

# The effect of particle size and composition on the performance of styrene/butyl acrylate miniemulsion-based PSAs

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## Abstract

Styrene/butyl acrylate batch miniemulsion copolymerizations were performed in a 1.2 L stainless steel reactor. Conversions were monitored off-line using gravimetry and in-line using ATR-FTIR spectroscopy. The final latexes were coated on a polyethylene terephthalate carrier and dried at room temperature for 2 days. Their performance as pressure-sensitive adhesives (PSAs) was evaluated by measuring their tackiness, peel strength and shear strength. By using a constrained mixture design, the influence of particle size and copolymer composition was investigated. Particle size was found to be the most influential factor for both tack and peel strength models. Tack showed a concave upward trend whereas peel strength decreased with increasing particle size. Shear strength decreased with increasing particle size but was also significantly influenced by copolymer composition. The final forms of the models allowed 3D response surfaces to be built and an optimal adhesive performance region (highest combined tack, peel strength and shear strength) was located near the smallest particle diameter investigated with the highest styrene composition. The positive effect of smaller particles on every adhesive property relates to the tighter packing provided by smaller particles during the drying process, thus increasing the area of contact between the adhesive and the substrate.

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## 1. Introduction

Adhesives are defined as substances capable of holding at least two surfaces together. A class of adhesives called pressure-sensitive adhesives (PSAs) is characterized by instantaneous adhesion upon application of light pressure [1]. The most common applications for PSAs are tapes, labels and protective films. The polymerization process chosen to produce PSAs can be carried out in different media such as bulk, solution or emulsion. Because of environmental concerns and government regulations to substitute solvent-based systems by water-borne products, there is a growing interest in producing PSAs by emulsion polymerization. In conventional emulsion polymerizations, the main ingredients are monomer(s), water, surfactant and initiator. When the concentration of surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate to form small colloidal clusters referred to as micelles. In principle, polymer particles can be

formed by the entry of radicals into the micelles (heterogeneous nucleation), precipitation of growing oligomers in the aqueous phase (homogeneous nucleation), and radical entry in monomer droplets. The monomer droplets are relatively large (1–10  $\mu\text{m}$ ) compared to the size of monomer-swollen micelles (10–20 nm), and hence the surface area of the micelles is much greater than that of the monomer droplets [2]. Consequently, the probability for a radical to enter the monomer droplets is very low, and most particles are formed by homogeneous and heterogeneous nucleation.

An alternative to conventional emulsion polymerization, miniemulsion polymerization, provides a simpler means of controlling particle size [2]. The basis for the miniemulsion polymerization process is an energetic homogenization of the reaction mixture to reduce the size of the monomer droplets and the use of both a hydrophobe and an emulsifier to protect these droplets against degradation. An efficient miniemulsion polymerization (in terms of particle formation) is very useful as it allows one to control the number and size of particles being formed in a manner different from particles formed by micellar or homogeneous nucleation. That is, miniemulsions are conducted at emulsifier concentrations well below the CMC, thus avoiding micellar nucleation altogether. The droplet size can range from 50 to 500 nm in diameter [3] and the latex

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produced by miniemulsion is characterized by a broader particle size distribution (PSD) ranging from 50 to 1000 nm in diameter [2]. If one manages to reduce the size of the droplets sufficiently, the resulting large surface area of the droplets allows them to compete effectively against the micelles to capture the oligomeric radicals and to become the main loci of polymerization.

In order to develop new application-specific PSA products and improve existing processes, there is a need to identify the factors that influence the performance of PSAs. Reaction components and process conditions will affect latex properties such as copolymer composition, molecular weight distribution (MWD) and PSD. Those latex properties will, in turn, affect rheological properties and the film formation process. Eventually, the latex rheology and the film formation process can affect the performance of the adhesive. Furthermore, many industrial applications require materials with specific properties that can only be achieved through the use of two monomers, i.e. by copolymerization. One example is the styrene (St) and butyl acrylate (BA) system. Depending on their composition and molecular weight, among other properties, the resulting polymers from this system can be used to produce different types of adhesives, coatings and paints.

A PSA must be soft and tacky hence, its glass transition temperature ( $T_g$ ) should be low, ranging from  $-20$  to  $-60$  °C. Polymers with low  $T_g$ , typically from a class of alkyl acrylates such as poly(BA) and poly(2-ethylhexyl acrylate) are inherently soft and tacky but do not possess adequate shear strength. A balanced combination of tack, peel strength and shear strength is of primary concern for PSA production. As a consequence, the copolymerization of an alkyl acrylate having a low  $T_g$  with a thermoplastic such as St or methyl methacrylate having a high  $T_g$  is useful to regulate this combination of tack, peel strength and shear strength. In addition, monomers with functional groups such as acrylic acid (AA) or methacrylic acid (MAA) could be added to improve peel and shear strength although their addition often reduces tack [4]. Since tack, peel strength and shear strength are the three general adhesive properties that determine PSA performance, a brief description of each property follows.

Tack is defined as the property that enables an adhesive to form a bond of measurable strength with a surface of another material upon brief contact under light pressure [5] or no pressure [6]. Tackiness should increase when the  $T_g$  of the copolymer decreases [7] and  $T_g$  should in turn decrease when the copolymer composition is enriched with a soft polymer like poly(BA). Because  $T_g$  depends on chain flexibility, all factors affecting chain flexibility such as sequence length distribution, MWD, and cross-linking density will affect  $T_g$ . This concept was supported by Satas [8,9] who concluded that tackiness should increase with molecular weight. He demonstrated that an initially high value of tack associated with a low molecular weight would decrease and eventually level off when the molecular weight was increased. An increase in surfactant concentration could result in a decrease of tackiness if the water resistance is reduced or the surfactant molecules migrate to interfaces [10]. On the other hand, Brooks et al. [11] reported

that the influence of a proprietary stabilizer on the tack of a BA/vinyl acetate/MAA emulsion-based PSA was low.

Peel strength represents the force required to remove a standard PSA strip from a specified test surface under a standard test angle (90 or 180°) under standard conditions. The incorporation of a high  $T_g$  component like poly(St) should improve peel strength up to the point where the adhesive becomes too stiff and does not wet the surface, thus decreasing peel strength [1]. Low molecular weight polymers will show a mediocre resistance to peel and as the molecular weight continues to increase, the resistance to peel will eventually reach a maximum before starting to deteriorate at higher molecular weights [8,9]. When surfactant molecules migrate to the film-substrate interface, peel strength could be affected. Charneau et al. [12] suggested that the increase in peel strength when the concentration of surfactant was also increased corresponded to the formation of a monolayer of surfactant at the PSA surface while a decrease in peel strength corresponded to the formation of a similar but much thicker layer that would behave as a weak boundary layer.

Shear strength is the internal or cohesive strength of the adhesive mass. Usually, it represents the length of time it takes for a standard strip of PSA to fall from a test panel after application of a load. Shear resistance increases as the concentration of the high  $T_g$  component increases [1]. The resistance to shear will also depend on the MWD of the polymer [8,9]. High molecular weight polymers present a good resistance to shear but this property will degrade rapidly at lower molecular weights. As well, a broad MWD will result in a lower shear resistance compared to a narrow one [1]. The presence of highly mobile small molecules like surfactant molecules are expected to decrease shear resistance.

### 1.1. Modeling adhesive performance

The performance of an adhesive depends heavily on its latex properties. Latex properties such as copolymer composition, MWD, PSD and gel content can be controlled by adjusting the operating conditions. Therefore, a good knowledge of the effect of operating conditions on the latex properties is required. In addition, the relationship between the latex properties and the performance of the adhesive is of equivalent importance. The relationship between the operating conditions and the latex properties can be obtained by mathematical modeling of the polymerization reactor and extensive experimentation. Considerable efforts have already been devoted to the modeling and control of at least some of the latex properties mentioned above [13,14] and hence, this study focuses on the impact of latex properties on adhesive performance. The development of these relationships in the context of miniemulsions has been limited. In the exploratory investigation by Jovanovic et al. [4], the performance of BA/methyl methacrylate PSAs produced in a conventional emulsion and a miniemulsion was compared. Structure–property relationships between the adhesive properties and the weight–average molecular weight and average particle size were also examined. They found that adhesives made from

both polymerization processes (conventional and miniemulsion) showed similar characteristics that could be tailored to obtain the desired properties. They also concluded that miniemulsions could provide greater control over the latex properties because of the compartmentalized nature of the particles and finer control of the particle size.

There are no adhesive property studies for free radical copolymerizations of styrene/butyl acrylate in miniemulsion, to our knowledge. Adhesive studies on similar systems using conventional emulsion could, however, provide a basis for comparison [15–17]. However, none of these studies focused on the effect of particle size on PSA properties.

The improved control of the PSD by miniemulsion polymerization coupled with a control over the MWD and composition of the copolymer could offer the possibility of tailoring the desired properties of PSAs. In this study, miniemulsion polymerization was used to develop our understanding of the relationships between particle size and copolymer composition on the adhesive performance of a St/BA-based PSA.

## 2. Experimental section

### 2.1. Reagents

The reagents: St, BA, AA, octadecyl acrylate (ODA), the chain transfer agent (CTA) *n*-dodecyl mercaptan, sodium dodecyl sulfate (SDS, EM Science), Triton X-405, sodium hydrogen carbonate ( $\text{NaHCO}_3$ ), and potassium persulfate (KPS) were all purchased from Aldrich Chemical, unless otherwise indicated and were used without any further purification. All components used to perform the characterizations, i.e. toluene, ethanol, methanol, chloroform-*d*, tetrahydrofuran (THF), sodium hydroxide (NaOH), and calcium chloride ( $\text{CaCl}_2$ ) were used as received.

### 2.2. Experimental procedure

The reactions were performed in a jacketed 1.2 L stainless steel reactor with a Labmax™ setup (Mettler Toledo) and stirred at 200 rpm. The reactor was equipped with a nitrogen purging/pressurizing line, reflux condenser, sampling line and a port for the IR insertion probe. Stirring speed and temperature were automatically controlled using Camille™ software (Mettler Toledo).

St, BA and ODA were mixed for 15 min in a beaker while water, Triton X-405, and SDS were mixed for 15 min in a separate vessel. Both solutions were then combined and mixed for 1 h with a magnetic stirrer. The mixture was then sonicated using a Fisher Scientific 550 sonic dismembrator for 3 min at level 6. The mixture was simultaneously cooled in an ice bath and well mixed while undergoing sonication.

The polymerizations were run at 80 °C. The reaction mixture was then heated and purged of oxygen by bubbling  $\text{N}_2$  through it for at least 40 min. When the set point temperature was reached, a deoxygenated initiator solution made with KPS and distilled deionized water was charged into

the reactor. This corresponded to time zero for the polymerization. At suitable time intervals, samples were taken through the sampling port for further analysis.

### 2.3. Characterization

Mass conversion based on the total polymer in the reaction mixture and percent solids were measured using gravimetry.

Proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) was used to determine the average or cumulative composition of copolymers. Analyses were carried out at room temperature in deuterated chloroform (about 2% weight per volume solution) with a Bruker AMX-500 Fourier transform  $^1\text{H}$  NMR spectrometer. The acquisition time was 4.6 s and 16 scans were performed per sample. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. The spectral peaks for the  $-\text{OCH}_2$  group in BA were located at  $\sim 3.4$ – $4$  ppm and the cyclic (5H) group in St was located at  $\sim 6.6$ – $7.2$  ppm.

Average molecular weights were measured using GPC. Polymer molecular weight averages and distributions were determined with a Waters Associates GPC system equipped with three Waters Styragel-HR columns ( $10^3$ ,  $10^4$ , and  $10^6$  Å pore size) installed in series, thermostated to 30 °C, and a Waters 410 differential refractometer thermostated to 38 °C. THF was used as the mobile phase and was delivered at 0.3 mL/min. Polymer samples were dissolved in THF to produce solutions with a concentration of approximately 0.005 g/10 mL and filtered through 0.45  $\mu\text{m}$  filters to remove any high molecular weight gel. A quantity of 200  $\mu\text{L}$  of each solution was injected into the GPC and the data were analyzed using the Millennium 32™ (version 3.05) chromatography manager software. The polymer molecular weights were calculated by using the universal calibration principle. The following Mark–Houwink parameters determined in THF were used for the calculations: for polystyrene,  $K$  and  $\alpha$  were  $16 \times 10^3$  mL/g and 0.700, for polybutyl acrylate,  $K$  and  $\alpha$  were  $11 \times 10^3$  mL/g and 0.708 [18]. The values of  $K$  and  $\alpha$  for the copolymers were obtained using weighted averages based on the cumulative copolymer composition data.

The particle size and PSD of the final latexes were determined using a Brookhaven disc centrifuge photosedimentometer (BI-DCP). A gradient fluid containing 0.1 mL of dodecanol, 0.2 mL methanol, and 15 mL of water was first prepared and injected into a spinning disc. A narrow polystyrene standard was used to check the accuracy of the system prior to the determination of the particle size. A volume of 0.2 mL of each sample solution, which consisted of 3 mL of distilled de-ionized water, 1 mL of methanol, and three drops of the latex sample, was then injected into the spinning disc ( $\sim 10,000$  rpm).

Gel content was determined using the membrane partitioning method [19]. A known amount of sample was sealed between two polytetrafluoroethylene membranes (pore size of 0.2  $\mu\text{m}$  and diameter of 47 mm). Enclosed samples were shaken for 72 h in THF. Sealed pouches were air-dried until a

constant weight was achieved. The difference between the initial and final weight of the sample was used to calculate the gel content.

Once the latexes were characterized, PSAs were produced by casting the latex film onto a carrier. Before casting the film, particle agglomerates were removed from the latexes using a size #30 mesh. Each latex were then coated onto a polyethylene terephthalate carrier using a Meyer rod #30 to give a dry film thickness of 30  $\mu\text{m}$  when dried at room temperature. The films were dried for 2 days before testing. All the tests were performed according to the test methods for pressure sensitive tapes [6] with stainless steel substrates. Three adhesive tests were performed to evaluate the tack, peel strength and shear strength of the PSAs. Two films were cast per latex and three specimens from each film were used for each adhesive test for a total of six tests per latex. A hierarchical design was used to test run-to-run and film-to-film differences. No film-to-film differences were found and therefore, the average of the six measurements was used in the analysis of the results.

Tack was measured using the PSTC-16 (loop tack) standard. A specimen of 25.4 mm  $\times$  177.8 mm was cut and one inch on both sides was masked with masking tape. A loop with the adhesive facing outside was formed and placed in the upper grip of an Instron 1100 universal 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  $\times$  25.4 mm, the upper grip was brought up at a crosshead speed of 300 mm/min. The maximum force required to remove the specimen was recorded as the loop tack.

Peel was measured using the PSTC-101 (180° peel) standard. A specimen of 25.4 mm  $\times$  304.8 mm was cut and laminated onto the substrate using a 2040 g rubber coated roller. The average force per 10 mm to peel the specimen from the substrate was recorded. The testing speed for the Instron tester was 300 mm/min.

Shear was measured using the PSTC-107 standard. A specimen of 25.4 mm  $\times$  152.4 mm was cut and an area of 25.4 mm  $\times$  25.4 mm was laminated onto the 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™ software (National Instruments).

#### 2.4. Experimental design

A series of experiments was designed to further our understanding of the relationships between the latex properties (particle size and polymer composition) and PSA performance (tack, peel strength and shear strength). All recipes were performed as miniemulsions with a sonication time of 3 min, a reaction temperature of 80 °C and a solids content of 50 wt%. The following ingredient concentrations were also kept constant: water=90 phm, NaHCO<sub>3</sub>=1 phm (to control pH), KPS=0.75 phm, AA=4 phm, CTA=0.25 phm, where phm represents parts per 100 parts of monomer.

In order to properly understand the relationships between particle size and copolymer composition on the adhesive

performance of the PSA, a three-level factorial design for two variables was planned. Because the emulsifier concentration was used to control particle size, it was decided to choose three levels of emulsifier concentration as a design variable. A system of three emulsifiers was used to prevent monomer droplet degradation and all three concentrations were changed proportionally for each level. Three polymer compositions were also chosen. Based on previous knowledge, it was assumed that certain compositions would produce PSAs with poor performance. Hence, the following constraints (in phm) were used in order to choose those three levels of compositions: 85 < BA < 95 and 5 < St < 15. As a result of this 3<sup>2</sup> factorial design, 11 runs (9+2 replicates of run 5) were performed as described in Table 1.

A full second order polynomial model was used to model each dependent variable (tack, peel strength, shear strength):

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{12}x_1x_2 \quad (1)$$

where  $y$  is the dependent variable,  $\beta$ 's are the fitted parameters in the model,  $x_1$  represents the St concentration in phm and  $x_2$  represents the particle diameter in micrometer. The variables were coded as follows:

$$\text{Coded value} = \frac{(\text{value} - ((\text{max} + \text{min})/2))}{|\text{max} - \text{min}|/2} \quad (2)$$

The models were evaluated using standard statistical tools such as residual plots, the correlation coefficient ( $R^2$ ), the significance  $F$ , and by performing a lack of fit test with  $\alpha=0.05$ . The number of parameters in the models was then reduced by considering the precision of the parameter estimates. Finally, the models were decoded to obtain the form shown in this paper.

### 3. Results and discussion

Gravimetric results indicated fast reaction rates for all of the runs and are shown in Fig. 1 for runs 1, 4 and 7. Similar results were obtained for the other runs with runs at the same feed composition having similar polymerization rates. All the runs were completed successfully with conversions exceeding 99 wt% in most cases.

Table 1  
Batch recipes (all values in phm)

Run	St	BA	Triton X405	SDS	ODA
1	5	95	0.5	0.03	0.5
2	5	95	1	0.06	1
3	5	95	2.5	0.15	2.5
4	10	90	0.5	0.03	0.5
5-1	10	90	1	0.06	1
5-2	10	90	1	0.06	1
5-3	10	90	1	0.06	1
6	10	90	2.5	0.15	2.5
7	15	85	0.5	0.03	0.5
8	15	85	1	0.06	1
9	15	85	2.5	0.15	2.5

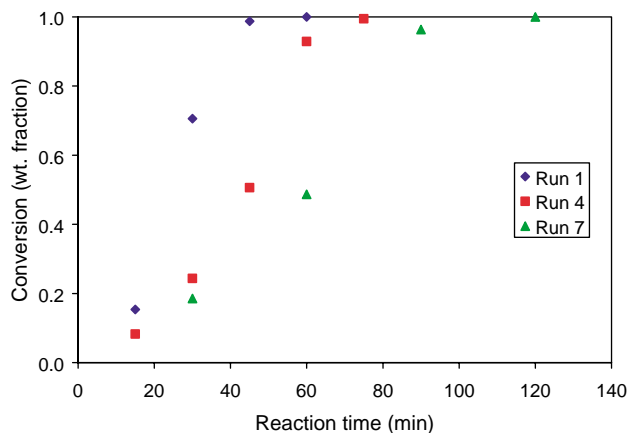


Fig. 1. Conversion vs. time for runs 1, 4, 7.

As stated earlier, a small amount of AA was added to improve the peel and shear strength of the final PSA. It should be noted that the partitioning of AA in the water and oil phase was strongly influenced by the pH of the reaction mixture. In the St/BA/AA system, Dos Santos et al. [20] found AA to be equally distributed between the water and oil phases when the pH was between 2 and 4. An increased pH of 6 and higher resulted in the presence of AA mainly in the water phase. Furthermore, at a pH of 6–7, the AA propagation rate decreased. With this in mind, the pH of the reactions in this study was maintained between 4 and 5 to encourage the incorporation of AA into the polymer particles.

The impact of monomer feed composition on cumulative copolymer composition is shown in Fig. 2 for runs 1, 4, and 7. Similar results were obtained for the other runs with the feed composition having the expected effect on copolymer composition.

An important factor affecting the performance of PSAs is the  $T_g$  because it reflects the softness necessary for the adhesive to flow and bond with a surface. However, Benedek and Heymans [1] warned that while  $T_g$  was a good predictor, it was not an absolute measure of an adhesive's suitability to become a PSA. When the amounts of all other components in the recipe are kept constant, the final observed value should only be dependent on the ratio of monomers used in the recipe. Hence,

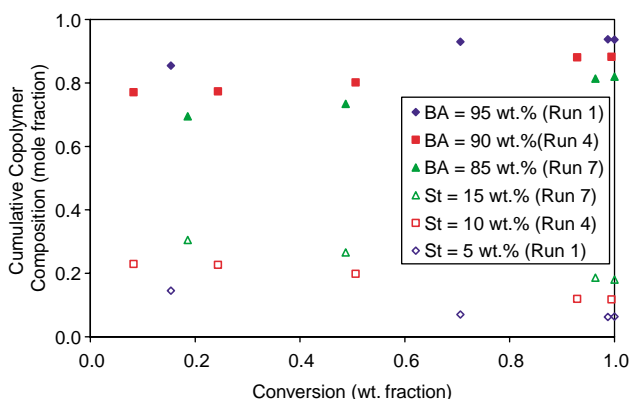


Fig. 2. Cumulative copolymer compositions for different feed compositions.

the  $T_g$ s in this study ranged from 229 to 239 K, based on the final copolymer composition.

Polymer molecular weight has a great influence on adhesive properties, especially in the low molecular weight range. As the molecular weight increases, its effect starts to level off. Low molecular weight PSAs exhibit good tack but their ability to peel is generally unacceptable for typical PSA applications unless they can be crosslinked. Changes in PSA properties as a function of molecular weight are known [8]. Both tack and peel strength increase with increasing molecular weight until a maximum is reached. Shear strength increases with increasing molecular weight but decreases strongly at a fairly high molecular weight. The molecular weights obtained in this study are shown in Table 2 and their polydispersity indexes (PDI) ranged from 2.1 to 3.6. There were no detectable trends in PSA performance with respect to molecular weight from the data at the conditions studied herein. Other factors (e.g. particle size and  $T_g$  or polymer composition) likely had stronger effects on the properties. Of course, it is also known that the molecular weight between crosslinks and the entanglement molecular weight may show more representative trends in the PSA properties [19]. However, these were not measured in this study.

The gel content is another factor that could affect the performance of PSAs. An increase in gel content should increase the shear strength of PSAs while reducing tack [21]. The gel contents obtained in this study are shown in Table 2. A major contributor for the formation of gel in the latex is likely the BA monomer. A high BA content can lead to 'backbiting' or chain transfer to polymer, resulting in the formation of double bonds that can further polymerize and form branches or cross-links [22]. In addition, the relatively low CTA concentrations used in this study could have enhanced this effect because CTA is normally added to a recipe to lower the molecular weight and gel content. Hence, with a lower concentration of CTA, the gel content could be expected to increase. Since the BA content remained fairly high for every recipe in this study (between 85 and 95 phm), it was difficult to appropriately assess the effect of gel content on PSA properties. In other words, the effects of other factors (particle size,  $T_g$ ) were strong enough to mask the effects of gel content under the conditions studied.

### 3.1. Modeling adhesive performance

All values for the dependent variables (tack, peel strength, shear strength) and the independent variables (particle diameter, monomer feed composition) used in the derivation of the models are shown in Table 2. The polydispersity indexes of the particle diameters ranged from 1.05 to 1.20.

For the determination of tack, six specimens from two films were tested. Prior to any analysis, a fully nested (hierarchical) analysis of variance (ANOVA) was performed to provide an estimate of the components of variance in the data. This hierarchical experimental design was used to investigate run-to-run and film-to-film differences. The analysis of variance (ANOVA) results, shown in Table 3, were obtained with

Table 2  
Experimental results ( $d_p$  = number-average particle size)

Run	St feed composition (phm)	Tack (N/cm <sup>2</sup> ) ± 0.1	Peel strength (N/10 mm) ± 0.3	Shear strength (h) ± 2	$d_p$ (μm) ± 0.005	$M_w$ (g/mol) × 10 <sup>-4</sup>	Gel content (wt%) ± 6
1	5	1.6	2.2	68	0.371	9.2	13
2	5	1.0	2.9	71	0.327	8.8	11
3	5	1.6	2.6	56	0.282	5.7	19
4	10	1.2	1.8	127	0.372	9.0	0
5	10	0.9	3.4	178	0.321	8.3	28
5-2	10	1.2	4.2	326	0.306	7.6	22
5-3	10	1.2	4.2	253	0.302	7.5	34
6	10	1.0	3.8	252	0.305	8.9	25
7	15	0.5	1.4	219	0.348	8.6	0
8	15	0.6	2.5	302	0.326	7.4	9
9	15	0.8	3.2	356	0.311	8.3	19

MS-Excel. Because the ANOVA revealed no statistically significant film-to-film differences, the average of six measurements was reported as a single value of tack (Table 2). As expected, the run-to-run differences were significant at the 0.05 level and were the major contributors to the total variability in the data. Similar results were obtained for peel and shear measurements and are reported elsewhere [23].

All samples showed adhesive failure except for runs 1, 2 and 3 where a residue was left on the stainless steel substrate. The ‘softer’ adhesives (runs 1, 2 and 3) showed a lack of cohesive strength with superior performance under loop tack conditions. In general, higher tack values could be associated with lower  $T_g$ s (i.e. lower St content) or, to a lesser degree, higher gel contents. Despite the cohesive nature of some samples, they were included in the analysis because of their consistent behaviour with respect to the model. The coded (Eq. (3)) and final decoded (Eq. (4)) forms for the tack model are

$$\text{tack} = -0.4589 - 0.3914f_{St} - 0.4079d_p + 1.0880d_p^2 - 0.4174f_{St}d_p \quad (3)$$

$$\text{tack} = 31.370 + 0.2928f_{St} - 189.46d_p + 297.74d_p^2 - 1.0279f_{St}d_p \quad (4)$$

where  $f_{St}$  is the mole fraction St in the copolymer and  $d_p$  is the

number-average particle diameter. There were no trends in the residuals and no lack of fit was found. The model explained a significant amount of variation in the data and the correlation coefficient ( $R^2$ ) was 0.9790. From the coded form of the model, the most influential parameter was the  $d_p^2$  parameter ( $\beta_{22}$ ) indicating a strong curvature (with a minimum) for the relationship between particle size and tack. The model also revealed a synergistic interaction effect (see  $\beta_{12}$  parameter) between particle size and polymer composition (or feed composition or  $T_g$ ) on tack. A representation of the model is shown in Fig. 3. When the St content (or  $T_g$ ) was decreased, tack increased; this is consistent with the work of Aubrey [7]. As for particle size, a possible explanation for the positive effect of smaller particles on tack could involve the film formation process. It can be speculated that smaller particles could pack more tightly during the drying process, thus increasing the area of contact between the adhesive and the substrate. The incorporation of a molecular weight variable was attempted for the tack model but its inclusion rendered the model inadequate to explain the data. This was likely due to the strong correlation exhibited between particle size and molecular weight. The data in Table 2 demonstrate how an increase in particle size was often associated with an increase in molecular weight.

For the case of peel strength analysis, only the latexes associated with the higher  $T_g$  values (high St content runs 7, 8

Table 3  
Analysis of variance (ANOVA) for tack

Fully nested ANOVA						
Source	DF	SS	MS	$F$ -calculated	$F$ -tabulated	$p$
Run	10	7.6192	0.7619	59.160	2.1	$3.48 \times 10^{-22}$
Film	11	0.0000	0.0000	0.001	4.1	0.98
Error	4	0.5667	0.0129			
Total	65	8.1859				
Variance components						
Source	Variance component		Percent of total		Standard deviation	
Run	0.117		93.08		0.342	
Film	0.000		0.00		0.000	
Error	0.009		6.92		0.093	
Total	0.126					

DF, degrees of freedom; SS, sum of squares; MS, mean square. Significant difference exists if  $F$ -calculated >  $F$ -tabulated or if  $p < 0.05$ .

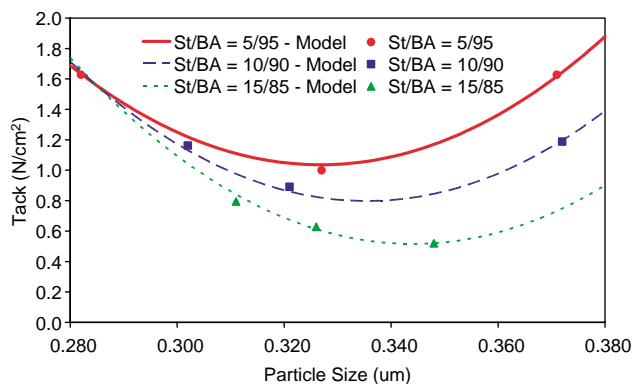


Fig. 3. Tack vs. particle size and polymer composition.

and 9) or with no gel content (runs 4 and 7) showed adhesive failure (no residue was left on the stainless steel substrate). The ‘softer’ adhesives with some gel content (runs 1, 2, 3, 5 and 6) showed a lack of cohesive strength. In general, higher peel strength values could be associated with higher gel contents. Similar to tack, the consistent behaviour with respect to the model allowed the samples exhibiting cohesive strength to be included in the analysis. The coded (Eq. (5)) and final (Eq. (6)) forms for the peel strength model are

$$\text{peel} = 0.3389 - 0.0322f_{St} - 1.0044d_p - 0.5671f_{St}^2 - 0.8047f_{St}d_p \quad (5)$$

$$\text{peel} = -5.7541 + 2.2125f_{St} - 18.398d_p - 0.0310f_{St}^2 - 4.8943f_{St}d_p \quad (6)$$

There were no trends in the residuals and no lack of fit was found. The model explained a significant amount of variability in the data and the correlation coefficient ( $R^2$ ) was 0.9614. From the coded form of the model, the most influential parameter was the  $d_p$  ( $\beta_2$ ) parameter indicating a strong linear relationship between particle size and peel strength. The coded model also showed a pronounced synergistic effect of particle size and polymer composition on peel strength. A representation of the model is shown in Fig. 4. At the lowest particle sizes, the increased St content (or higher  $T_g$ ) produced effects consistent with the work of Benedek and Heymans [1] who

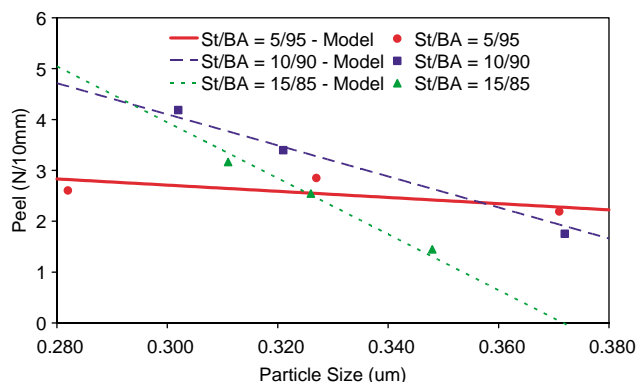


Fig. 4. Peel strength vs. particle size and polymer composition.

found that it should increase the peel strength. At the highest particle sizes, the impact of increasing the St content reduced the peel strength. They also found that increasing the St content should increase the peel strength up to a maximum. Beyond this maximum, the adhesive becomes too stiff and does not wet the surface appropriately, hence reducing the peel strength. During the drying process, perhaps the largest particle sizes imparted some inherent weaknesses to the peel strength property and the smallest styrene content tested already exceeded the optimum value.

In the case of shear strength, all the samples showed cohesive failure where a residue was left on the stainless steel substrate. In general, higher shear strength values could be associated with higher  $T_g$ s. The coded (Eq. (7)) and final (Eq. (8)) forms for the shear strength model are:

$$\text{shear} = 0.8011f_{St} - 0.6398d_p - 0.1976f_{St}^2 + 0.0910d_p^2 - 0.6545f_{St}d_p \quad (7)$$

$$\text{shear} = 191.93f_{St} - 3201.1d_p - 1.3377f_{St}^2 + 8226.7d_p^2 - 431.12f_{St}d_p \quad (8)$$

There were no trends in the residuals and no lack of fit was found. The model was statistically significant, in terms of describing variation in the data, and the correlation coefficient ( $R^2$ ) was 0.9347. From the coded form of the model, the most influential parameter was the  $f_{St}$  ( $\beta_1$ ) parameter indicating a strong linear relationship between polymer composition and shear strength. The coded model also showed an appreciable linear relationship with respect to particle size ( $\beta_2$ ) and a pronounced synergistic effect of particle size and polymer composition ( $\beta_{12}$ ) on shear strength. A representation of the model is shown in Fig. 5. When the St content (or  $T_g$ ) was increased, shear strength increased; this is consistent with the work of Benedek and Heymans [1]. As for particle size, a possible explanation for the positive effect of smaller particles on shear strength relates to a similar concept described for tack wherein the smaller particles could pack more tightly together during the drying process, thus increasing the area of contact between the adhesive and the substrate. Similar to the tack and peel strength models, the possible correlation between particle

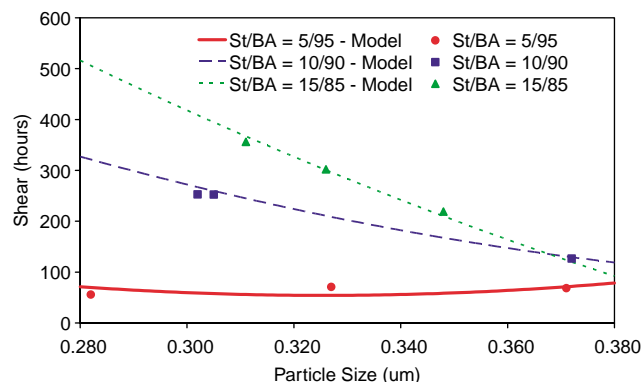


Fig. 5. Shear strength vs. particle size and polymer composition.

size and molecular weight probably rendered the shear strength model inadequate to explain the data when a molecular weight variable was introduced.

The final forms of the models allowed 3D response surfaces to be constructed for tack, peel strength and shear strength; these are shown in Figs. 6–8, respectively. From the tack response surface, a minimum is located in the middle of the investigated particle diameter region. Although moving away from this region in both directions would increase tack, more freedom over the polymer composition could be achieved if the particle diameter became smaller. The peel and shear strength response surfaces both indicate maximums in the smallest particle diameter region with high styrene composition. After investigating all three response surfaces, the optimal adhesive performance region should be located near the smallest particle diameter investigated, with the highest styrene composition. In order to properly assess those conclusions, a more in depth study should be conducted in this optimal region.

#### 4. Conclusions

A series of St/BA miniemulsion copolymerizations was carried out in a 1.2 L stainless steel reactor. All recipes were performed as miniemulsions with a solids content of 50 wt%. All the runs were completed successfully with conversions exceeding 99 wt% in most cases. The pH of the reactions in this study was maintained between 4 and 5 to allow the incorporation of AA into the polymer particles. The  $T_g$ s ranged from 229 to 239 K, the molecular weights ranged from  $6 \times 10^4$  to  $9 \times 10^4$  and the gel contents ranged from 0 to 33.6 wt%.

By using a constrained mixture design, the influence of particle size and polymer composition on PSA performance was investigated. As a result of a  $3^2$  factorial design (nine runs and two replicates), loop tack, peel strength and shear strength were measured and modeled empirically using a full second order polynomial. The models all described a statistically significant amount of variation in the data, showed no trends in the residuals and showed no lack of fit.

In general, higher tack values were associated with a lower  $T_g$  and, to a lesser degree, higher gel contents. This concurs with well-known concepts relating a decrease in  $T_g$  (or St

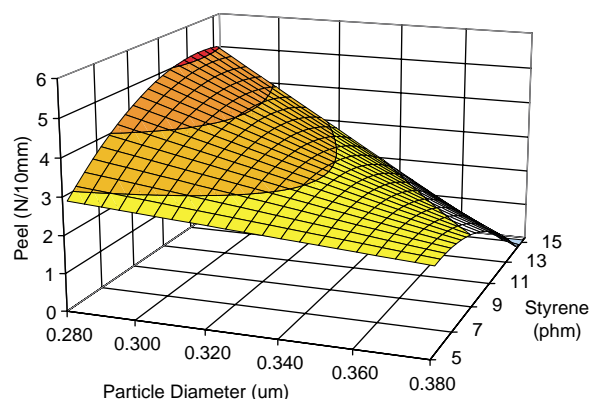


Fig. 7. 3D response surface for the peel strength model.

content in the polymer composition) with an increase in tack [7]. At the lowest particle sizes studied, the peel model agreed with known relations between  $T_g$  and peel strength [1]. That is, an increase in styrene content (or  $T_g$ ) resulted in higher peel strengths. However, at the largest particle sizes, the impact of adding more styrene to the recipe lowered the peel strength. As stated by Benedek and Heymans [1], if the maximum peel strength is achieved with a certain St composition, the addition of more St to the polymer chain could only result in a reduced performance. Hence with the largest particle sizes, it is likely that the optimum St content was already exceeded. Higher shear strength values were usually associated with higher  $T_g$ s (or increased St content), which is consistent with the literature [1].

In all three models, the particle size played a significant role. That role was associated with the packing of particles during the adhesive film drying process. For example, the increased contact area afforded by smaller particles resulted in an increase in tack and shear strength. For tack, however, as particle size was further increased an increase in tack resulted. In other words, a concave upwards relation between tack and particle size was shown to exist. In addition, the peel model showed that an increase in particle size resulted in a decreased peel strength.

The final forms of the models allowed for the construction of 3D response surfaces. An optimal adhesive performance

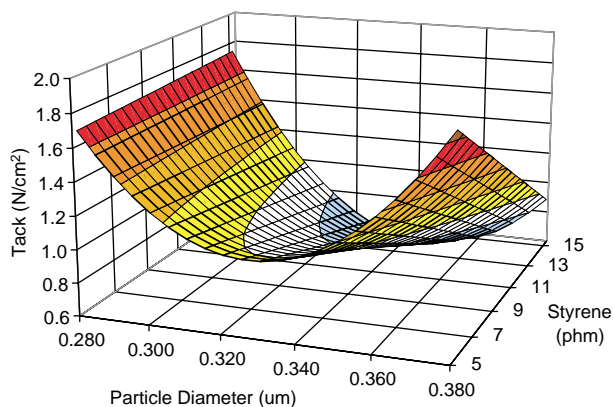


Fig. 6. 3D response surface for the tack model.

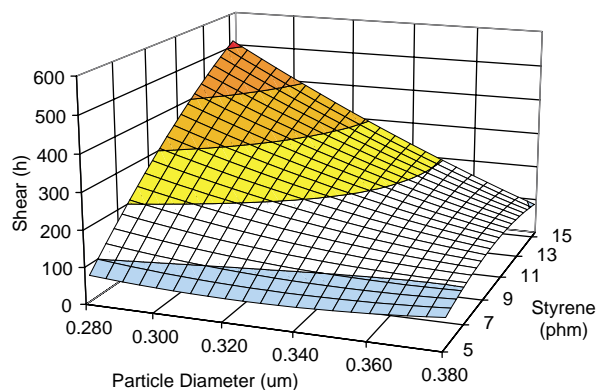


Fig. 8. 3D response surface for the shear strength model.



region (high tack, peel strength and shear strength) was located near the smallest particle diameter investigated with the highest St composition. Further exploration of the experimental space in the optimal adhesive performance region would be the next logical step. Ultimately, this study has shown that the control over particle sizes afforded by miniemulsions 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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