the shear-holding power.[14] Meanwhile, a reduction in molecular weight reduced the level of chain entanglement in the bulk polymer. When the particle size was large, the chain ends from the micronetworks could entangle with the soluble polymer chains from another particle after the film formation. The micronetworks were no longer entangled with the soluble polymer chains when the particles were small. Chain entanglements behaved as pseudocrosslinks that eventually disentangled under shear stress but contributed to the measured shear resistance. As the overall gel content was the same for all latexes, the high soluble molecular weight fractions were desirable for improved shear strength of PSAs.

Shear resistance (T) is directly proportional to zero shear viscosity as given by the following equation[15]:

$$T = \frac{L^2 W \eta}{2tMg} \tag{4}$$

where T is the time to failure, L is the length of overlap, W is the width of the tape, η is the zero shear viscosity, t is the adhesive thickness, M is the load, and g is the gravitational constant. When the particle size of the latex increased, molecular weight of the soluble polymers increased, i.e., the soluble polymers with low molecular weights acted as plasticizer to decrease the zero shear viscosity. Because the failure was cohesive in each case, the increasing level of low-molecular-weight soluble polymer at the interface clearly resulted in a decrease in the cohesive strength of the PSA film. From the results of measuring the soluble polymers listed in Table II, the effect was evident in the data for shear resistance, which increased as the particle size increased, as shown in Figure 12.

Another reason for the changes of shear resistance might belong to an effect of surfactant in the interfaces between latex particles in the dried films, which would be expected to be more significant as the surfactant level increased in the conventional emulsion polymerization.

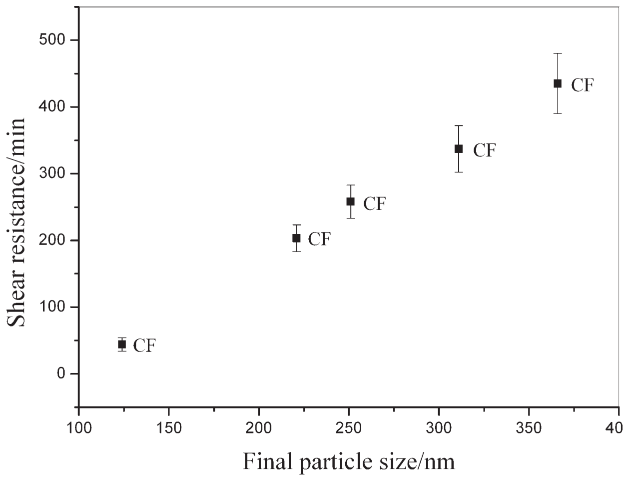

Figure 12 Variation of PSA shear resistance with latex particle size (CF, cohesive failure).

As the emulsion polymerization process for all five latexes was under monomer-starved conditions, as described earlier, and there was no secondary nucleation at the growth stage,[16] the surfactant content per unit area (A) on the surface of each latex particle could be calculated by the following equation:

$$A = \frac{M_s}{M_m} \cdot \frac{D_s^3}{D_f^2} \cdot \rho \cdot \frac{V}{6} \times 10^{-19} \tag{5}$$

where $M_s(g)$ is the total mass of the surfactant in the seed stage and all of the surfactant in the growth stage, M_m (g) is the total mass of the monomer in the seed stage, D_s (nm) is the average particle diameter at the end of the seed stage, D_f (nm) is the final average particle diameters at the end of emulsion polymerization, ρ (g/cm^3) is the density of the particles, and V (L) is the volume of water.

Some parameters used in the emulsion polymerization process are listed in Table III. Assuming A equal to unity for 20-g surfactant latex system, we can get that the weight ratio of the surfactant per square nanometer on the latex particles is 1 : 1.17 : 1.22 : 1.25 : 1.35, respectively, for latexes with particle sizes of 124, 221, 251, 305, and 366 nm, that is, the surfactant contents on the surface of the latex particles increase slightly with the increase of the particle size.

Generally, the surfactants have adverse effects on the cohesion strength of the adhesive. The effects of the surfactant distribution on the adhesive properties have been studied by several authors.[17–19] At medium and high rate, the peel energy versus surfactant concentration curves showed either a maximum or a minimum, depending on the surfactant.[17] The poorer physical properties of adhesives from waterborne PSAs could be avoided by controlling the distribution of water-soluble species within the film.[18,19] At the end of the drying process, the formation of a dense array of latex spheres was facilitated by the expulsion of residual water and compaction of the latex to ensure a closely packed environment. This action brought the absorbed outer layers of the particles into close contact and caused them to interpenetrate, and thus the sulfonic headgroup of the MA Series surfactant molecule came into close contact with the acrylate groupings on the polymer chain. The net result was the formation of hydrogen bonds between the sulfonic and acrylate groups, which limited the surfactant migration in a small region. The presence of surfactant-related hydrogen bonds could outweigh the effects imposed by the surfactants on the adhesive properties. That is, the surfactant level added in the experiments did not cause detrimental effect on adhesion. The mechanism of the MA Series surfactant action in the drying PSAs is complex, but it is errorous to think that the higher the surfactant, the lower is the shear resistance for the polyacrylic PSAs studied herein. The interfacial entanglement between the particles from the soluble polymers with the network structures was dominant for the increase of the shear resistance with the increase of poly(BA-*co*-AA) particle size.

TABLE III
Summary of Some Parameters for Emulsion Polymerization Process

Monomer (mass/g)	Particle (size/nm)		Surfactant (mass/g)	
Seed stage	Seed stage	Final	Seed stage	Growth stage
145	64	124	20.0	11.88
50	82	221	7.5	11.88
50	95	251	5.0	11.88
50	115	305	2.5	11.88
50	138	366	1.0	11.88

CONCLUSIONS

PSA latexes with different particle sizes and narrow size distributions were successfully prepared by monomer-starved semibatch emulsion polymerization. The particle's ξ-potential decreased as the particle size increased (corresponding to a reduction in the surfactant level). Moreover, the PSA copolymers had similar glass transition temperatures and gel fractions. The particle size of the latex had a substantial effect on the adhesive properties. 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. For tack, however, a concave upward relation between tack and particle size was shown to exist. The shear resistance reduced as the particle diameter decreased because of the presence of the low-molecular-weight soluble polymers in the interface of the dried latex film. The interfaces, enriched in the low-molecular-weight soluble species, would play an important role in determining the linear viscoelastic properties of the dry film. These results might be due to the strong correlation exhibited between particle size and the soluble molecular weight to affect the adhesive properties. Finally, this study has shown that the control over particle sizes afforded by emulsion polymerization could enable us to affect the properties of PSA in a controlled manner. The approach used in this work could be easily adapted to study other factors influencing PSA properties.

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