

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231375750>

Effect of Bimodality on the Adhesive Properties of Pressure Sensitive Adhesives: Role of Bimodal Particle Size and Molecular Weight Distributions

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JULY 2010

Impact Factor: 2.59 · DOI: 10.1021/ie100204x

CITATIONS

3

READS

34

3 AUTHORS, INCLUDING:



Timothy F.L. McKenna

Centre National de Recherche Scientifique,...

215 PUBLICATIONS 2,548 CITATIONS

SEE PROFILE

Effect of Bimodality on the Adhesive Properties of Pressure Sensitive Adhesives: Role of Bimodal Particle Size and Molecular Weight Distributions

Gabriela E. Fonseca,[†] Timothy F. L. McKenna,[‡] and Marc A. Dubé^{*,†}

Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada, and Department of Chemical Engineering, Queen's University, Kingston, Canada

A one-pot, two-step miniemulsion polymerization approach was successfully used to create poly(2-ethyl hexyl acrylate/methyl methacrylate/acrylic acid) pressure sensitive adhesives with well-defined and predictable bimodal particle size distributions (PSDs) or bimodal molecular weight distributions (MWDs). The resulting viscoelastic (shear storage and loss moduli) and adhesive properties (i.e., loop tack, peel strength, and shear strength) were tested and compared to monomodal distributions of either particle size or molecular weight along with bimodal distributions created by postpolymerization blending. The results indicated that in situ bimodal MWDs offered superior values of PSA properties when compared to either monomodal MWDs or postpolymerization blends. Viscoelastic analysis of the in situ bimodal MWD samples showed that the proposed approach can effectively vary the MWDs and cross-linking densities of the resulting PSAs, thus tailoring the final properties. In comparison, the in situ bimodal PSD latexes did not show significant differences in viscoelastic behavior, but they exhibited large differences in PSA properties.

Introduction

Pressure sensitive adhesives (PSAs) are used in applications ranging from ordinary tapes and labels to highly complex structures such as those used in drug delivery technology.¹ Their ability to adhere to practically any surface with slight pressure, commonly referred to as tack, is likely the main reason for the extensive application of this category of adhesive.² Up until very recently, they were most commonly produced using solution polymerization, a process that requires the monomers to be reacted in a solvent such as toluene or xylene, among others. They can also be produced by water-based polymerization (e.g., suspension, conventional emulsion, microemulsion, and miniemulsion polymerization), where the monomers are dispersed in water as opposed to organic solvents, making these techniques more environmentally friendly. Stringent environmental regulations have influenced a push toward the reduction of volatile organic compounds in PSA products. As a consequence, a great deal of research has been carried out to attempt to understand the differences in the microstructure of polymers formed by solvent-based versus water-based polymerizations.^{3,4}

In addition to tack, which represents the ability of an adhesive to bond to a substrate, PSAs must exhibit a certain peel strength (i.e., the ability to debond easily from the substrate) and shear strength (i.e., the cohesive strength to resist flow and be removed without leaving a residue).¹ This set of properties is usually tailored to a specific application through adjustment of the molecular microstructure. This is achieved by modification of the molecular features [molecular weight distribution (MWD), glass transition temperature (T_g), entanglement molecular weight (M_e), and molecular weight between cross-links (M_c)]⁵ as well as the particle size distribution (PSD). While the PSD mainly influences film formation and latex viscosity,⁶ it has also been shown to affect adhesive properties.^{7,8} Nevertheless, care should be taken when modifying the molecular microstructure as, most often, increasing the properties associated with adhesion (tack and peel strength) tends to decrease cohesion (shear strength).¹

In order to compensate for the decrease in cohesion mentioned above, it has been suggested that a small fraction of high molecular weight material can make a substantial contribution to shear strength.¹ A number of studies have reported on the influence of broad⁹ or blended multimodal¹⁰ MWDs on different polymer or adhesive properties. A comparison of adhesive properties for films produced from latex blends to achieve a bimodal MWD with films produced from latexes with an “in-reaction” bimodal MWD showed that the latter yielded better PSA properties.¹¹

There are several means to produce multimodal MWDs besides postpolymerization blending. These include various semibatch monomer-feed strategies^{12,13} as well as sequential polymerization processes.¹⁴ Ouzineb et al.¹⁵ presented an approach using a miniemulsion/semibatch emulsion polymerization technique to create latexes with high molecular weights followed by the addition of another miniemulsion to create the low molecular weight portion of the same polymer.

Broad or multimodal PSD latexes offer advantages over narrow PSD latexes such as high solids contents and reduced viscosity.¹⁶ Multimodal distributions have been achieved by postpolymerization blending of two or more latex types (i.e., different particle sizes) into a film so that the desired final PSA properties are achieved.¹⁷ Latexes with bimodal PSDs have been shown to exhibit improved rheological and film formation properties compared to their monomodal counterparts.^{18,19} The influence of the latex PSD of a model acrylic PSA with monomodal and postpolymerization blended bimodal PSD on tack was studied.²⁰ Blends with 40 wt % or more small particles yielded films with superior adhesive properties compared to those of the parent monomodal particle distributions. However, the M_w values of the two particle populations they produced were different. Nevertheless, for a fixed copolymer composition, it was possible to influence the adhesive properties by changing the latex PSD. A number of approaches have been investigated to produce multimodal PSD systems without postpolymerization blending such as seeded semibatch processes^{16,21–23} and unseeded multistep processes²⁴ and by exploiting miniemulsion polymerization techniques.²⁵

* To whom correspondence should be addressed. E-mail: Marc.Dube@UOttawa.ca. Fax: (613) 562-5172.

[†] University of Ottawa.

[‡] Queen's University.

Jovanovic et al.²⁶ compared the PSA performance of latexes prepared by either conventional emulsion or miniemulsion polymerization. Although they were successful in creating bimodal MWD/PSD latexes, the peaks of particle size and molecular weight obtained by conventional emulsion and miniemulsion were different and, thus, it was not easy to discriminate between the effects that a different PSDs or MWDs had on these PSA properties. Overall, these studies established three main points: (i) it is possible to affect the PSA performance through careful modification of the multimodal PSD or MWD; (ii) they showed that multimodal distributions generated during the reaction produced higher tack, peel, and shear strength values compared to latex blends; (iii) the decoupling of the MWD and PSD effects on PSA properties has yet to be studied. These three points motivated the present study.

Miniemulsion polymerization is especially attractive for the production of latexes since it can provide a means to finely control the MWD and PSD due to its compartmentalized nature.^{15,27} Miniemulsion polymerization differs from conventional emulsion polymerization in that the reaction proceeds under droplet nucleation conditions and not via micellar or homogeneous nucleation. Proceeding under droplet nucleation conditions favors so-called compartmentalization in miniemulsion polymerization. A properly formulated miniemulsion is able to reach a kinetically stable state in which the droplets with diameters on the order of 100 nm act as nanoreactors and diffusion of monomer through the aqueous phase could be minimized.²⁸ It is this compartmentalized characteristic that could allow for the production of a bimodal MWD or PSD in situ without the need of multiple seeds.

In this work, a one-pot, two-step miniemulsion polymerization strategy is presented for the production of bimodal MWD or bimodal PSD latexes. The impact of the bimodal MWD or PSD on PSA performance is presented. As opposed to previous studies, the initial reaction conditions were carefully designed so that, for bimodal PSD latexes, the molecular weight and gel fraction were identical for small and large particles. Similarly, for the bimodal MWD latexes, the surfactant and monomer concentrations were carefully selected to produce identical particle diameters for the low and high molecular weight polymer fractions. Thus, the effects of the MWD and PSD on PSA properties were decoupled. It should be pointed out that the main goal of the current study was to gain a general understanding of the effect of multimodal distributions (either of particle size or molecular weight) on adhesive performance for future optimization studies.

Experimental Details

Materials. All of the materials were reagent grade, were used as supplied by the manufacturer, and were obtained from Sigma Aldrich, unless otherwise indicated. The monomers were 2-ethyl hexyl acrylate (EHA), methyl methacrylate (MMA), and acrylic acid (AA). Octadecyl acrylate (ODA) was used as the polymerizable hydrophobe and 1-dodecanethiol (DDM) was used as the chain transfer agent (CTA). The ionic surfactant was sodium dodecyl sulfate (SDS) (GC grade) and the nonionic surfactant was Disponil A3065 donated by Cognis Canada. Sodium bicarbonate (NaHCO_3) was used as a buffer. Distilled deionized water (DDI H_2O) was used throughout the study.

Preparation of the Miniemulsion. ODA, DDM, and the three monomers (EHA, MMA, and AA) were mixed until they formed a homogeneous, clear solution. Disponil A3065, SDS, and NaHCO_3 were dissolved in DDI H_2O . Subsequently, the organic phase was added slowly to the aqueous phase and stirred

Table 1. Detailed Experimental Recipes

Bimodal MWD			
	first population step 1		second population step 2
EHA [wt %]	63.0		63.0
MMA [wt %]	35.0		35.0
AA [wt %]	2.0		2.0
ODA [phm]	4.0		4.0
DDM [phm]	0		0.5
SDS [phm]	0.09		0.09
Disponil A3065 [phm]	4.57		4.57
NaHCO_3 [phm]	0.15		0.15
APS [phm]	0.30		0.30
Bimodal PSD			
	first population step 1	step 2	second population step 3
EHA [wt %]	63.0	63.0	63.0
MMA [wt %]	35.0	35.0	35.0
AA [wt %]	2.0	2.0	2.0
ODA [phm]	4.0	0.0	4.0
DDM [phm]	0.20	0.30	0.20
SDS [phm]	0.09	0.0	0.09
Disponil A3065 [phm]	4.57	1.20	4.57
NaHCO_3 [phm]	0.15	0.15	0.15
APS [phm]	0.30	0.40	0.30

until the emulsion appeared as a milky solution. Then 100 mL batches were sonicated in an ice bath for 4 min each at an output amplitude level of 9 using a Fisher Scientific Sonicator Model 550. Finally, the total volume was combined in one vessel.

Polymerization Procedure for Bimodal Molecular Weight Distributions. The polymerization reactions were performed in a 1.1 L Labmax automated stainless steel reactor (Mettler Toledo) equipped with a stirrer, condenser, and three feed ports. The two miniemulsions, each with different CTA concentrations, were prepared separately prior to the reaction. The first miniemulsion was charged to the reactor and heated while stirring. Nitrogen gas was bubbled through the reaction mixture to remove any dissolved oxygen. The temperature and stirring speed were automatically controlled at 70 °C and 200 rpm, respectively. The reaction was initiated with a single shot of the initiator solution. The first miniemulsion was left to polymerize for 180 min, after which time the second miniemulsion was added to the reactor with a second shot of initiator solution. The total reaction volume was then left to polymerize for an additional 180 min. It is important to note that the second miniemulsion was not a seed but rather was a miniemulsion. The resulting latexes will be referred to as in situ bimodal MWD latexes to distinguish them from typical postpolymerization blends. The five latexes in this set of experiments are labeled “HL” (high/low M_w). The two monomodal MWD latexes are considered the extremes and are labeled as HL1 and HL5. The three bimodal MWD latexes are referred to as HL2, HL3, and HL4 depending on the formulation.

All the miniemulsion polymerizations carried out in this study were prepared using the recipe shown in Table 1. The monomer composition and the ODA concentration (which acted as the hydrophobic compound delaying Ostwald ripening) were kept constant. The difference in terms of preparation between miniemulsions with high M_w and miniemulsions with low M_w lay solely in the CTA concentration; i.e., the first miniemulsion contained no CTA while the second contained 0.5 parts per hundred parts monomer (phm) CTA, as shown in Table 1.

Due to the acid group present in AA, this monomer can partition between the particles (either buried in the core or at the surface) and the aqueous phase depending on the pH of the

reaction mixture.^{29,30} It has also been shown that changes in the amount of carboxylic acid present in the particles can affect the mechanical and adhesive properties of the resulting polymer.³¹ In this sense and considering that the pK_a of AA is 4.25,³² the pH of all the reactions was kept constant at ~ 5 .

Polymerization Procedure for Bimodal Particle Size Distributions. The polymerization reactions to produce latexes with a bimodal PSD were performed in the same reactor as mentioned above (cf. Table 1). The first miniemulsion was prepared to produce monomer droplets with a diameter of ~ 200 nm. This miniemulsion was charged to the reactor and heated to 70 °C, and the reaction was initiated with an initiator shot. The miniemulsion was left to polymerize for 180 min, and at this point, monomer and surfactant solutions (cf. Table 1) were fed semicontinuously until the required particle diameter was achieved (~ 450 nm). The second miniemulsion with an average monomer droplet diameter of ~ 200 nm was then charged to the reactor, and the polymerization continued for 180 min. Similar to the bimodal MWD case, the five latexes of this set are labeled “LS” (large/small D_p). The two monomodal PSD latexes are referred to as LS1 and LS5, while the three bimodal PSD latexes are referred to as LS2, LS3, and LS4.

Sample Characterization. Monomer conversion was obtained using conventional gravimetric procedures. Droplet and particle sizes were obtained using a NanoS dynamic light scattering (DLS) instrument (Malvern Instruments) with a scattering angle of 176° for the monomodal distributions and a Laser Diffraction LS 13320 multiwavelength particle analyzer (Beckman Coulter) for the bimodal particle size distributions. One drop of the emulsion or latex was placed in a 4 mL polystyrene cuvette (in the case of the DLS instrument) and diluted with distilled deionized water. The drop of emulsion or latex was diluted 200 times or until the mean count rate in the DLS equipment was between 200 and 400 kcps (the number of photons detected in kilocounts per second) in order to maximize the accuracy of the results. The reported diameter is an intensity weighted average particle size, also known as z -average, made of three measurements that were analyzed in 10 runs of 30 s each. Given the water solubility of some of the monomers used herein (such as MMA), it is likely that some of the monomer could have been stripped from the sample and dissolved in the water phase, thus decreasing the diameter of the droplet/particle. According to calculations performed to estimate measurement error, there was a 5–10% decrease in the droplet diameter, which represented an 8–15 nm error in particle sizes reported, which is well within the experimental error of the technique. Finally, as long as the error of the technique would remain constant, comparisons within our experiments would be valid and allow us to make sound conclusions. The polydispersity indices given throughout this study are those reported by the Malvern dynamic light scattering instrument. The polydispersity indices given by this instrument indicate that a family of particles with a polydispersity under 0.01 is considered to be monodisperse. MWDs were analyzed by gel permeation chromatography.³³ The universal calibration curve included a set of standards (EasiCal from Polymer Laboratories) with a range of 162–6 035 000 g/mol. The values of K and α used for EHA were 1.24×10^{-4} dL/g and 0.67, while those for MMA were 1.28×10^{-4} dL/g and 0.69, respectively.^{34,35}

Gel fraction was analyzed on the final latex samples. A 200 mg sample of dry polymer was placed in a pouch formed by two 25-mm-diameter PTFE membranes with a pore size of 0.2 μ m. The membranes were heat sealed and placed in a glass jar with 50 mL of THF. The jars were placed in a shaker for at

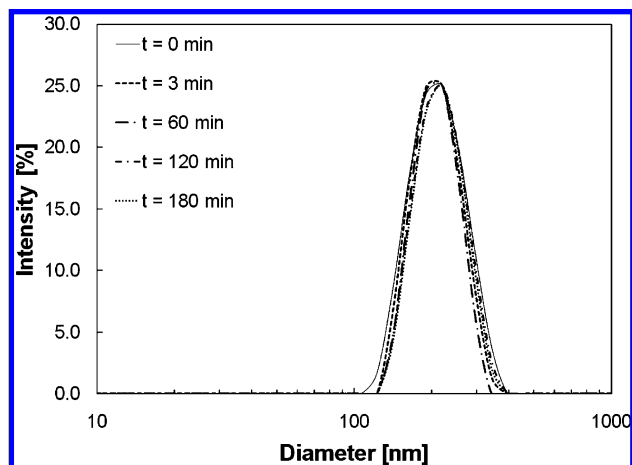


Figure 1. Droplet size distribution and evolution of particle size distribution of reaction HL1.

least 48 h, after which time the pouches were removed and allowed to dry. The gel fraction was calculated from the difference between the final and initial weights of the polymer. T_g was determined using a differential scanning calorimeter (DSC) Model Q1000 (TA Instruments). The analysis was performed using a modulated DSC method with a modulation amplitude of ± 1 °C every 60 s. The sample was cooled to -80 °C and followed by a heating ramp of 2 °C/min. The T_g was calculated from the inflection point in the reversed heat flow curve using the software provided. If the transition was broad and, thus, the result ambiguous, the T_g was taken as the peak in the curve of the derivative heat capacity (C_p). Master curves and temperature sweeps were carried out by dynamic mechanical analysis (DMA; Rheometrics RDA III).

Tack, peel strength, and shear strength were measured according to the Pressure Sensitive Tape Council standards PSTC-6, PSTC-1, and PSTC-7, respectively.^{2,36} The latex was filtered using glass wool and cast onto a 50 μ m Mylar sheet. The cast film was dried at room temperature and conditioned for 24 h at standard conditions of temperature and humidity (23 ± 2 °C and $50\% \pm 2$ relative humidity).

Results and Discussion

The key to successful compartmentalization in miniemulsion polymerization lies in the careful selection of the stabilization system, i.e., the surfactants, which protect the miniemulsion against coalescence, and the hydrophobic compound, which protects the miniemulsion against diffusional degradation, or Ostwald ripening. Figure 1 presents the initial droplet size distribution (DSD) and the evolution of the PSD of a typical run in this study. All of the miniemulsion polymerizations exhibited the same trend as that shown in Figure 1.

The initial droplet diameter, D_d , of sample “ $t = 0$ ” (cf. Figure 1) is 202 nm, and the average particle diameter, D_p , did not change significantly throughout the reaction, exhibiting a final value of 220 nm. These results led us to presume that the reactions indeed proceeded via droplet nucleation since there was no indication of secondary nucleation despite the presence of MMA and AA (monomers with appreciable water solubility), and thus, this formulation was used for the production of bimodal distributions.

Bimodal Molecular Weight Distributions. Table 2 summarizes the weight fractions and the ratio between the number of particles with high M_w and low M_w . Our goal was to evaluate the influence of the concentration of high M_w domains (which

Table 2. Composition of Latexes for the Monomodal and in Situ Bimodal Distributions

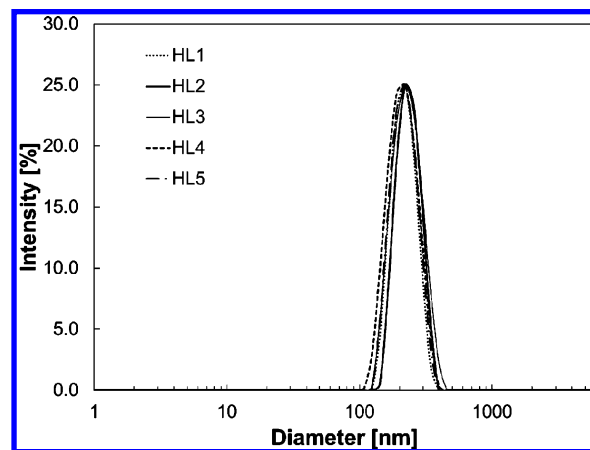
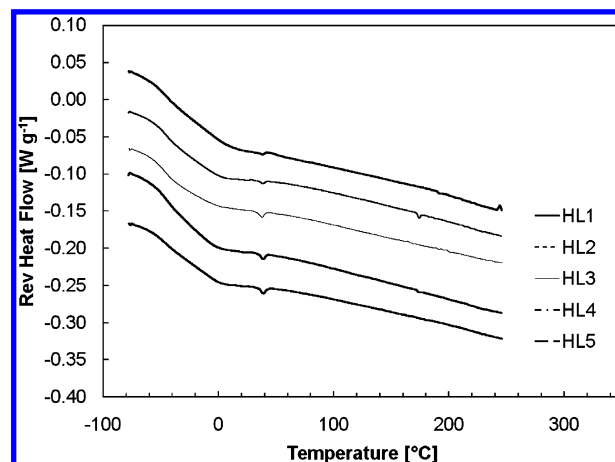
Bimodal MWD				
run	mass % ^a high M_w	mass % low M_w		
HL1	100	0		
HL2	75	25		
HL3	50	50		
HL4	25	75		
HL5	0	100		

Bimodal PSD				
run	mass % ^a small D_p	number % small D_p	mass % large D_p	number % large D_p
LS1	100	100	0	0
LS2	27	75	73	25
LS3	11	50	89	50
LS4	4	25	96	75
LS5	0	0	100	100

^a The solids content of all miniemulsion-based latexes prepared was ~52 wt % and since D_p 's in the bimodal MWD latexes were equal, volume and number percentages were used interchangeably.

would be expected to be highly elastic and provide high shear strength) and low M_w domains (which would be viscous and be able to dissipate energy easily) on PSA performance. As shown in Table 2, three ratios were tested to assess the changes in viscoelastic behavior and adhesive properties. Along with that of the bimodal MWD films, the properties of films cast from monomodal MWD latexes were measured. As mentioned earlier, the copolymer composition was fixed at 63/35/2 wt % EHA/MMA/AA so that the only observable effect on the PSA properties would be that of the molecular weight. In order to verify that the PSD did not change after addition of the second unreacted miniemulsion, the PSD was measured before and after charging the second miniemulsion. The miniemulsions were designed to have a D_p of approximately 200 nm, and any significant deviation from this value would indicate that miniemulsion compartmentalization did not take place. The z -average D_d values of the two miniemulsions were 210 and 213 nm, respectively. The sample taken just prior to the addition of the second miniemulsion presented a conversion of ~95 wt %, and the D_p was equal to 218 nm. The next sample was taken 30 min after the addition of the second unreacted miniemulsion. Upon addition of the unreacted miniemulsion, the PSD did not show any indication of secondary nucleation, which would likely appear as smaller particles or as a broader distribution; i.e., the addition of the miniemulsion did not change the z -average diameter or the polydispersity. The DSD of the final sample of this latex was, in fact, close to that of the initial miniemulsion with a z -average diameter of 225 nm.

Figure 2 shows the final PSD of the in situ bimodal MWD latexes as well as that of the monomodal MWD latexes. The PSDs of the latexes were all comparable, thus eliminating any effect that particle size could have on the PSA properties. Copolymer composition could also have an effect on the adhesive properties. Figure 3 shows the DSC thermographs of both monomodal and in situ bimodal MWD polymers. There was no significant difference between the copolymer compositions of the five latexes, thus eliminating its influence. The monomodal and in situ bimodal MWD of the five samples are shown in parts a and b, respectively, of Figure 4. As shown in Table 1, the monomodal MWD with low M_w polymer was produced using a CTA concentration of 0.5 phm producing a weight-average M_w of ~121 000 g/mol, while the high M_w polymer was produced without the addition of CTA, giving a weight-average M_w of ~878 000 g/mol as seen in Figure 4a.

**Figure 2.** PSD of bimodal MWD (HL2, HL3, and HL4) and monomodal MWD (HL1 and HL5).**Figure 3.** DSC thermographs of polymers with monomodal MWD (HL1 and HL5) and in situ bimodal MWD (HL2, HL3, and HL4).

The production of the in situ bimodal MWD was carried out in two steps as outlined earlier. The first step involved a miniemulsion designed to produce a polymer with the same M_w as sample HL1 in Figure 4a. The reactor contents were allowed to react until most of the monomer in the first population had reacted. At this point, the second unreacted miniemulsion was introduced to the reactor. This miniemulsion was prepared to produce a polymer with the same M_w as sample HL5.

Figure 4b shows the GPC results of the in situ bimodal MWD and offers two pieces of information. First, it suggests that there was no transfer between the two populations of particles since the location of the two peaks in the in situ bimodal MWDs corresponds to the location of the peaks obtained in the monomodal MWDs when only one population of particles was used. This was also corroborated by the PSD of the in situ bimodal MWD latexes shown in Figure 2, which did not display evidence of transfer. Second, it also shows that the peak that corresponds to the high M_w decreases as the weight fraction decreases. However, the high M_w peak was also considerably smaller than the peak that corresponds to the low M_w even though the mass fraction (or N_p) in two of the runs was at least equal to or larger than the mass fraction of low M_w . In this case, this is due to the fact that no CTA was added to the high M_w miniemulsion, which in turn produced high gel fractions, which were likely separated from the fraction that is soluble in the GPC mobile phase solvent (in this case, tetrahydrofuran) during the sample preparation process. The peaks were also not completely separated from each other due to the relatively small

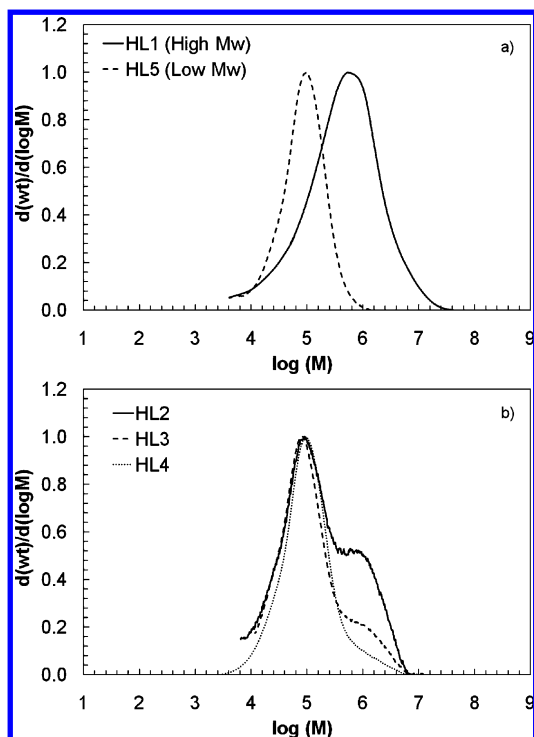


Figure 4. (a) Monomodal MWD of runs HL1 (low M_w) and HL5 (high M_w) and (b) in situ bimodal MWD of latexes HL2, HL3, and HL4. Ratios of high-to-low M_w are 3, 1, and 0.3, respectively.

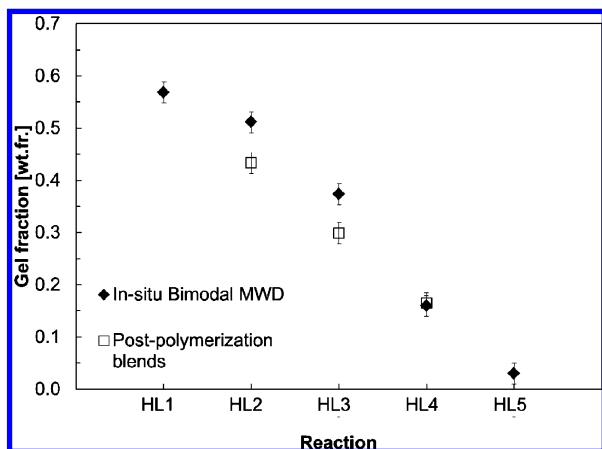


Figure 5. Gel fraction of in situ bimodal MWD (filled diamonds) and postpolymerization blended bimodal MWD (empty squares).

difference between the two M_w 's. However, the M_w 's were chosen keeping in mind the final application as PSAs.

It is known that, in water-borne acrylic polymers, intermolecular chain transfer to polymer contributes to the formation of gel fractions and this effect decreases in the presence of a CTA. Figure 5 shows the gel fractions for the monomodal and in situ bimodal MWD polymer samples. The gel fraction of the monomodal MWD with high M_w (sample HL1) was ~ 0.56 , and the gel fraction for the monomodal MWD with low M_w (sample HL5) was ~ 0.03 . Gel fractions for the bimodal MWD had values in between these two extremes, and gel fractions increased with the weight fraction of the high M_w particles, which was expected since the high M_w domains increased. These results were compared to gel fractions obtained for latexes with a bimodal MWD obtained by postpolymerization blending of latexes HL1 and HL5 using the same weight fractions as for the in situ bimodal MWD. These samples are referred to as

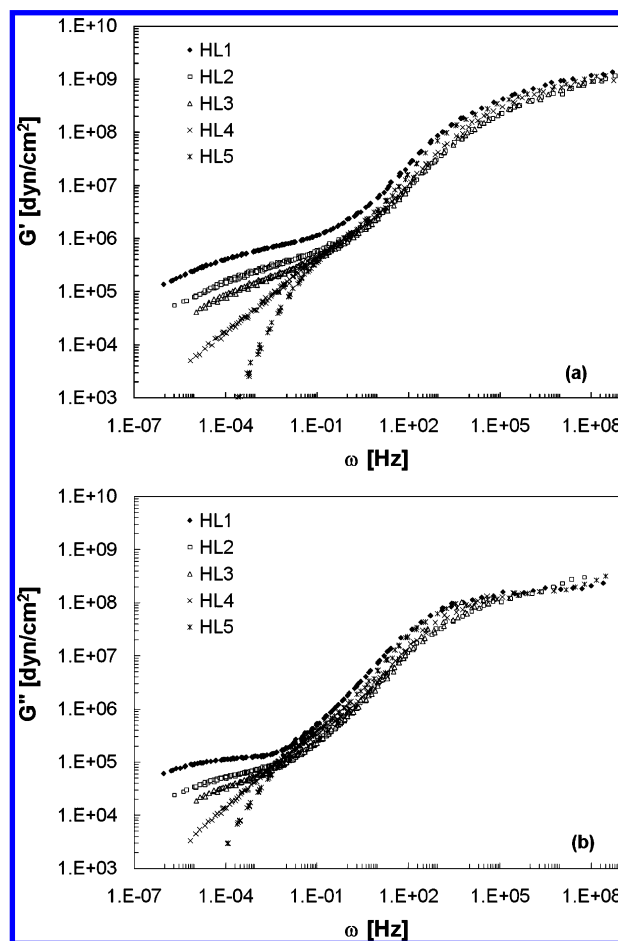


Figure 6. Frequency master curves of (a) storage modulus (G') and (b) loss modulus (G'') for monomodal MWDs of high (HL1) and low M_w (HL5), and in situ bimodal MWD (HL2, HL3, and HL4).

postpolymerization blends, and the corresponding sample name is designated with an "X".

Surprisingly, the results showed that the gel fractions of the postpolymerization blends were lower for samples HL2X and HL3X and about the same value for HL4X. Molecular weight and particle size results suggest that compartmentalization indeed took place or that it remained compartmentalized. However, the number of "gel-forming events" increases when one operates on a starved-feed basis because the higher polymer concentration leads to more chain transfer to polymer reactions.³⁷ The difference in gel fractions between the "in situ bimodal MWD" and the postpolymerization blends lies likely in the additional intermolecular chain transfer reactions of the population of particles that contained no CTA (high M_w particles), which remained inside the reactor for a longer period of time after the addition of the second miniemulsion.

Figure 6 shows the storage (G') and loss shear moduli (G'') for the monomodal and in situ bimodal MWDs. The transition region showed no significant variation between the different samples indicating similar copolymer compositions, which was consistent with DSC measurements. The differences among the five curves appeared exclusively in the rubbery plateau and terminal regions, where it is known that changes in M_w and MWD are strongly noticeable. One can see that the rubbery plateau region of sample HL1 extended further to lower frequencies without a clear presence of the terminal region. The rubbery plateau region became more evident for samples HL2, HL3, and HL4, while sample HL5 showed a very short rubbery plateau region and decayed into the terminal region at a much

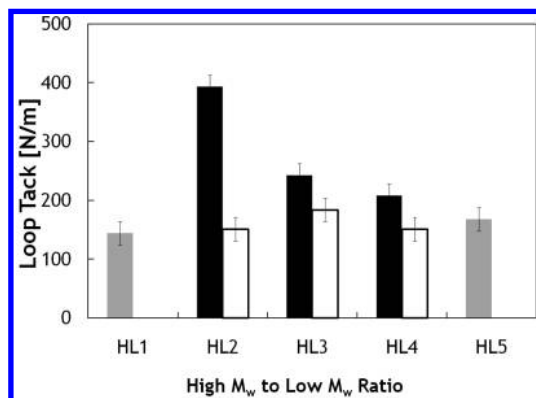


Figure 7. Loop tack results for monomodal MWD (gray), in situ bimodal MWD (black), and postpolymerization blended bimodal MWD (white). Ratios represent the N_p of high M_w by N_p of low M_w .

higher frequency. These results indicate that sample HL1 had a higher M_w (which is also known from GPC measurements) and the absence of the terminal region gives an indication of a cross-linked structure.³⁸ G' sequentially decreased with lower weight fractions of the high M_w miniemulsion, indicating that cross-linking sequentially decreased. It is beyond the aim of this study to quantify the molecular weight between cross-link points, but the extent of cross-linking can be seen from the curves and qualitatively compared. From Figure 6a, one can see that G' in the rubbery plateau region of sample HL1 is higher than that for sample HL2. Both are cross-linked, but HL1 is likely more cross-linked since its values of G' are higher and the terminal region starts to decay at a much lower frequency compared to sample HL2. Overall, the three bimodal MWD samples had characteristics of the high and low M_w monomodal MWDs. It is expected that samples HL2, HL3, and HL4 offer the characteristics of, on the one hand, high compliance and good contact with the surface and, on the other hand, a cross-linked network that will give the necessary cohesion.

Figures 7–9 present the results of the PSA properties (loop tack, peel strength, and shear strength) for the monomodal MWD (gray bars), in situ bimodal MWD (black bars), and postpolymerization bimodal MWD blends (white bars). As can be seen in Figure 7, the loop tack values of the films cast from monomodal MWD latexes were lower compared to those films cast from in situ bimodal MWD latexes. The higher values of loop tack were attributed to two effects. The first effect was due to the bimodality of the MWD since all other factors had been kept constant (e.g., copolymer composition, D_p , and adhesive testing conditions). Sample HL2 exhibited the highest loop tack values of the three samples at a ratio of high-to-low M_w of 3, which means that most of the polymer particles in sample HL2 had a very high M_w with only a portion of the particles with low M_w acting to provide a high compliance. Figure 7 also shows that loop tack values decreased as the weight fraction of low M_w increased. The second effect offered by these results is noticed when they are compared against the bimodal MWD prepared by postpolymerization blending, which displayed lower loop tack values. If the bimodality of the MWD was the only effect responsible for the higher values of loop tack, then it would be expected that the bimodal MWD latexes obtained by postpolymerization blending would have similar values. As can be observed in Figure 7, the postpolymerization blends had considerably lower values compared to the in situ bimodal MWD samples. This behavior was likely due to the lower gel fraction observed earlier. In general, the results observed for the in situ bimodal MWD samples are due to a combined effect of the bimodality of the distribution and the in

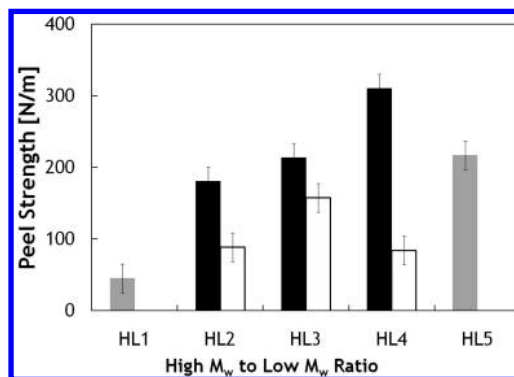


Figure 8. Peel strength results for monomodal MWD (gray), in situ bimodal MWD (black), and postpolymerization blended bimodal MWD (white). Ratios represent the N_p of high M_w by N_p of low M_w .

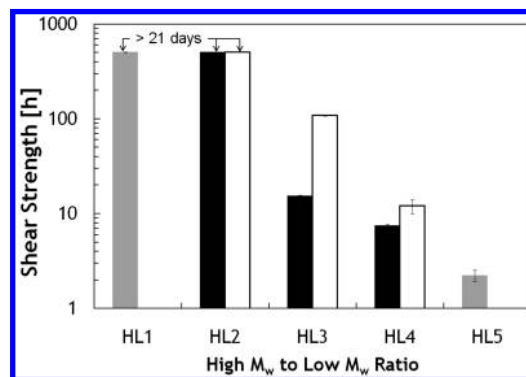


Figure 9. Shear strength results for monomodal MWD (gray), in situ bimodal MWD (black), and postpolymerization blended bimodal MWD (white). Ratios represent the N_p of high M_w by N_p of low M_w .

situ process itself, which led to higher gel fractions. Both characteristics improved loop tack values.

Similarly, Figure 8 shows the peel strength results for the in situ bimodal MWD samples (black bars), postpolymerization blends (white bars), and monomodal MWD (gray bars) samples. The difference in peel strength between the two monomodal MWD samples (HL1 and HL5) was clearly due to their M_w and gel fraction, where HL1 presented a much higher value of both M_w and gel fraction, effectively decreasing the peel strength.¹ The in situ bimodal MWD samples, on the other hand, displayed significantly higher values of peel strength, which is again attributed to the bimodality of the MWD and gel fractions. The sample with the lowest weight fraction of low M_w particles (i.e., HL4) displayed the highest peel strength. In this sample, the low M_w domains acted as a plasticizer. The low M_w domains and a gel fraction of 0.16 were sufficient to provide cohesive strength but not high enough to provide high levels of cross-linking,³⁹ which would markedly diminish peel strength as also observed in the viscoelastic measurements. As cross-linking levels presumably increased (cf. Figure 6) with higher weight fractions of the high M_w domains, peel strength values clearly decreased. The postpolymerization bimodal MWD blends exhibited lower values of peel strength compared to the in situ bimodal MWD samples.

Finally, Figure 9 shows the results of shear strength for the three types of samples: monomodal MWD, in situ bimodal MWD, and postpolymerization blended bimodal MWD. It is known that shear strength is directly proportional to the amount of cross-linking and entanglement.⁴⁰ It has also been reported that the concentration of CTA has a strong influence on the static shear strength.⁴¹ As can be observed in Figure 9, shear strength values decreased as the weight fraction of high M_w

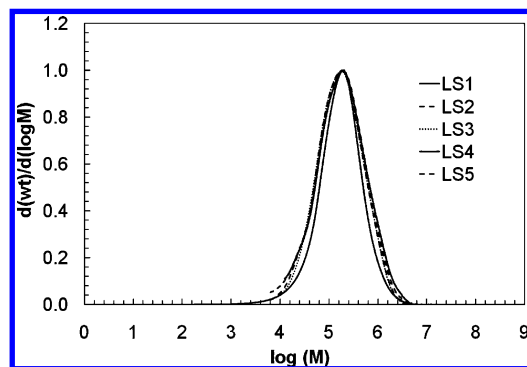


Figure 10. MWD of monomodal PSD for small (LS1) and large (LS5) particle diameters and in situ bimodal PSDs (LS2, LS3, and LS4).

particles decreased, which was also related to the fact that gel fractions became smaller. The results showed that the PSA properties can be tailored and improved using the approach proposed herein.

Bimodal Particle Size Distributions. Once it was established that miniemulsion compartmentalization facilitated the production of bimodal MWD latexes, bimodal PSD latexes were also produced using a similar, three-step, one-pot miniemulsion polymerization approach (cf. Table 1). A miniemulsion with a small D_d (~ 200 nm) was prepared first and charged to the reactor. Once the particles reached a high conversion (>95 wt %), additional monomer and surfactants were added in a semicontinuous fashion to increase the D_p to ~ 450 nm. As soon as the particles reached the specified diameter, a second miniemulsion with a small D_d (~ 200 nm) was loaded to the reactor and the two populations (i.e., small and large D_p particles) were left to polymerize to full conversion. Table 1 in the experimental section shows the recipe for the production of the bimodal PSD.

In order to test the influence of having more or less small D_p particles, similarly as in the bimodal MWD case, three weight ratios of small to large D_p particles were tested and the corresponding weight fractions are shown in Table 2. The CTA concentrations were adjusted to produce medium weight-average M_w gel-free samples (gel fraction of ~ 3 wt %) that would still ensure good PSA properties but with the same MWD in both small and large D_p particle populations. A change in the MWD would likely affect the PSA properties,⁴² and it would not be possible to differentiate between the effect of the MWD and that of the PSD. It is known that a certain amount of gel is required to produce PSAs. Moreover, any significant difference between the cross-linking of two given samples would interfere with our ability to distinguish between the effect of different particle sizes. Figure 10 shows the MWD of the five samples, i.e., the monomodal PSD of small and large D_p values and the in situ bimodal PSD. Finally, the copolymer composition was another aspect that was carefully considered in the preparation of the bimodal PSD. There were not observable deviations in the T_g values of the three in situ bimodal PSD latexes measured by DSC (not shown here).

The initial miniemulsion followed the same PSD trend as that exhibited previously for the bimodal MWD case (cf. Figure 1), and it is thus not shown again here. Figure 11 shows the final PSDs of the small and large D_p populations. The difference between the two D_p 's was constrained by the typical particles sizes used in PSA applications, which ranged from 100 to 1000 nm.⁴³ The average D_p 's for the two populations were 167 and 310 nm, respectively. These values were obtained using a laser diffraction multiwavelength particle analyzer (Beckman Coulter).

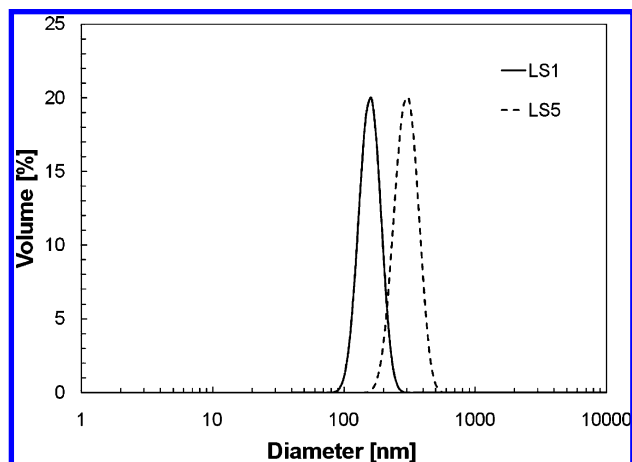


Figure 11. Particle size distribution of small D_p (LS1) and large D_p (LS5) polymer particles prepared by miniemulsion polymerization.

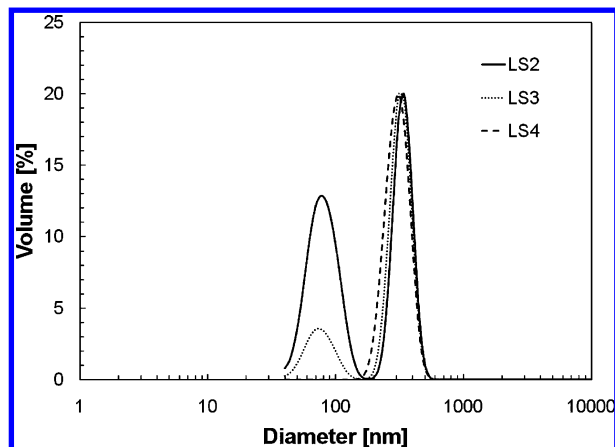


Figure 12. Particle size distribution of in situ bimodal latexes (LS4, LS3, and LS2).

The PSDs of monomodal PSD samples were analyzed using a dynamic light scattering instrument (Malvern Instrument). The D_p 's obtained using the laser diffraction multiwavelength particle analyzer were smaller than the measurements carried out previously by dynamic light scattering (such as the PSD reported earlier in this study), which has been observed before.⁴⁴

Figure 12 shows the particle size analysis of the three samples with in situ bimodal PSD. As can be observed in the plot, the samples with 75 and 50% in number (or 27 and 11 wt %) of small D_p particles were evidently bimodal distributions. However, sample LS4 did not exhibit a peak of the smaller D_p particles possibly due to the fact that this sample contained the lowest weight percentage of the small D_p particles (4 wt %). It is likely that the amount of these particles was low enough to avoid detection by the laser diffraction instrument.

Once it was confirmed that the latexes had indeed a bimodal PSD, the viscoelastic and adhesive behaviors were measured. Figure 13 shows G' and G'' of the monomodal PSDs of the small (LS1) and large (LS5) D_p 's and of the in situ bimodal PSDs. Surprisingly, there was no difference in the viscoelastic behavior in the transitions, rubbery plateaus, or terminal regions of the samples analyzed. These results differ from those found by do Amaral et al.,²⁰ who found a significant difference between the viscoelastic behavior of postpolymerization latex blends prepared from small D_p and large D_p latexes. However, it is difficult to draw conclusions from their study since the adhesives were prepared by two different polymerization techniques (conventional emulsion and miniemulsion polym-

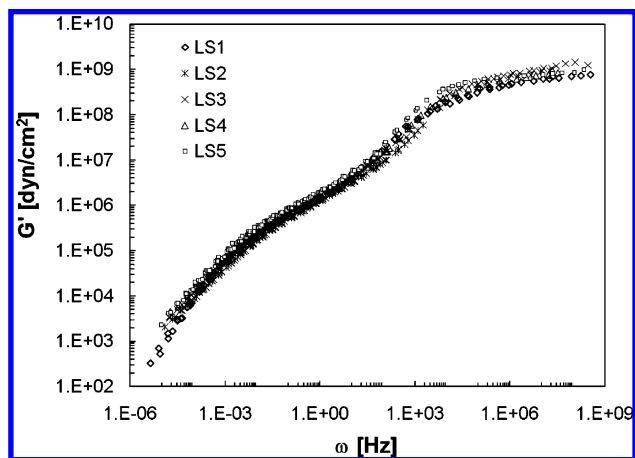


Figure 13. Frequency master curves of storage modulus (G') for polymer with monomodal PSD of small D_p (LS1) and large D_p (LS5) and for polymers with in situ bimodal PSD.

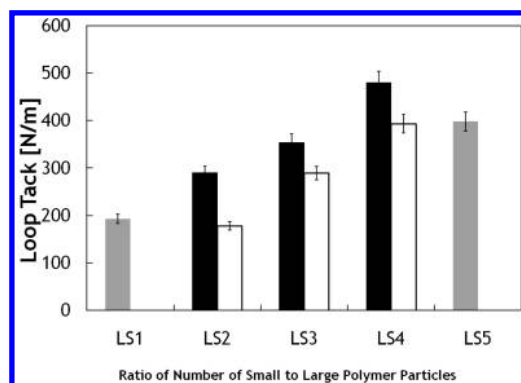


Figure 14. Loop tack results for monomodal PSD of small and large D_p (gray), in situ bimodal PSD (black), and postpolymerization blended bimodal PSD (white).

erization), which produced two different MWDs and likely two different microstructures. Since the rheology is very sensitive toward M_w and MWD,⁴³ it is clear that, in this study, all the samples had the same M_w and MWD and particle size did not contribute to their viscoelastic behavior. In other words, all the particles (large and small) had the same bulk properties.

Figures 14–16 show the results of the PSA properties of the monomodal, in situ bimodal, and postpolymerization blended bimodal PSD latexes. As can be observed, while loop tack and shear strength exhibited considerable differences among the three types of latexes, this was not the case for peel strength, for either in situ bimodal or postpolymerization blended bimodal PSDs. Differences were only encountered in the peel strengths of monomodal small and large D_p latexes. Even though the overall copolymer compositions, gel contents, and MWDs were the same for all the latexes studied herein, it is likely that the semicontinuous feeding stage introduced different compositional drifts in the larger particles. It is evident from Figure 14 that the latexes with smaller particles gave lower values of loop tack compared to the larger particles. As well, it was those blends with the highest number of large particles that resulted in much larger values of loop tack. Moreover, the values of loop tack of films cast from in situ bimodal PSD latexes were larger than those of the postpolymerization blend bimodal PSD latexes. However, as can be seen in Figure 14, the values of loop tack for the bimodal PSD latexes were not an average of the loop tack values obtained for the two monomodal PSDs. Since the viscoelastic behavior shows no difference between the samples analyzed, i.e., the PSD (either monomodal or bimodal) had no

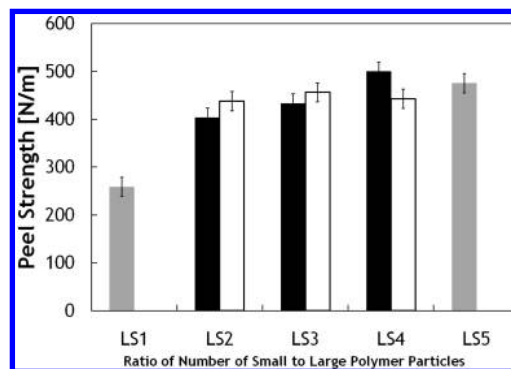


Figure 15. Peel strength results for monomodal PSD of small and large D_p (gray), in situ bimodal PSD (black), and postpolymerization blended bimodal PSD (white).

effect on the viscoelastic behavior (not to be confused with the influence that PSD has on the latex rheology which is of large industrial importance), the differences in the resulting values of loop tack are likely due to an interfacial phenomenon. In terms of film formation, it has been reported that smaller particles deform faster and take less time to fill interstitial voids while larger particles show only superficial deformation in the same time frame because, in larger particles, the polymer chains have to flow over longer distances.^{45,46} This means that the three bimodal PSD latexes prepared in this study led to various film formation paths and, thus, different particle surfaces which in turn affected loop tack. It must also be considered that small and large particles could contain different surfactant amounts. Even though the polymerization was designed to cover approximately the same surface area for both diameters, it is acknowledged that larger particles had a larger monomer to surfactant ratio compared to the smaller particles (39 versus 22). Nevertheless, the monomer to surfactant ratios between the three in situ bimodal PSD latexes and their respective postpolymerization blend counterparts should be equal, and thus, the monomer to surfactant ratios per se did not account for the differences observed. It was then concluded that a combination of the bimodality of PSD and the proposed in situ polymerization method were the main factors contributing synergistically to the improved loop tack values.

Peel strength, on the other hand, did not show discernible differences between the bimodal PSDs, as mentioned previously. Nevertheless, we can see in Figure 15 that there was a noteworthy difference between the two monomodal distributions. For example, sample LS1 (monomodal PSD with small particles) exhibited a peel strength value of ~ 258 N/m while sample LS5 (monomodal PSD with large particles) had a peel strength value of ~ 475 N/m, which is about twice as much as the former. This difference was the result of similar reasons as in the loop tack results, i.e., differences in composition drift between the large and small particles or different film formation paths leading to different contact area or different roughness at the interface with the substrate since all other variables (copolymer composition, MWD, gel content) were kept equal. As for the bimodal PSDs (in situ or postpolymerization blends), it was noticeable that they gave a peel strength closer to the value obtained from large particles, which could be due to the fact that the mass fraction of the large particles was considerably larger than that of the small particles.

Finally, the results displayed in Figure 16 show the films cast from bimodal PSD latexes. As can be observed, the bimodal PSD sample with the highest number of large particles (LS4) displayed the highest shear strength values while the monomodal

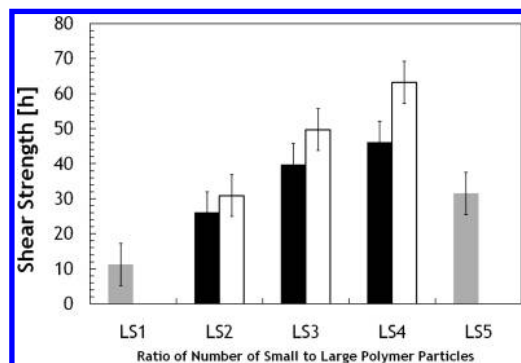


Figure 16. Shear strength results for monomodal PSD of small and large D_p (gray), in situ bimodal PSD (black), and postpolymerization blended bimodal PSD (white).

PSD exhibited much lower values. The differences in shear strength observed between the in situ bimodal MWD and postpolymerization blended bimodal MWD latexes were likely within experimental error. Nevertheless, one can see that higher amounts of large particles led to an increase in shear strength. At this point, it is still not clear what PSD or film formation related mechanisms were playing a role in the resulting shear strength values of the PSAs produced, a subject which may require further investigation.

Conclusions

The study described in this paper detailed a one-pot, two-step miniemulsion polymerization strategy for the production of well-defined bimodal MWD or bimodal PSD latexes. The strategy exploits the compartmentalization nature of miniemulsion polymerization to create populations of polymer particles of either different particle diameters or different molecular weights. The latexes produced by this approach were termed in situ bimodal, and their viscoelastic and PSA properties were compared to the properties of monomodal distributions as well as bimodal distributions produced via postpolymerization blending.

The results indicated that gel fractions of the in situ bimodal MWD latexes were higher than those obtained by postpolymerization blending, suggesting that additional intermolecular chain transfer reactions occurred during the miniemulsion polymerization. It was speculated that these additional reactions occurred inside the first population of particles, which did not contain CTA, during the second step of the polymerization that subjected this particle population to a longer time inside the reactor. The viscoelastic analysis clearly showed that increasing the fraction of particles with low M_w modified the microstructure from a cross-linked structure (as noted in the rubbery plateau region of sample HL2) to a lightly cross-linked structure (as noted in the terminal region in sample HL4). PSA performance analysis showed that the loop tack and peel strength resulted in higher values when the latexes were prepared in situ as opposed to postpolymerization blending. They also displayed higher values than the monomodal MWDs. This effect was attributed to the higher gel fractions as well as to the bimodality of the MWD since all other properties (e.g., T_g and PSD) were carefully kept equal.

Bimodal PSD latexes were also successfully prepared using a similar approach. There were no significant differences in the viscoelastic behavior when comparing the different in situ bimodal PSD latexes (i.e., different ratios of large-to-small particles) or when they were compared to the monomodal PSD samples. Nevertheless, two of the PSA properties (loop tack

and shear strength) were significantly different depending on the ratio of large-to-small particles used, and in most of the cases, they displayed values larger than their corresponding monomodal PSD. Peel strength, on the other hand, did not exhibit differences between the different ratios, and it was only observed that the bimodal PSD took on a value similar to the large particle population. The in situ bimodal PSD latexes were also compared to postpolymerization blends similarly, and it was found that they both fell within the same range. It is important to stress that the benefit offered by the in situ bimodal distributions lies in the preparation technique since it uses a one-pot, two-step approach as opposed to the postpolymerization blends. The polymer produced in this study had the same copolymer composition, but it is suggested that it can also be used to create PSAs (or latexes for that matter) with different compositions. Overall, the study showed that the approach proposed can be effectively used to create PSAs with bimodal MWDs and PSDs simultaneously. The knowledge obtained can be used as a basis for a more in-depth analysis of the nonlinear elastic behavior of the PSAs produced herein. Such a study would expand on the information provided by the tests used herein and provide a path toward the optimization and manipulation of PSA properties for specific applications.

Acknowledgment

The authors gratefully acknowledge the financial support of the Natural Science and Engineering Research Council (NSERC) of Canada and the University of Ottawa. G.E.F. thanks the National Council of Science and Technology (CONACYT) of Mexico for the doctoral scholarship provided.

Literature Cited

- (1) Satas, D. *Handbook of Pressure Sensitive Adhesive Technology*; Van Nostrand Reinhold: New York, 1989.
- (2) Pressure Sensitive Tape Council. *Test Methods for Pressure Sensitive Adhesive Tapes*; Pressure Sensitive Tape Council: Northbrook, IL, 2004.
- (3) Tobing, S. D.; Klein, A. Mechanistic Studies in Tackified Acrylic Emulsion Pressure Sensitive Adhesives. *J. Appl. Polym. Sci.* **2000**, *76*, 1965.
- (4) Tobing, S. D.; Klein, A. Molecular Parameters and Their Relation to the Adhesive Performance of Emulsion Acrylic Pressure-Sensitive Adhesives. II. Effect of Crosslinking. *J. Appl. Polym. Sci.* **2001**, *79*, 2558.
- (5) Jovanovic, R.; Dubé, M. A. Emulsion-Based Pressure-Sensitive Adhesives: A Review. *J. Macromol. Sci., Polym. Rev.* **2004**, *C44*, 1.
- (6) Schneider, M.; Claverie, J.; Graillat, C.; McKenna, T. F. High Solids Content Emulsions. I. A Study of the Influence of the Particle Size Distribution and Polymer Concentration on Viscosity. *J. Appl. Polym. Sci.* **2002**, *84*, 1878.
- (7) Qu, X. W.; Wang, N. Y.; Lovell, P. A. Preparation and Characterization of the Latexes With Different Particle Sizes by Semibatch Emulsion Polymerization and the Influence on Properties of Waterborne Pressure-Sensitive Adhesives. *J. Appl. Polym. Sci.* **2009**, *112*, 3030.
- (8) Roberge, S.; Dubé, M. A. The Effect of Particle Size and Composition on the Performance of Styrene/Butyl Acrylate Miniemulsion-Based PSAs. *Polymer* **2006**, *47*, 799.
- (9) Baus, R. E.; Swift, G. Emulsion Polymer of Heterogeneous Molecular Weight and Preparation Thereof. U.S. Patent 4,501,845, 1985.
- (10) O'Connor, A. E.; Willenbacher, N. The Effect of Molecular Weight and Temperature on Tack Properties of Model Polyisobutylenes. *Int. J. Adhes. Adhes.* **2004**, *24*, 335.
- (11) Elizalde, O.; Vicente, M.; Leiza, J. R.; Asua, J. M. Control of the Adhesive Properties of N-Butyl Acrylate/Styrene Latexes. *Polym. React. Eng.* **2002**, *10*, 265.
- (12) Sayer, C.; Lima, E. L.; Pinto, J. C.; Arzamendi, G.; Asua, J. M. Molecular Weight Distribution in Composition Controlled Emulsion Copolymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1100.
- (13) Vicente, M.; Leiza, J. R.; Asua, J. M. Simultaneous Control of Copolymer Composition and MWD in Emulsion Copolymerization. *AIChE J.* **2001**, *47*, 1594.
- (14) Lenzi, M. K.; Cunningham, M. F.; Lima, E. L.; Pinto, J. C. Producing Bimodal Molecular Weight Distribution Polymer Resins Using

Living and Conventional Free-Radical Polymerization. *Ind. Eng. Chem. Res.* **2005**, *44*, 2568.

(15) Ouzineb, K.; Graillat, C.; McKenna, T. F. Study of Compartmentalization in the Polymerization of Miniemulsions of Styrene and Butyl Methacrylate. *J. Appl. Polym. Sci.* **2004**, *91*, 115.

(16) Schneider, M.; Graillat, C.; Guyot, A.; McKenna, T. F. High Solids Content Emulsions. III. Synthesis of Concentrated Latices by Classic Emulsion Polymerization. *J. Appl. Polym. Sci.* **2002**, *84*, 1916.

(17) Steward, P. A.; Hearn, J.; Wilkinson, M. C. An Overview of Polymer Latex Film Formation and Properties. *Adv. Colloid Interface Sci.* **2000**, *86*, 195.

(18) Geurts, J. M.; Lammers, M.; German, A. L. The Effect of Bimodality of the Particle Size Distribution on Film Formation of Latices. *Colloids Surf., A* **1996**, *108*, 295.

(19) Peters, A. C. I. A.; Overbeek, G. C.; Buckmann, A. J. P.; Padgett, J. C.; Annable, T. Bimodal Dispersions in Coating Applications. *Prog. Org. Coat.* **1996**, *29*, 183.

(20) do Amaral, M.; Roos, A.; Asua, J. M.; Creton, C. Assessing the Effect of Latex Particle Size and Distribution on the Rheological and Adhesive Properties of Model Waterborne Acrylic Pressure-Sensitive Adhesives Films. *J. Colloid Interface Sci.* **2005**, *281*, 325.

(21) Chu, F. X.; Graillat, C.; Guyot, A. High Solid Content Multisized Emulsion Copolymerization of Styrene, Butyl Acrylate, and Methacrylic Acid. *J. Appl. Polym. Sci.* **1998**, *70*, 2667.

(22) Chu, F. X.; Guillot, J.; Guyot, A. Study of Poly(St/BA/MAA) Copolymer Latexes With Trimodal Particle Size Distribution. *Polym. Adv. Technol.* **1998**, *9*, 844.

(23) Chu, F. X.; Guillot, J.; Guyot, A. Study of Poly(St/BA/MAA) Copolymer Latexes With Bimodal Particle Size Distribution. *Polym. Adv. Technol.* **1998**, *9*, 851.

(24) Boutti, S.; Graillat, C.; McKenna, T. F. High Solids Content Emulsion Polymerisation Without Intermediate Seeds. Part II. In Situ Generation of Bimodal Latices. *Polymer* **2005**, *46*, 1211.

(25) Ouzineb, K.; Graillat, C.; McKenna, T. F. High-Solid-Content Emulsions. V. Applications of Miniemulsions to High Solids and Viscosity Control. *J. Appl. Polym. Sci.* **2005**, *97*, 745.

(26) Jovanovic, R.; Ouzineb, K.; McKenna, T. F.; Dubé, M. A. Butyl Acrylate/Methyl Methacrylate Latexes: Adhesive Properties. *Macromol. Symp.* **2004**, *206*, 43.

(27) Ouzineb, K.; Hua, H.; Jovanovic, R.; Dubé, M. A.; McKenna, T. F. Monomer Compartmentalisation in Miniemulsion Polymerisation Studied by Infrared Spectroscopy. *C. R. Chim.* **2003**, *6*, 1343.

(28) Landfester, K.; Bechthold, N.; Forster, S.; Antonietti, M. Evidence for the Preservation of the Particle Identity in Miniemulsion Polymerization. *Macromol. Rapid Commun.* **1999**, *20*, 81.

(29) Mendizabal, E.; Hernandez, P. J.; Puig, J. E.; Canche-Escamilla, G.; Katime, I.; Castano, V. Effect of PH on the Mechanical Properties of Functionalized Polymers Prepared by Emulsion Polymerization. *J. Appl. Polym. Sci.* **1999**, *74*, 3299.

(30) Martins Dos Santos, A.; McKenna, T. F.; Guillot, J. Emulsion Copolymerization of Styrene and N-Butyl Acrylate in Presence of Acrylic and Methacrylic Acids: Effect of pH on Kinetics and Carboxyl Group Distribution. *J. Appl. Polym. Sci.* **1997**, *65*, 2343.

(31) Garrett, J.; Lovell, P. A.; Shea, A. J.; Viney, R. D. Water-Borne Pressure-Sensitive Adhesives: Effects of Acrylic Acid and Particle Structure. *Macromol. Symp.* **2000**, *151*, 487.

(32) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 90th ed. (Internet Version 2010); CRC Press/Taylor and Francis: Boca Raton, 2010.

(33) Fonseca, G. E.; McKenna, T. F.; Dubé, M. A. Influence of Particle Nucleation in Pressure Sensitive Adhesive Properties: Miniemulsion Versus Emulsion Polymerization. *Macromol. Symp.* **2008**, *271*, 83.

(34) Hua, H.; Dubé, M. A. Off-Line Monitoring of Butyl Acrylate, Methyl Methacrylate and Vinyl Acetate Homo- and Copolymerizations in Toluene Using ATR-FTIR Spectroscopy. *Polymer* **2001**, *42*, 6009.

(35) Lathova, E.; Lath, D.; Pavlinec, J. The Behavior of Poly(2-Ethylhexyl Acrylate) in Dilute-Solution-Viscosity Measurements. *Polym. Bull.* **1993**, *30*, 713.

(36) Jovanovic, R.; McKenna, T. F.; Dubé, M. A. Empirical Modeling of Butyl Acrylate/Vinyl Acetate/Acrylic Acid Emulsion-Based Pressure-Sensitive Adhesives. *Macromol. Mater. Eng.* **2004**, *289*, 467.

(37) Gonzalez, I.; Leiza, J. R.; Asua, J. M. Exploring the Limits of Branching and Gel Content in the Emulsion Polymerization of N-BA. *Macromolecules* **2006**, *39*, 5015.

(38) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980.

(39) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Alberdi, J. M.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. Seeded Semibatch Emulsion Polymerization of Butyl Acrylate: Effect of the Chain-Transfer Agent on the Kinetics and Structural Properties. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1106.

(40) Tobing, S. D.; Klein, A. Molecular Parameters and Their Relation to the Adhesive Performance of Acrylic Pressure-Sensitive Adhesives. *J. Appl. Polym. Sci.* **2001**, *79*, 2230.

(41) Gower, M. D.; Shanks, R. A. The Effect of Chain Transfer Agent Level on Adhesive Performance and Peel Master-Curves for Acrylic Pressure Sensitive Adhesives. *Macromol. Chem. Phys.* **2004**, *205*, 2139.

(42) Chauvet, J.; Asua, J. A.; Leiza, J. R. Independent Control of Sol Molar Mass and Gel Content in Acrylate Polymer/Latexes. *Polymer* **2005**, *46*, 9555.

(43) Benedek, I. *Pressure-Sensitive Adhesives and Applications*; Marcel Dekker, Inc.: New York, 2004.

(44) Schneider, M.; McKenna, T. F. Comparative Study of Methods for the Measurement of Particle Size and Size Distribution of Polymeric Emulsions. *Part. Part. Syst. Charact.* **2002**, *19*, 28.

(45) DuChesne, A.; Bojkova, A.; Rottstegge, J.; Glasser, G.; Neher, D.; Krieger, S. Film Formation of Heterogeneous Latex Systems—a Comparative Study by Mechanical Testing, Electron Microscopy, Interferometry and Solid State NMR. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3871.

(46) Eckersley, S. T.; Rudin, A. Film Formation of Acrylic Copolymer Latexes: A Model of Stage II Film Formation. In *ACS Symposium Series*; Provder, T., Winnik, M. A., Urban, M. W., Eds.; American Chemical Society: Washington, DC, 1996; Vol. 648, pp 2–21.

Received for review January 28, 2010

Revised manuscript received July 1, 2010

Accepted July 1, 2010

IE100204X