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Influence of Particle Nucleation in Pressure Sensitive Adhesive Properties: Miniemulsion *versus* Emulsion Polymerization

Gabriela E. Fonseca,[1] *Timothy F. McKenna,*[2] *Marc A. Dubé**[1]

Summary: Miniemulsion polymerization is a promising approach to produce and tailor pressure sensitive adhesives (PSAs). In this paper, a systematic comparison of the adhesive properties of latexes produced by miniemulsion and conventional emulsion polymerization is presented. Specifically, the influence of the total surfactant concentration, chain transfer agent concentration and chemical composition on the final adhesive properties of the polymer 2-ethyl hexyl acrylate/methyl methacrylate/acrylic acid was discerned using a 2^3 factorial design for each polymerization method. In addition to the adhesive properties (i.e., loop tack, peel strength and shear strength), molecular weight distribution, particle size distribution (PSD) and glass transition temperature were analyzed. The results show that under the conditions used in this work, it is possible to produce PSAs using miniemulsion polymerization, a process wherein monomer droplet nucleation is the dominant particle nucleation mechanism. The use of a miniemulsion polymerization process, as opposed to the conventional emulsion technique, produced several differences such as larger particles sizes and narrower molecular weight distributions. Focusing on the PSA films that exhibited adhesive rather than cohesive failure, the PSA films generated via miniemulsion polymerization displayed higher values of loop tack and peel strength compared to those produced via conventional emulsion polymerization. Shear strength results were strongly dependent on the amount of gel content and sol molecular weight for both cases.

Keywords: 2-ethyl hexyl acrylate; methyl methacrylate; miniemulsion polymerization; pressure sensitive adhesives

Introduction

A global need for environmentally friendly technologies and products has led to the replacement of volatile organic compounds (VOCs) used in the production of pressure sensitive adhesives (PSAs), for water. Water-based technologies such as emulsion polymerization are now widely used in PSA production. In particular, water-based PSAs produced with acrylic polymers are now common commercial products[1].

The performance of these pressure sensitive products (PSPs) is characterized by their adhesive and cohesive behaviour, which is defined by three main application properties, namely, tack, peel strength and shear strength. Tack represents the ability to form an instant bond; peel strength represents the resistance to removal from the adherend and shear strength is a measure of the cohesive strength.[2] However, there is a known conflict between these three application properties since an increase in tack and peel strength (adhesive component) often leads to a decrease in

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[1] Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada
E-mail: Marc.Dube@UOttawa.ca

[2] Department of Chemical Engineering, Queen's University, Kingston, Ontario, K7L 3N6, Canada

shear strength (cohesive component) and *vice versa*.[3] Depending on the application, it is usually desirable to find a means to decouple this property interdependence.

The behaviour of a PSP is a consequence of its viscoelastic properties which are influenced by several polymer properties such as the molecular weight distribution (MWD), particle size distribution (PSD) and glass transition temperature (T_g), which in turn are affected by the type of process, reaction conditions, monomers used and addition of other components (surfactants, initiator, crosslinkers, etc.).

It is also known that broad or multimodal MWDs can help in the improvement of PSA properties.[1] For example, tack and peel strength improve with an increase in molecular weight (up to a maximum); however, they can be further improved by adding a fraction of low molecular weight polymer. In addition, it is recognized that multimodal PSDs can promote the achievement of higher solids contents latexes at a reduced viscosity, which is beneficial from a processing and economics point of view.[4,5]

Emulsion polymerization is a heterogeneous polymerization process wherein monomer droplets are suspended in an aqueous phase containing surfactant micelles. The surfactant also stabilizes the monomer droplets. Typically, an emulsion polymerization system consists of three phases, namely a monomer droplets phase, a continuous phase (surfactant, micelles, a free-radical initiator and other components dissolved in the water) and the polymer particles phase. Micelles will be present in the continuous phase if the surfactant concentration is above the critical micelle concentration (CMC) and these are normally the setting for the nucleation of polymer particles. Usually, the main locus of the reaction takes place inside the polymer particles (i.e., the nucleated monomer-swollen micelles.[6]

Miniemulsion polymerization has gained interest in the last twenty years because of its potential for commercial polymer production. This type of polymerization is formulated to change the particle nucleation location from monomer-swollen micelles to the monomer droplets. This is accomplished by using an appropriate surfactant system and a highly hydrophobic compound, together with the use of high shear mixing. The hydrophobic compound decreases the monomer droplets' solubility and the combination of high shear mixing and a stabilizer serves to adjust or control the droplet sizes and their distribution. Together, these will delay Ostwald ripening, creating a kinetically stable emulsion and producing so-called "particle compartmentalization".[7] In a miniemulsion, the mean monomer droplet diameter is considerably smaller (50–500 nm) than in conventional emulsions (>1 μm), which greatly increases the droplets' surface area. Also, the amount of free surfactant after the initial emulsification present in the medium is kept well below the CMC. The larger surface area occupied by the monomer droplets and the absence of micelles cause the nucleation of polymer particles to occur in the droplets as opposed to micelles. The result is that monomer droplets act as independent batch nano-reactors keeping their individual characteristics throughout the reaction, wherein no significant amount of material is transferred between the droplets or towards the continuous aqueous phase. This could allow the simultaneous polymerization of various sets of particles with different characteristics, and potentially, the fine-tuning of PSA properties without the need for blending. In addition, the preparation of high solids content/low viscosity latexes can be made possible using this technique.[8,9]

Previous studies have established the viability of producing miniemulsion-based PSA with multimodal MWDs and PSDs and confirmed the compartmentalized nature of the technique.[10,11] The aim of this study was to evaluate the difference between the PSA produced by the two polymerization processes, i.e. miniemulsion and conventional emulsion polymerization. The ultimate goal was to increase one property (i.e., loop tack) without decreasing another (i.e., shear strength). Miniemulsion polymerization could help in this goal, but in order to do so, it was necessary to know if different nucleation mechanisms would lead to different PSA application properties or if the compartmentalised and more stable nature of miniemulsion polymerization was producing different polymer microstructures, e.g. lower molecular weights or broader particle size distributions. In other words, it was indispensable to identify the range of PSA properties achievable by miniemulsion polymerization and how they were compared to those produced by similar conditions in conventional emulsion polymerization.

We present the results of a systematic comparison of the adhesive properties obtained by miniemulsion and conventional emulsion polymerization. A factorial design was used to discern the effects of chain transfer agent concentration (CTA), total surfactant concentration (TS) and the EHA fraction in the copolymer composition (EHA), which are three important parameters that affect the polymer properties and in turn, the PSA properties.

Experimental Part

The monomers used in this study were 2-ethyl hexyl acrylate (EHA) (Aldrich), methyl methacrylate (MMA) (Aldrich) and acrylic acid (AA) (Aldrich). Octadecyl acrylate (ODA) (Aldrich) was used as a polymerizable hydrophobe, and the initiator was ammonium persulfate (APS) (Sigma-Aldrich). 1-dodecanethiol (DDM) (Aldrich) was used as chain transfer agent (CTA). The surfactant system consisted of a mixture of an ionic (Sodium dodecyl sulphate (SDS) (Sigma-Aldrich) and a non-ionic surfactant (Disponil® A3065) (donated by Cognis Canada). Sodium bicarbonate ($NaHCO_3$) (Sigma-Aldrich) was used as buffer. Distilled deionized water was used in all the experiments as the continuous phase. All ingredients were used without further purification.

The conventional emulsions and miniemulsions were prepared by mixing the aqueous phase, which contained SDS, Disponil® A3065, $NaHCO_3$ and water, with the organic phase which contained EHA, MMA, AA, ODA and DDM. The organic phase was slowly added to the aqueous phase and stirred until a homogeneous emulsion was obtained. For the miniemulsion polymerization, the emulsion was then sonicated for 4 min using a Fisher Scientific Sonic Dismembrator model 550 at level 9. It should be noted that ODA was added to both the miniemulsion and conventional emulsion recipes, although previous studies have not done so due to the fact that it is considered merely as the hydrophobic compound. In this work, the possibility that this component might pose an influence in the PSA properties was considered, since it would certainly be incorporated into the polymer matrix and could possibly create a bias in the comparison between the two adhesives. Therefore, the ODA concentration was kept constant for both polymerization methods.

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 temperature and stirring speed were automatically controlled at 70 °C and 200 rpm, respectively. Conversion was obtained from gravimetric measurements. Droplet and particle sizes for the monomodal distributions were obtained using a Dynamic Light Scattering (DLS) instrument (Malvern NanoS Zetasizer) with an angle of 176°. Two drops of the latex were diluted and placed in a polystyrene cuvette and analyzed 3 times. The reported diameter is the z-average (intensity-based) of 3 measurements that were analyzed in 10 runs of 30 s each. The number of particles and number of droplets were calculated based on the average polymer particle or monomer droplet diameter obtained from DLS and conversion measurements. The osmotic pressure (P_O) and Laplace pressure (P_L) were calculated according to the method used by Ouzineb et al.[12] The P_O considers only the concentration of ODA and do not includes that of DDM.

The MWDs were obtained using Gel Permeation Chromatography (Waters). A small sample of dry polymer was dissolved in tetrahydrofuran (THF) to give a concentration of ~0.015 g/mL. The solution was then filtered with a 0.45 μm filter to eliminate the presence of large particles and gel. The instrument is equipped with a refractive index detector and three Waters Styragel columns used in series (10^3, 10^4 and 10^6 Å). THF was used as the eluent at a flow rate of 0.3 mL/min. The calibration was done with polystyrene standards with molecular weights ranging from 1.8×10^2 to 6.0×10^6 g/mol. The analysis of the data was done using the Universal Calibration method with Empower2 software (Waters). The Mark-Houwink constants used are $K = 0.0001254$ dL/g and $\alpha = 0.67$ for poly(2-ethyl hexyl acrylate)[13] and $K = 0.000128$ dl/g and $\alpha = 0.69$ for poly(methyl methacrylate).[14]

Copolymer compositions were obtained using ^{1}H-NMR spectroscopy (Bruker). Each sample of dry polymer was dissolved in d-CCl_4 at a concentration of 5% w/v. Further details about the procedure can be found in Jovanovic and Dubé.[15]

Adhesive testing was performed following Pressure Sensitive Tape Council (PSTC) standards PSTC-1, PSTC-6 and PSTC-7 for peel strength, loop tack and shear strength, respectively.[16] The latexes were cast on a 50 μm Mylar® film using a Meyer rod to obtain approximately 65 g/m^2 (dry basis) of applied adhesive and were conditioned under controlled temperature (23 ± 2 °C) and humidity (50 ± 5%) for 24 h prior to testing. The substrate used for these tests was stainless steel.

A 2^3 factorial design with 2 center points was used to discern the effect of EHA, CTA and TS in both, miniemulsion and conventional emulsion polymerization (see Table 1) for a total of 20 runs. Statistical analysis was performed with the statistical software Minitab® version 14.

Results

The goal of this work was to determine the range of properties that a true miniemulsion polymerization could achieve and make an unbiased comparison between the PSA properties produced by both miniemulsion and conventional emulsion polymerization. As a first step, it was first necessary to evaluate whether the miniemulsion reactions had proceeded via droplet nucleation and if the presence of secondary nucleation could also influence the PSA application properties in a way that would be more in line with conventional emulsion polymerization than miniemulsion polymerization. In order to make such an evaluation, the ratio between the number of polymer particles and number of droplets (N_p/N_d) was calculated (see Table 2). The N_p/N_d values were more or less constant throughout each experiment. From these results, it was observed that, as expected, the ratio N_p/N_d was sensitive to the amount of surfactant involved in the recipes and to a lesser extent to the amount of EHA (see Figure 1).

In order to get a better idea of this dependence, the amount of the polymer particle surface covered by surfactant, which was calculated according to a method used by Fortuny-Heredia[17], was investigated. Figure 2 illustrates the dependence of N_p/N_d with the particle surface covered by surfactant. This figure shows that in

Table 1.
Miniemulsion recipes[a)].

Factor	Levels		
	−1	0	1
Chemical composition [EHA/MMA wt.%]	65/35	75/25	85/15
CTA [phm]	0.50	0.75	1.00
Surfactant [phm]	4.50	5.00	5.50

[a)] For all experiments, initiator = 0.30 phm, buffer = 0.15 phm, AA = 2.00 phm, ODA = 4.00 phm.

Table 2.

Miniemulsion and conventional emulsion polymerization: stability and particle diameter.

Run ID	N_p/N_d	P_O [bar]	P_L [bar]	MP D_p [nm]	CEP D_p [nm]
1	1.145	2.91	1.65	177	160
2	1.005	2.89	1.64	182	153
3	1.307	2.92	1.52	170	138
4	1.099	2.95	1.64	197	155
5	0.884	2.91	1.5	191	138
6	1.073	2.92	1.77	196	150
7	1.140	2.86	1.77	162	100
8	1.139	2.92	1.64	160	125
9	1.220	2.86	1.6	178	124
10	1.084	2.9	1.64	180	154

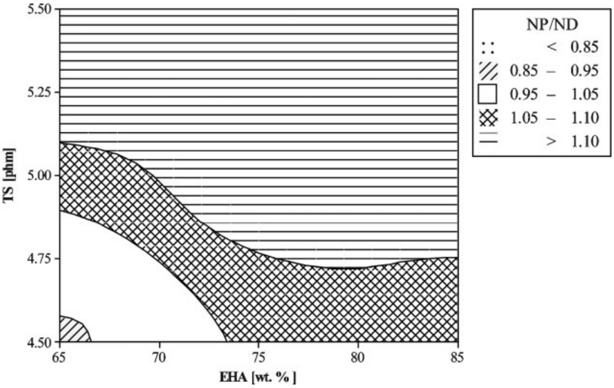

Figure 1.

Relationship between of N_p/N_d versus amount of EHA and TS.

order to obtain a relatively stable miniemulsion, the amount of surfactant would have to be kept at concentrations that would result in surface coverages of no more than 38%, which could possibly restrict the particle sizes achievable. As mentioned before, it was seen that N_p/N_d was sensitive to the amount of EHA

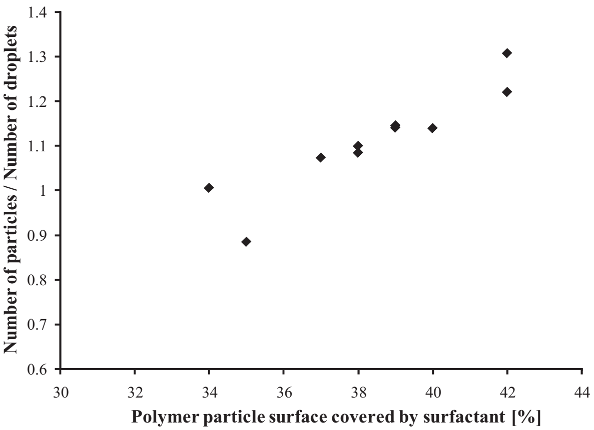

Figure 2.

Percentage of polymer particle surface covered by surfactant.

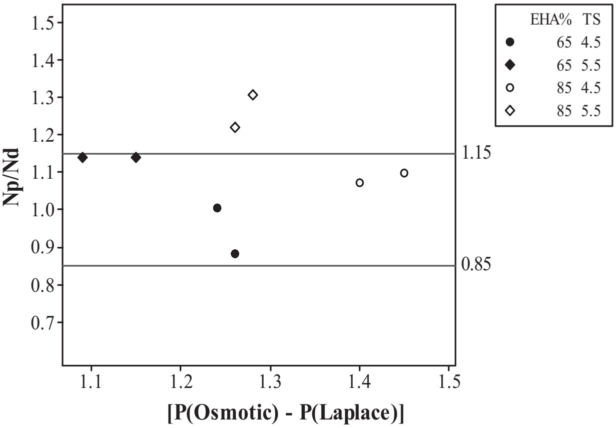

Figure 3.
(P_O - P_L) vs. N_p/N_d at two EHA levels (65 and 85 wt.%) and two TS levels (4.5 and 5.5 phm).

present in the emulsion (see Figure 1). Table 2 also shows the values of the resulting P_O and P_L. One could think that high EHA level runs would require a lower amount of ODA to be stable. This could be explained by looking at the difference between P_O and P_L. A plot of the differences between these two pressures was generated (see Figure 3) to corroborate this reasoning. As it can be observed, moving to a higher amount of EHA increases the difference between P_O and P_L, leaning towards the limits of colloidal stability. A decrease of P_O by means of decreasing the ODA concentration would likely overcome this effect. Also, moving to a higher surfactant concentration decreases this difference and in this case, an increase in P_O to compensate for it would be recommended. In the end, a judicious balance between these two pressures must be achieved to yield a stable miniemulsion.[7]

In summary, eight out of ten of the runs were polymerized within the stability limits. The results of the miniemulsion and conventional emulsion polymerization showed some important differences. First of all, the miniemulsion polymerizations resulted in somewhat larger particles compared to the conventional emulsion polymerizations. Table 2 shows the results for the particle diameters.

Statistical analysis for all samples suggests that in the case of miniemulsion polymerization (ME), both TS and EHA influenced the final D_p, while in the case of conventional emulsion (CE) polymerization, the three factors studied (i.e., CTA, TS and EHA) all affected the final D_p:

$$\begin{aligned} D_{p\_ME} = {} & (178.5 \pm 6.1) \\ & + (5.7 \pm 3.1)(EHA) \\ & - (12.0 \pm 3.1)(TS) \end{aligned} \tag{1}$$

$$\begin{aligned} D_{p\_CE} = {} & (157.0 \pm 10.6) \\ & + (6.4 \pm 5.3)(EHA) \\ & - (7.4 \pm 5.3)(CTA) \\ & - (13.6 \pm 5.3)(TS) \\ & - (21.6 \pm 11.9)(EHA^2) \end{aligned} \tag{2}$$

In all equations, only the statistically significant model parameters (along with their 95% confidence intervals) are presented. In both cases (see Equation 1 and 2), TS was the major effect, a result that was expected since particle size is usually manipulated by the concentration of surfactant. Figure 4 shows how a change in TS resulted in different final PSDs for the two techniques. This figure also shows how conventional emulsion polymerization produced a narrower PSD at the high level of TS compared to miniemulsion polymerization. As well, the effect of a change in

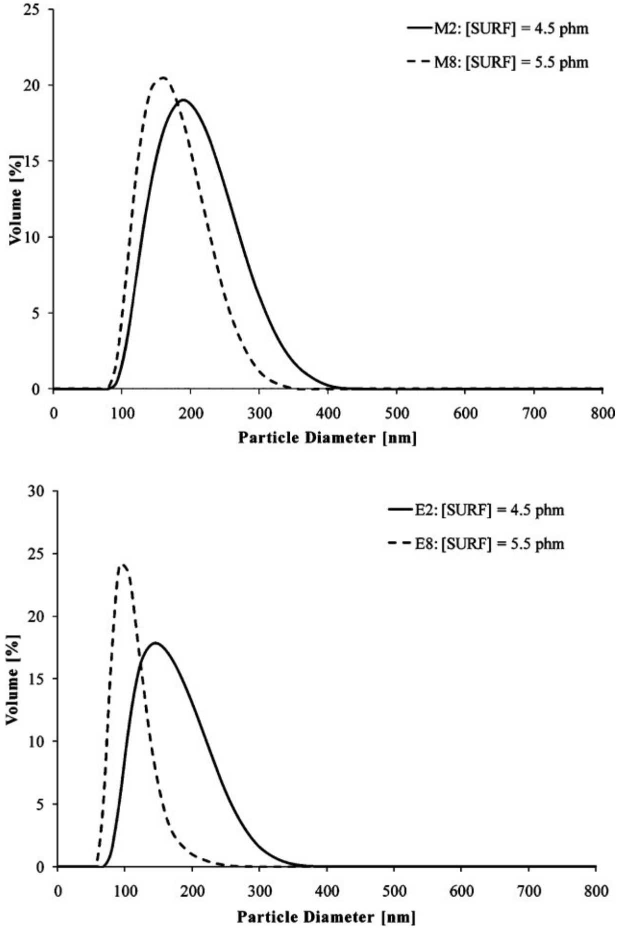

Figure 4.
PSD for miniemulsion (top) and conventional emulsion (bottom) polymerization; effect of surfactant concentration.

surfactant was more pronounced for conventional emulsion polymerization, where the PSD was determined by the particle formation and subsequent growth, while in the miniemulsion polymerization case, the PSD was determined a priori (as is typical of miniemulsion polymerization[10]). The PSD produced by miniemulsion polymerization was dependent on the initial droplet size distribution (DSD), which in turn was influenced by TS, the high shear applied to the miniemulsion, and to a lesser extent, by the EHA.

As there was no significant effect of CTA concentration on the PSD for the miniemulsion case, it is implied that the PSD can be manipulated independently of MWD in a miniemulsion polymerization, i.e., it should be possible to modify *a priori* the PSD without changing MWD or vice-versa.

For both polymerization methods, the weight- and number-average molecular weights, M_w and M_n, respectively, were affected only by the CTA concentration. However, the miniemulsion polymerizations produced lower values of M_w and narrower polydispersity indexes compared to the conventional emulsion polymerizations, as can be seen in Figure 5. The lower sol M_w and narrower polydispersity encountered in miniemulsion based latexes would be due to the lower polymer concentration, on average, in the growing

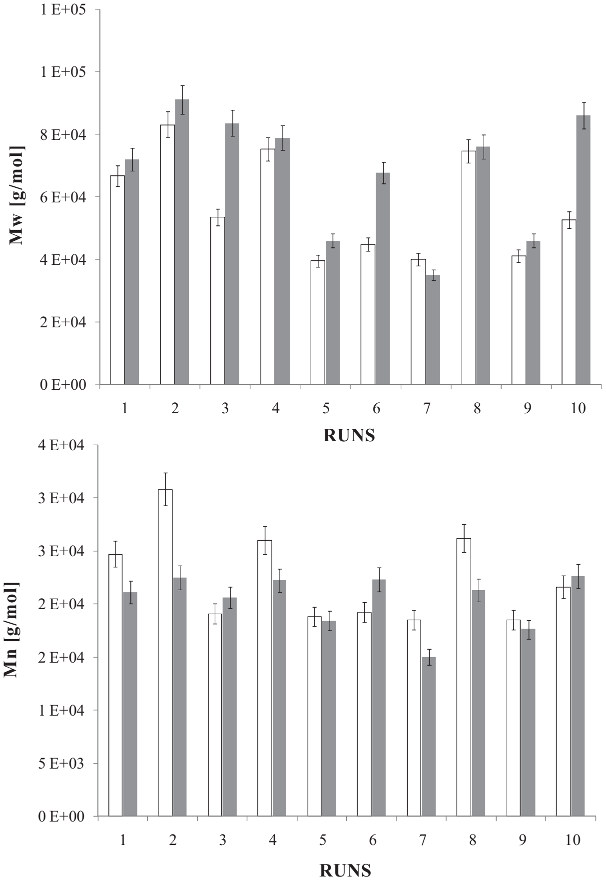

Figure 5.

Weight- and number-average molecular weight results. ☐ = Miniemulsion Polymerization and ■ = Conventional Emulsion Polymerization.

particles over the course of the polymerization.

The next step in the analysis was the evaluation of the PSA properties and how the different particle nucleation mechanisms had impacted the results. Table 4 shows results for the three main PSA properties for both the miniemulsion and conventional emulsion polymerizations. Some of these runs presented a cohesive failure characterized by transfer of adhesive material to the substrate; i.e., some residual PSA was found on the substrate. Only those latexes prepared with a EHA/MMA composition of 65/35 wt.% presented adhesive failure (no residue left on the substrate) for both techniques. The reason for having a cohesive failure in this case is related to the T_g of the polymer. The lower T_g values resulted in PSA materials that were too fluid at the testing temperature, i.e., room temperature (see Table 3). In addition, in cases where the gel content of the PSA films was low, insufficient cohesion (i.e., low internal strength of the PSA) resulted.

The regression model describing loop tack was:

$$\begin{aligned}\text{Loop Tack} = {} & (0.67 \pm 0.5) \\ & - (0.66 \pm 0.2)(\text{EHA}) \\ & - (0.25 \pm 0.2)(\text{CTA})\end{aligned} \tag{3}$$

From Equation 3, it is evident that loop tack was primarily influenced by the EHA concentration, which was expected since it

Table 3.
Loop tack, peel strength and shear strength results for miniemulsion (MP) and conventional emulsion polymerization (CEP).

Run	MP				CEP			
	Loop tack $[N/cm^2]$	Peel strength [N/10 mm]	Shear strength [min]	T_g [°C]	Loop tack $[N/cm^2]$	Peel strength [N/10 mm]	Shear strength [min]	T_g [°C]
1	0.49	0.189	0.47	−52	1.46	0.964	1.31	−52
2	2.48	3.133	3.15	−47	1.06	0.552	22.00	−52
3	0.50	0.213	0.39	−57	1.66	1.582	1.25	−57
4	0.70	0.279	0.74	−56	1.11	0.824	1.22	−57
5	1.39	5.545	3.59	−43	0.57	0.446	1.48	−51
6	0.35	0.156	0.16	−57	0.50	0.223	0.15	−55
7	1.45	1.066	1.38	−46	0.35	0.288	0.19	−65
8	1.81	5.299	5.12	−50	1.08	0.874	0.84	−52
9	0.32	0.173	0.13	−57	0.26	0.174	0.16	−60
10	0.86	0.638	1.70	−48	0.55	0.346	2.71	−52

is known that changes in EHA will modify the T_g, which in turn affects tack. Since a good PSA exhibits adhesive rather than cohesive failure, it was decided to investigate the influence of the other design factors using only those runs that exhibited adhesive failure.

Figure 6a and 6b show the influence of M_n, M_w and gel content on loop tack for both polymerization techniques. Higher values of M_n and M_w resulted in higher loop tack values. However, miniemulsion polymerization gave higher values compared to conventional emulsion polymerization, even though the latter resulted in a higher M_w. It was established that there was no relation between loop tack and gel content, which can be due in part to the low levels of gel produced under the reaction conditions studied. Higher gel contents may reveal such a dependence. Another factor that could have influenced loop tack and created the differences in the adhesive results was the PSD. The conventional emulsion polymerizations produced narrower PSDs with smaller mean particle diameters compared to the miniemulsion polymerizations.

Peel strength, on the other hand, is known to be affected mainly by the modulus through the molecular weight. In this work, miniemulsion polymerization gave higher values of peel strength compared to conventional emulsion polymerization (see Figure 6c and 6d), although it had lower or equivalent values of the M_w. One reason could be attributed to the gel content, which was higher for miniemulsion based films than it was for conventional emulsion based films. A sample with higher gel content would present less polymer mobility, which would improve its cohesion and peel strength at these levels of gel content. It should also be mentioned that the miniemulsion-based latexes exhibited narrower MWDs than the conventional emulsion-based latexes, a fact that could have contributed to an improvement of the cohesive strength even though the former exhibited somewhat higher values of M_w.

Finally, both polymerization methods showed similar trends for shear strength (see Figure 6e and 6f). In both cases, it can be seen that shear strength values increased with M_w and gel content since a higher cohesive strength was attained when the polymer chains were not able to move freely, which is possible when molecular weight is increased or under the presence of a gel or network. If considering only those films that presented adhesive failure, miniemulsion polymerization produced higher gel content values compared to conventional emulsion polymerization. However, the resulting shear strength values depended on the combination of both parameters, which does not allow for a straightforward conclusion regarding whether one technique is improved over the other.

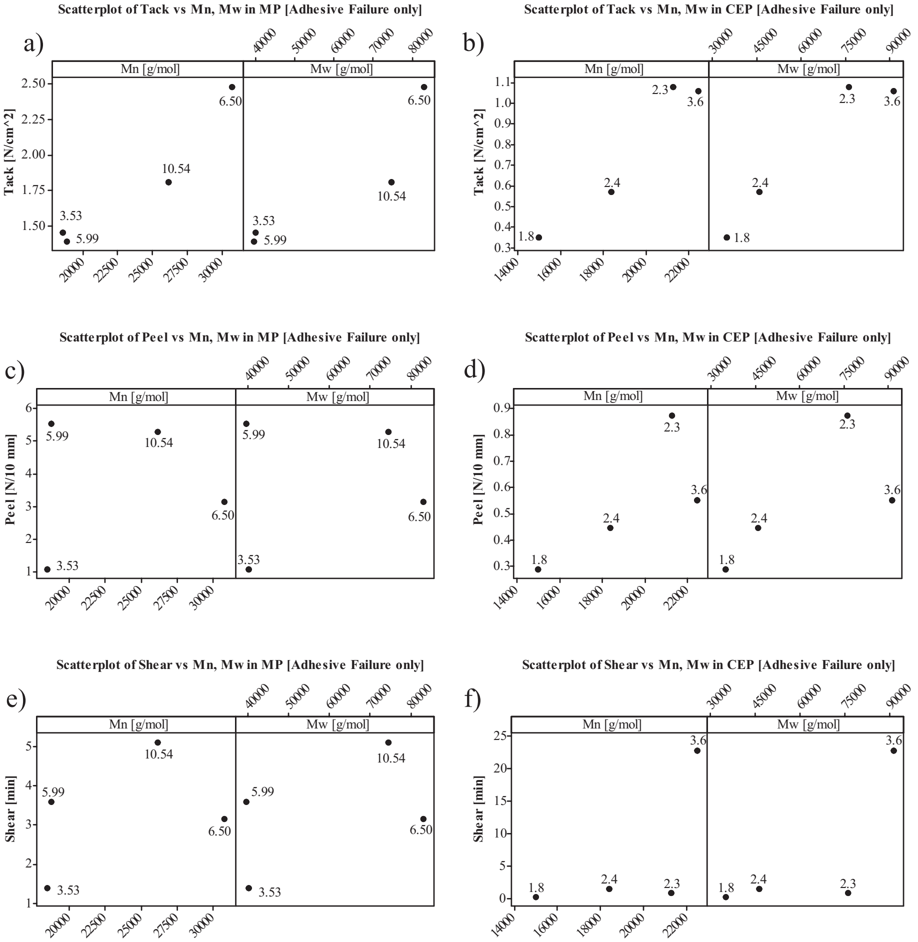

Figure 6.
Loop tack (a & b), peel strength (c & d) and shear strength (e & f) vs. M_n and M_w for miniemulsion (MP) and conventional emulsion polymerization (CEP). Values next to points indicate gel content in %.

Conclusions

The aim of this study was to carry out a comparison between PSAs produced by miniemulsion and conventional emulsion polymerization. We were able to discern the range of properties for miniemulsion based latexes and to highlight the differences between PSAs created by two polymerization techniques with different nucleation mechanisms (droplet *vs.* micellar nucleation). The miniemulsion stability strongly relies on a judicious balance between the P_O and P_L and it should be kept in mind that if one wants to modify the size of the polymer particles (e.g., through a modification of TS or EHA), the concentration of the hydrophobe, in this case ODA, must be modified to adjust this pressure balance and obtain a stable miniemulsion.

In general, miniemulsion based EHA/MMA adhesives yielded higher values of loop tack and peel strength to those produced by its conventional emulsion counterpart. This can be attributed in part to the differences in the PSD, which were broader with higher mean particle diameter for those films cast from conventional emulsion-based latexes. It can be speculated that somewhat larger particles and a larger polydispersity contributed to higher loop tack values. Also, miniemulsion-based latexes showed narrower MWD, lower M_w and somewhat larger gel contents. These characteristics could be the reason for the higher values of peel strength exhibited by those films prepared by the miniemulsion polymerization technique. Finally, shear strength results were dependent on the amount of gel content, which was expected. However, gel content values of miniemulsion polymerization samples were generally higher when compared to those produced by conventional emulsion polymerization. The film cast from conventional emulsion-based latexes that displayed higher shear strength values also displayed a larger M_w than its counterpart, which could be well the reason for the higher cohesion in that film.

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