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Butyl Acrylate/Methyl Methacrylate Latexes: Adhesive Properties

Renata Jovanović,[1] *Keltoum Ouzineb,*[2] *Timothy F. McKenna,*[2] *Marc A. Dubé**[1]

[1]Department of Chemical Engineering, University of Ottawa, Ottawa, Canada
[2]LCPP-CNRS/ESCPE—Lyon,Villeurbanne, France
E-mail: dube@genie.uottawa.ca

Summary: In this study, butyl acrylate/methyl methacrylate (BA/MMA) latexes of bimodal molecular weight and particle size distribution were prepared in a multi-step process by seeded conventional emulsion and seeded miniemulsion polymerization. For the conventional emulsion case, a BA/MMA batch copolymerization was conducted as a first step (seed generation) and was followed by a monomer addition step to ensure particle growth. In a third step, a BA/MMA pre-emulsified mixture was added to generate a second particle population. For the miniemulsion case, a BA/MMA copolymerization was carried out as a first step (seed generation) and was followed by a monomer addition step. The addition of a BA/MMA miniemulsion served to generate a bimodal particle size and molecular weight distribution. The final latexes were coated onto a polyethylene terephthalate carrier, dried and their performance as pressure-sensitive adhesives was evaluated using tack, peel and shear adhesion measurements. Structure-property relationships between the adhesive properties and the weight-average molecular weight and average particle size were examined. Even though the polymers obtained by miniemulsion showed better shear resistance, their shear resistance was low. There was no statistically significant difference in peel resistance of the polymers obtained by the two reactions. While a significant difference in tackiness between the two emulsion procedures was found when the adhesives were tested using the less sensitive, rolling ball test, no differences were found when they were tested using a loop tack test.

Keywords: butyl acrylate; methyl methacrylate; pressure-sensitive adhesives, emulsion polymerization, miniemulsion polymerization

Introduction

Pressure-sensitive adhesives (PSA) are a class of adhesives that instantaneously form a bond upon application of light pressure. Tapes, labels and protective films are common pressure-sensitive products with a variety of applications such as in the automotive, aerospace and electronic industry,[1] bioelectrodes,[2] and "smart adhesives" used for transdermal drug delivery.[3]

A basis for a PSA is a polymer with a low glass transition temperature (T_g) typically from

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a class of alkyl acrylates such as poly(butyl acrylate) and poly (2-ethylhexyl acrylate). Although inherently tacky and soft with a T_g of –52 and –70°C, respectively, their homopolymers do not possess adequate shear strength. A balanced combination of tack, peel strength and shear strength is a major requirement for a PSA. Therefore, co- or multicomponent polymerizations are necessary. The addition of co-monomers such as alkyl methacrylates (e.g. methyl methacrylate, MMA), vinyl esters (e.g. vinyl acetate) or vinyl aromatics (e.g. styrene and its derivatives) with homopolymer T_g's above 0°C is common.[4,5] In addition, monomers with functional groups such as acrylic or methacrylic acids providing possible crosslinking sites are added to improve shear and peel resistance. However, their addition often reduces tack. Thus, the presence of other formulation components such as tackifiers is used to counteract this.

Although butyl acrylate and methyl methacrylate have been indicated in the literature as possible major components of PSAs, there are only a few studies on the adhesive performance of their copolymers. Garrett et al.[6] examined the performance of soft-soft and hard-soft pressure-sensitive adhesive latexes with a rigid core consisting of poly(methyl methacrylate)-co-poly(allyl methacrylate) and a soft shell of poly(butyl acrylate)-co-poly(acrylic acid). The presence of a rigid core provided very high shear adhesion, but at the cost of an almost complete loss of peel strength. Marçais et al.[7] investigated the adhesive performance of MMA/2-EHA (2-ethylhexyl acrylate) latexes obtained in batch and semi-batch emulsion polymerization. They found that the batch process yielded a PSA that behaved as a repositionable PSA while the semi-batch process resulted in a long-lasting PSA. This suggests that the selection of the appropriate polymerization mode may have an impact on the end use of PSAs. Shull et al.[8] investigated a series of triblock copolymers containing end blocks of poly(methyl methacrylate) and a poly(butyl acrylate) midblock. Used as a thermoreversible gel, this copolymer retained its underlying gel structure and exhibited good performance as a PSA when dried.

PSAs can be obtained by different polymerization modes such as bulk, solution and dispersion polymerizations or radiation curing. Solvent-based formulations were dominant in the past due to their excellent performance but water-based PSAs are now gaining in importance due to stricter environmental laws. With the use of reactive surfactants,[10] the formation of structured networks of crosslinked particles,[11] or specialty formulations,[12,13] the performance of emulsion-based PSAs is approaching the performance of solvent-based PSAs. Although there is considerable interest in the kinetics and different applications of miniemulsion polymerizations,[14,15] studies investigating the performance of the resulting products as adhesives are few. The unique characteristics of miniemulsion polymerization make it an attractive choice for PSA synthesis. In addition to the benefits of conventional emulsion polymerization such as the absence of organic solvents if polymerizable co-stabilizers are used, miniemulsions have other advantages: better control of particle nucleation because the polymerization *loci* are in the monomer droplets generated by mechanical mixing; direct generation of moderately high solids contents without the need for long semi-batch feeds; and easy manipulation of the MWD at high solids contents.[16] In water-based PSA production, high solids content latexes are preferable due to their better converting properties (i.e. coating, lamination and manufacture of a final product).[17] Also, it is estimated that the energy required to dry out water from a coated low solids content latex is five times higher than that requred for the removal of solvent from the same coating.[18] Hence, the increased interest in the production of high solids content latexes for PSAs.

The improved control of molecular weight and particle size distribution are key factors in latex film formation. This offers the possibility of "tailoring" the desired properties of water-based PSAs. In addition, miniemulsion polymerization offers a means of microencapsulation of different solid and/or liquid compounds into the particles[15] which can be used for the production of PSAs for transdermal drug delivery or other specialty products.

The objective of the work presented here was to propose a methodology for looking at different ways of making PSAs and this will be illustrated by investigating the adhesive performance of BA/MMA latexes obtained by seeded emulsion polymerizations. Latexes were obtained using two polymerization processes: clasical emulsion and miniemulsion.

Experimental procedures and techniques

Monomers, BA and MMA (Aldrich) were used without further purification. Sodium dodecyl sulphate (EM Science), ammonium persulfate (Aldrich), Triton X405 (Aldrich), stearyl methacrylate (Aldrich) and dodecyl mercaptan (Aldrich) as well as solvents tetrahydrofuran (EM Science), and methanol (ACP Chemicals) were also used as received. In all experiments, distilled de-ionized water was used.

Polymerization procedure

Preparation of the miniemulsions was performed one day prior to polymerization according to the following procedure. The aqueous phase containing water, Triton X405, and SDS was mixed using a magnetic stirrer. The monomer mixture containing octadecyl methacrylate was prepared in a separate flask also using a magnetic stirrer. Once the components in the different mixtures were completely dispersed, the contents of both flasks were mixed for approximately 1h. The reaction mixture was subsequently sonicated using a Fisher Scientific 550 sonic dismembrator at 30% power, Level 9 for 1 min. The mixture was simultaneously cooled in an ice bath and well mixed while undergoing sonication. Detailed polymerization recipes are given in Table 1.

Table 1. Polymerization recipes (All amounts are in parts per hundred monomer (phm) unless otherwise indicated. SDS – sodium dodecyl sulfate, APS – ammonium persulfate, SMA– stearyl methacrylate).

Run	**Step 1** (seed production)	**Step 2** (monomer addition)	**Step 3** (generation of the second particle population)
EE	BA = 77.91 MMA = 22.09 CTA = 0.47 SDS = 0.05 Triton X-405 = 0.25 Water = 183.6 APS = 0.23	BA = 79.99 MMA = 20.01 CTA = 0.49 APS = 0.22 Feed rate = 2 g/min	*Pre-emulsion:* BA = 80.00 MMA = 20.00 SDS = 0.76 CTA = 4.82 Water = 180.00 APS = 0.23 *Feed rate: 13.53 g/min*
MM	BA = 77.28 MMA = 22.72 SMA = 5.75 CTA = 0.52 SDS = 0.15 Triton X-405 = 7.12 Water = 183.6 APS = 0.23	BA = 79.79 MMA = 20.21 CTA = 0.53 APS = 0.22 Feed rate = 2 g/min	*Miniemulsion mixture:* BA = 78.81 MMA = 21.19 SDS = 0.15 Triton X405 = 7.08 CTA = 5.74 SMA = 4.22 Water = 180 APS = 0.23 *Feed rate: 13.53 g/min*

All reactions were performed in a 1.2L Labmax™ (Mettler Toledo) glass reactor equipped with a condenser, feed and sampling ports, and an anchor stirrer. Stirring speed (200 rpm), temperature (70°C) and feeding rates were automatically controlled using Camille™ software (Mettler Toledo). All reactions were repeated in a 1L jacketed glass reactor similarly equipped with a stirrer, feed and sampling ports, condenser and a feed pump.

Dynamic laser light scattering or quasi elastic light scattering (QELS) (Autosizer 4700, Malvern Instruments Ltd) was used to determine particle size and distribution. Only the repeated runs were analyzed using QELS. The particle size measurements were performed by diluting a drop of latex in approximately 4 mL of distilled, deionized water. Measurements were recorded at a 90° angle and an average of ten measurements was recorded. The CONTIN mode in the Malvern PCS software was used for the analysis of the results.

A Waters gel permeation chromatograph (GPC) was used for the determination of the molecular weight distribution of the latexes. Three Waters Ultrastyragel columns (10^3, 10^4 and 10^6 Å) were used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 mL/min at 38°C. Polystyrene standards (SHODEX) with molecular weights between 1.3×10^3 to 3.15×10^6 g mol^{-1} were used for calibration. Standards and samples were prepared in THF and filtered prior to injection through 0.45 μm filters to remove high molecular weight gel, if present. The injection volume was 200 μL. Millennium32^{TM} software (Waters) was used for data acquisition and analysis.

PSA testing

Prior to coating, particle agglomerates were removed from the latexes using a size #30 mesh. Latexes were coated using a wire-rod #30 onto a 50 μm polyethylene terephthalate carrier (Mylar®, DuPont) to give a dry film of 30 μm thickness and dried at room temperature. The films were conditioned 24h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity. Stainless steel panels were used as substrates in all tests. All tests were performed according to the Test Methods for Pressure Sensitive Tapes (Pressure Sensitive Tape Council or PSTC).[19]

PSTC 1 – Test method A (180° Peel) was used for peel adhesion testing. A 25.4 mm × 300 mm specimen was cut and laminated against a stainless steel substrate using a 2040 g rubber coated roller. Dwelling time was 1 min. The testing speed of a tensile tester (Instron Inc.) was 300 mm/min. The average force per 10 mm to peel the specimen from the substrate was reported. Six specimens were tested per sample.

PSTC 7 – Test method A was used to test shear adhesion. A specimen of 12 mm × 150 mm was cut. A 12.7 mm × 12.7 mm area of the specimen was laminated onto a stainless steel substrate using a 2040 g rubber coated roller. A 500 g weight was placed at the end of the specimen. Time to failure was recorded automatically using Labview^{TM} software (National Instruments). Six specimens were tested for each sample.

Tack was measured using the PSTC-6 (rolling ball tack) and PSTC-16 (loop tack) standards. For PSTC-6, a specimen of 25.4 mm × 300 mm was cut. The rolling ball test apparatus was placed at the beginning of the specimen. The distance that the ball travelled after being released was recorded. For PSTC-16 (loop tack), a specimen of 25.4 mm × 177.8 mm was cut. A loop with the adhesive facing outside was formed and 25.4 mm was masked using a masking tape and placed in the upper grip of a tensile tester (Instron Inc.). The loop was then brought into contact with the substrate mounted onto a loop tack fixture inserted into the bottom grip. When the loop covered an area of 25.4 mm × 25.4 mm, the upper grip was brought up at a crosshead speed of 300 mm/min. The maximum force necessary to detach the specimen was recorded as the loop tack. Six specimens were tested per sample.

Results and Discussion

EE process. The first step in the procedure was the production of seed latex by emulsion polymerization in batch mode (Table 1). Next, a semi-continuous addition of a monomer/CTA/initiator mixture was performed (see Figure 1). High conversion was maintained during the addition step to prevent secondary particle nucleation. Because the objective was to induce a second particle population of a well-defined size in the latter part of the procedure, the presence of a second particle population with uncontrolled particle sizes during the addition step was undesirable. At 200 min, the latex was diluted from an initial solids content of 50 to 27 wt.% to adjust the average number of particles per unit volume of emulsion. The addition of the monomer/CTA/initiator mixture continued for an additional 78 min. At that point, an additional pre-emulsified mixture of the same composition (see Table 1) was fed to the reactor at a high feedrate (13.5 g/min). The objective was to generate a second particle population of smaller particle size and lower molecular weight. Therefore, a higher CTA concentration was used compared to the first step in the reaction. Conversion vs. time data are shown in Figure 1.

To verify the existence of two particle populations for the EE process, a latex sample was taken immediately prior to the introduction of the pre-emulsied mixture. Its particle size distribution is compared to that of the final latex in Figure 2. From Figure 2, it is shown that large particles were generated prior to the addition of the pre-emulsified mixture and exhibited a broad PSD with a mean diameter around 486 nm. The production of a second population with a mean diameter around 200 nm during the final step was also observed (see Figure 2). However, the second population of particles was not clearly separated from the larger PSD. This illustrates the difficulty of controlling the particle nucleation in conventional emulsion polymerization as both particle populations presented a broad PSD.

MM process. In the MM process, miniemulsion polymerization was used to produce the seed and a miniemulsion was added in the final step of the reaction (see Table 1). The MM process also started in the batch mode and was followed by the addition of a monomer/CTA/initiator mixture.

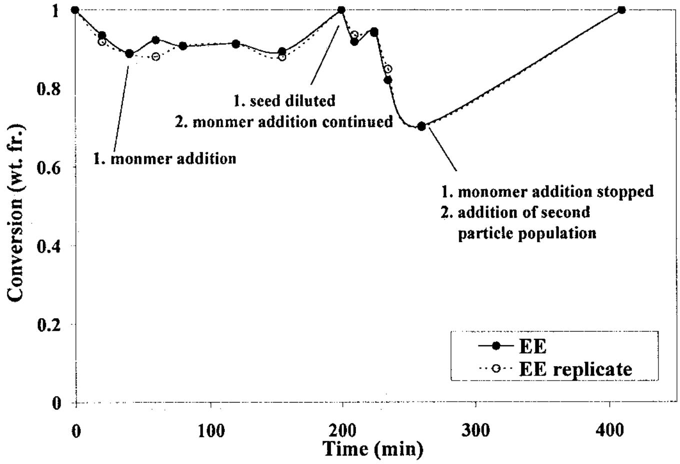

Figure 1. Conversion vs. time, EE process.

A sudden drop in the instantaneous conversion (see Figure 3) is evident at a reaction time of 75 min because the monomer mixture was fed to the reactor at that point to ensure further particle growth. At 308 min, in a way similar to the EE process, the seed latex was diluted from an initial 50 to 27% solids content to adjust the average number of particles per unit volume of emulsion. Further particle growth was ensured by continued addition of the monomer/CTA/initiator mixture. The addition was followed by feeding a miniemulsion at a high rate (13.5 g/min) into the reactor to generate a secondary particle population. As was the case for the EE process, this second particle population was of smaller particle size and lower molecular weight than that generated in the first part of the reaction.

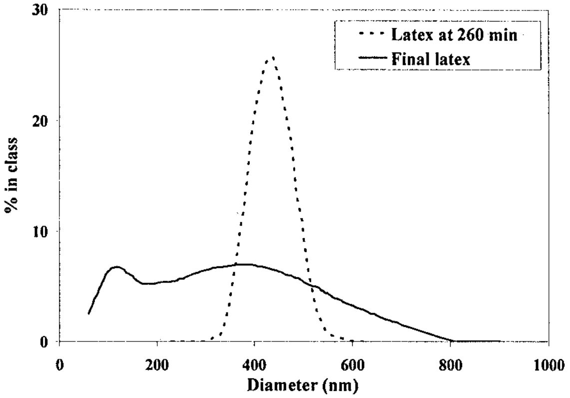

Figure 2. Particle size distribution, particles prior to addition of pre-emulsified mixture (sampled at 278 min) and final latex (EE process).

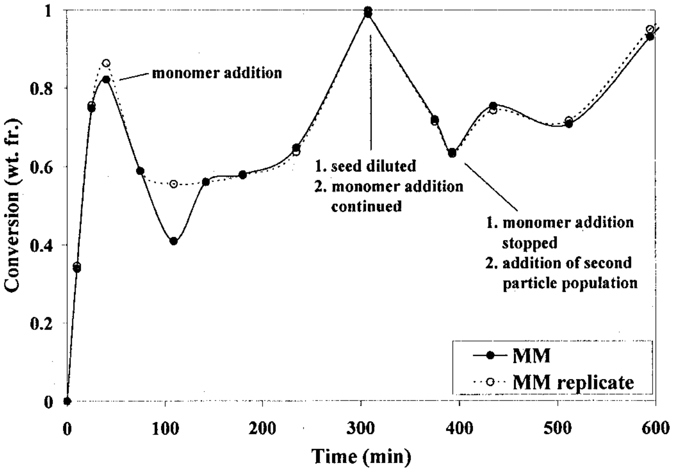

Figure 3. Conversion vs. time, MM process.

For the MM process, the particle size distribution prior to the addition of the final miniemulsion was monomodal with a mean particle size of 383 nm (see Figure 4). The final latex had a bimodal particle size distribution with mean particle sizes of 167.1 nm and 383.7 nm. The means and the width of the distributions indicate that the miniemulsion added during the final reaction step resulted in smaller particles and that existing larger particles were not affected by the addition of the second particle population. This concurs with recent findings that in miniemulsion polymerization, significant mass transfer of monomer between the particles does not occur under the conditions used here.[20] Using Differential Scanning Calorimetry and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy, Ouzineb et al.[20] have shown that, due to the dominance of droplet nucleation in miniemulsion, there is no significant monomer transfer between the polymerizing droplets. Controlling the initial droplet size by varying the sonication energy and duration, leads to better final particle size control compared to conventional emulsion polymerization, wherein monomer transfer from droplets to particles is essential for polymerization to occur.

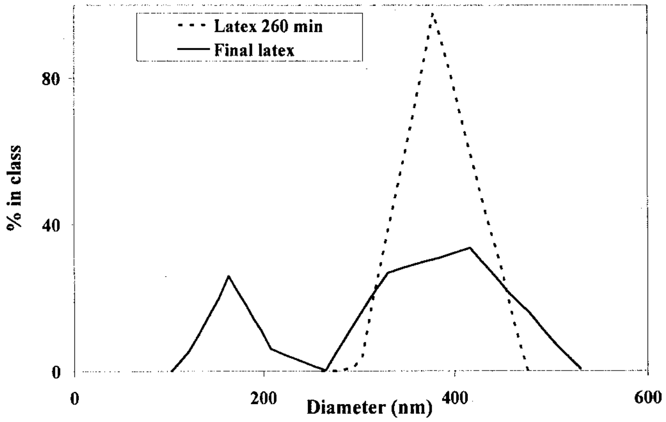

Figure 4. Particle size distribution, particles at reaction time 260 min and final latex (MM process).

Polymer molecular weight and distribution are important parameters governing pressure sensitive adhesive performance. Usually they have a conflicting influence on different properties. For example, good shear adhesion would require high molecular weight polymers with a high entanglement molecular weight. The molecular weight between the crosslink points can also be a factor if the formation of a crosslinked network is induced. On the other hand, to ensure good tack (i.e. formation of bonds in a short contact time), polymers with low T_g's and molecular weights are required. Thus, in this work, the objective was to generate BA/MMA polymers of a bimodal molecular weight distribution with both low and high molecular weight fractions that would satisfy the requirements for both shear adhesion and tack.

Similar to the particle size distribution, molecular weight distributions before and after the addition of the second particle population were determined. In both processes, a monomodal molecular weight distribution was observed for the seed latex while a bimodal molecular weight distribution was characteristic of the final latex. In Figures 5 and 6, respectively, are shown the molecular weight distributions of the EE and MM processes prior to the addition of the mixture leading to a second particle population and at the completion of the reaction. The number average molecular weights of the seed latex produced by the EE process (M_n=760,000) were almost double those obtained in the MM process (M_n=210,000). In both cases, the final latex showed a bimodal molecular weight distribution and extremely high average molecular weights (>3x10^6).

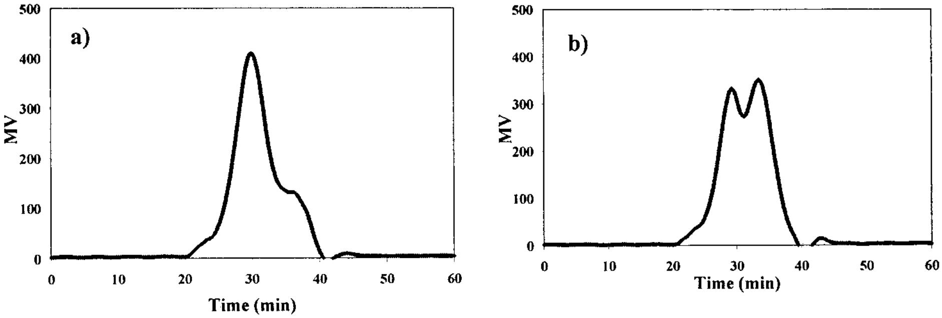

Figure 5. Molecular weight distribution, EE process prior to (a) and after (b) the addition of the pre-emulsion mixture.

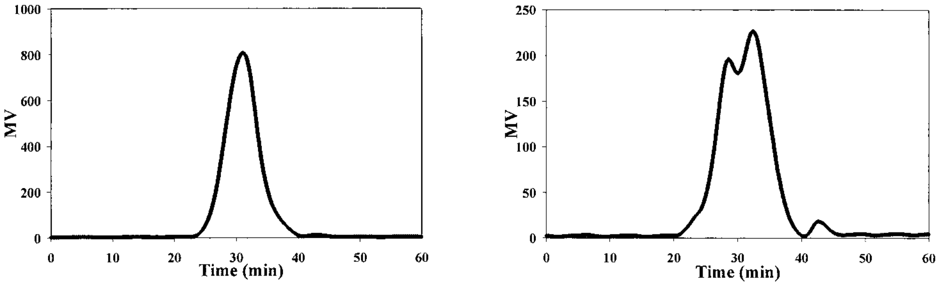

Figure 6. Molecular weight distribution, MM process prior to (a) and after (b) the addition of the pre-emulsion mixture.

Both final latexes were coated onto a poly(ethylene terephthalate) carrier and their performance as pressure sensitive adhesive tapes was evaluated. The PSA performance of the BA/MMA dry films is summarized in Table 2. It was possible to compare the different dry film performances because all tests were performed in six replicates and all other factors such as the thickness of the carrier and adhesive films, the drying time and temperature, as well as the testing conditions were kept constant.

Table 2. Adhesive properties of BA/MMA dried films.

	Peel (N/10mm)	**Loop Tack** (N/cm^2)	**Rolling Ball Tack** (cm)	**Shear** (min)
MM	6.2 ± 0.3	3.6± 0.4	6.0 ± 0.8	2.7± 0.3
EE	6.3 ± 0.3	3.8 ± 0.7	4.7 ± 0.3	1.4 ± 0.7

T-tests with a 0.05 significance level were used to compare the means in all tests. There was no statistically significant difference when the peel adhesion of the BA/MMA dry films obtained by the EE and MM processes was compared. Because of the high molecular weights obtained in both processes, this was not unexpected. It has been observed that peel adhesion increases with an increase in molecular weight of the polymer chains up to moderate molecular weights, after which it continuously decreases.[8] In both cases, adhesive failure was observed.

There was no statistically significant difference between the polymers when tack measured by the loop tack test was used for comparison. A relatively high loop tack was observed in both cases. The large amount of BA units in the polymer chains and the presence of a low molecular weight fraction in the molecular weight distribution which govern bond formation under short times are major factors affecting these results. It should be noted that the standard deviation for the measurements performed on EE adhesive films was almost double that for MM films. On the other hand, when tack was measured using a rolling ball tack test, a statistically significant difference was observed. In that test, BA/MMA dry polymers obtained from the EE process performed better. The tack measured by the different techniques is not comparable. Even though both copolymers were of high BA content, the number average molecular weight of the low molecular weight fraction was lower for the case of the EE polymer. Thus, it is possible that this reduction has caused improved tack. A similar trend in the loop tack measurement was not observed even though it was expected.

There was a statistically significant difference when shear adhesion was compared. BA/MMA films obtained by the miniemulsion process performed better. Even though they possessed higher molecular weights compared to the EE films, the MM films also showed extremely low shear adhesion. Both systems exhibited cohesive failure. It can be concluded that the presence of long chains alone is not sufficient to ensure good shear adhesion. It also has to be taken into account that both systems were emulsion based and thus, the formation of a continuous network upon drying, similar to that obtained in films dried from solution, which is known to contribute to improved adhesion, was not achieved here.

Overall, the performance of both BA/MMA latexes was similar, with high tack, moderate peel adhesion and low shear adhesion. This was despite the fact that one latex was obtained using a conventional emulsion while the other was achieved using a miniemulsion polymerization procedure.

Conclusions

Our objective was to compare BA/MMA polymers obtained in miniemulsion to those obtained by conventional emulsion polymerization. In both cases, we obtained a bimodal PSD. For the miniemulsion case, each PSD was clearly separated, whereas in the conventional emulsion polymerizations, the lower and upper limits of the larger and smaller PSDs were in the same particle size interval. Molecular weight distributions also revealed bimodal distributions with the number-average molecular weights of the lower fractions in the range of several thousands while the high molecular weight fractions were in the millions. The number-average molecular weights of the BA/MMA polymer obtained in the miniemulsion process was almost double those obtained in the conventional emulsion process.

When adhesive properties were tested and compared, both polymers showed similar characteristics: high tack, moderate peel and low shear adhesion. The confinement of low molecular weight polymer chains inside one particle size population was shown to improve the tackiness. Both polymerization processes showed good tack. On the other hand, the confinement of large molecular weight chains inside the other population did not improve shear considerably. The presence of long chains alone is not sufficient to improve this property. It would be necessary to introduce some crosslinking agents to ensure the development of a continuous network with a certain crosslink density to ensure better shear. Another possibility would be the introduction of interparticle crosslinking.[11]

This study has shown that a particular tailoring of PSA properties by selection of the polymerization process is possible. Depending on the objectives and economics, both, miniemulsion and emulsion polymerizations can be used to obtain desired properties. On the other hand, miniemulsion processes provide a greater ability to tailor polymer properties. Finer control of the MWD and our increased knowledge of nucleation in these systems will allow us to obtain an even better understanding of the influence of the different parameters involved in the generation of adhesive properties.

Acknowledgements

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