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Preparation of Stable Miniemulsions of Poly(2-ethyl hexyl acrylate-co-vinyl acetate)

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Summary: This paper presents the results of the preparation of miniemulsions as well as the subsequent copolymerizations of 2-ethyl hexyl acrylate and vinyl acetate. The miniemulsions were prepared using a mixture of an anionic and a non-ionic surfactant. Sodium dodecyl sulfate (SDS) was used as the anionic surfactant and two non-ionic surfactants were studied: Triton X-405 and Disponil A3065. The miniemulsions prepared with a 90/10 mol.-% Disponil A3065 were able to reach a kinetically-stable state to yield latexes with 43 wt.-% solids content with a maximum change in the number of particles (N_p) with respect to the number of droplets (N_d) of ~6%. A 2^3 factorial design was then used to discern the influence of monomer, chain transfer agent and surfactant concentration on the droplet size distribution (DSD) and particle size distribution (PSD). Pressure-sensitive adhesive (PSA) properties were also examined.

Keywords: 2-ethyl hexyl acrylate; adhesives; compartmentalization; copolymerization; vinyl acetate

Introduction

Miniemulsion polymerization is a heterophase polymerization process characterized by its compartmentalized nature. This type of emulsion is produced using a hydrophobic compound that stabilizes the emulsion against Ostwald ripening, together with the use of a high shear homogenization device which breaks down the monomer droplets present in a typical emulsion down to a droplet diameter between 50 and 500 nm. A properly-formulated miniemulsion is able to reach a kinetically-stable state in which the nanometre-sized monomer droplets act as nano-reactors and diffusion of monomer through the aqueous phase could be minimized[1].

Due to the fact that in miniemulsion polymerization monomer droplets are considerably smaller than in conventional emulsion polymerization, polymer nucleation does not proceed via a micellar mechanism and the available surfactant only partially covers the surface area of the monomer droplets. In this case, the monomer droplets do not act as reservoirs and the reaction proceeds under more or less strictly droplet nucleation conditions[2].

Miniemulsion polymerization offers a number of benefits that are attractive such as the production of high-solids content and low viscosity latexes[3,4], elimination of the oscillatory behaviour in continuous stirred tank reactors[5], encapsulation of organic and inorganic materials[6,7] and synthesis of hybrid nanocomposites[8]. Because it is possible to create nanocompartments and design a family of polymer particles with a specific set of properties (it has been called a 1 to 1 copy from monomer droplets to polymer particles[1]), the technique has great potential to generate tailor-made particle structures[6]. The success of com-

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partmentalization in miniemulsion polymerization lies in a careful selection of the stabilization system, i.e., the surfactant(s) and the hydrophobic compound, to prevent coalescence and Ostwald ripening. Nevertheless, the addition of the hydrophobic compound *per se* does not prevent Ostwald ripening completely. The miniemulsion droplet size distribution (DSD) is also critical in attaining a well-stabilized system. Miniemulsions with a broad DSD would inevitably lead to droplet instability due to Ostwald ripening despite the presence of the hydrophobe. It has been suggested that a narrower DSD would ensure a higher probability of polymerizing under droplet nucleation conditions[9].

If a miniemulsion has been adequately stabilized, the osmotic pressure (P_O) inside the droplets created by the addition of the hydrophobic compound would be able to counteract the Laplace pressure (P_L) produced by the interfacial energy at the monomer/water interface and the DSD[10]. Ideally, a zero pressure difference would completely stop diffusional degradation. Practically speaking, if this difference is close to zero, it would be sufficient to delay Ostwald ripening so that the miniemulsion could be polymerized.

Ouzineb et al.[11–13] studied monomer compartmentalization in the homopolymerizations of styrene (STY) and butyl methacrylate (BMA). In one of their studies[11], STY and BMA miniemulsions were prepared separately and copolymerized in the same reactor. Using an in-line Attenuated Total Reflectance-Fourier Transform InfraRed spectroscopy probe, they found that no significant mass transfer had occurred between the two miniemulsions since no detectable levels of copolymer had been found, i.e., if the compartmentalization had not taken place, a different spectra showing peaks that a copolymer had been formed would have appeared. They also showed that the change from the number of droplets (N_d) to the number of particles (N_p) was the least when the P_O was slightly higher than the P_L.

Miniemulsion polymerization has also been used to polymerize a number of hydrophobic monomers that are not suited for conventional macroemulsion polymerization[14,15] and to polymerize different pairs of monomers where at least one of them had a significant solubility in water[16–18]. Bohórquez and Asua[19] studied the nucleation mechanism of the miniemulsion copolymerization of VAc and vinyl ester of a highly branched decanoic acid. The influence of hydrophobe and type and concentration of initiator on the nucleation was examined. They observed that droplet nucleation was maximized when miniemulsion stability was improved using stearyl acrylate (SA) and efficient initiators, namely initiators with low water solubility such as lauroyl peroxide (LPO). However, they observed fluctuations in the N_p in most of the recipes prepared with the exception of those polymerized with potassium persulfate (KPS) as initiator and SA and polyvinyl alcohol (PVOH) as the stabilization system. Even with the latter stabilization system, the final particle diameter was larger than the initial droplet diameter with a ratio of N_d to N_p of ~1.4. It must be pointed out, however, that they obtained stable coagulum-free polyVAc latexes with a high solids content.

Wu and Schork[18] studied the copolymerization of VAc with butyl acrylate, dioctyl maleate and n-methylol acrylamide, systems with monomer pairs of different water solubilities and reactivity ratios. They found that miniemulsion polymerization was able to compensate for the poor monomer transport of highly water-insoluble monomers in corresponding macroemulsion polymerizations. However, they also observed that only a percentage of the initial droplets were nucleated into polymer particles.

Graillat and Guyot[20] studied the homopolymerization of VAc under different stabilization conditions and found that it was possible to obtain polyVAc latexes in conditions where the final N_p was close to the initial N_d. Nevertheless, these latexes had relatively low solids contents (~20%)

and in the case of polyVAc latexes with higher solids contents, the final N_p was lower than the initial N_d, a fact they attributed to the collision of polymer particles with unreacted monomer droplets. However, one can see from their study that even though the conditions for the nucleation of all monomer droplets in a miniemulsion of a slightly water soluble monomer such as VAc are hard to achieve, it is indeed possible to achieve a stable, compartmentalized miniemulsion system.

The question that arises is whether a functional compartmentalized system can be produced when the copolymer includes a slightly hydrophilic monomer such as VAc. The aim of this paper is to report the miniemulsion copolymerization of a commercial polymer used as PSA: 2-ethyl hexyl acrylate (EHA)/VAc. We first discuss the effect of different stabilization systems on the DSD and PSD of EHA/VAc miniemulsions. The following section shows the results of a 2^3 factorial design used to discern the influence of monomer, chain transfer agent and surfactant concentrations on the DSD and PSD. Finally, the PSA properties obtained for the copolymer EHA/VAc are presented and discussed.

Experimental Details

Materials

All the reagents were used as supplied by the manufacturer. The monomers used were EHA, VAc and methacrylic acid (MAA). Octadecyl acrylate (ODA) was used as the polymerizable hydrophobe and 1-dodecanethiol (DDM) as the chain transfer agent. All of these were reagent grade obtained from Sigma Aldrich. The ionic surfactant used was sodium dodecyl sulphate (SDS) GC grade (Sigma Aldrich) and the non-ionic surfactants were Disponil A3065 (Cognis Canada) and Triton X-405 (Sigma Aldrich). Sodium bicarbonate ($NaHCO_3$) (Aldrich) was used as buffer. Distilled deionized water (DDI H_2O) was used throughout the study. A 0.02 mol L^{-1} hydroquinone solution was used as inhibitor to stop conversion in the samples. Ammonium persulfate (APS) and benzoyl peroxide (BPO) (Sigma) were used as initiators.

Preparation of the Miniemulsion and Emulsion

The organic phase was prepared first. ODA, DDM and the monomers were charged to a 500 mL flask. The monomer mixture was stirred until it appeared as a homogeneous clear solution. The aqueous phase was prepared separately in a 1 L flask. The non-ionic surfactant and SDS as well as $NaHCO_3$ (if present) were dissolved in DDI H_2O. Subsequently, the organic phase was added slowly to the aqueous solution while stirring until the emulsion appeared as a milky solution. The mixture was sonicated using a Fisher Scientific Sonicator Model 550 with 600 W. In order to ensure that sufficient energy was supplied equally to the entire emulsion volume, the total mixture was sonicated in small batches of 100 mL. The mixture was kept in an ice-bath to avoid an increase in temperature and possible initiation of the reaction. The sonication time was 4 min at an output amplitude level of 9. After the sonication procedure, the entire volume was mixed and stirred.

Polymerization Procedure

The polymerization reactions were performed in a 1.1 L Labmax^{TM} automated stainless steel reactor (Mettler Toledo) equipped with a stirrer, condenser and three feed ports. The initial miniemulsion was charged to the reactor and simultaneously heated and mixed. Nitrogen gas was bubbled to the reaction mixture to remove any dissolved oxygen. The temperature and stirring speed were automatically controlled at 60 °C and 200 rpm, respectively. When the reaction temperature was reached, the initiator solution was injected into the reactor. Samples were taken at different times for conversion and D_p analysis. The sampling vials contained a few drops of a hydroquinone solution and were immediately placed in an ice-bath to shortstop the reaction. At the end of the reaction time, the mixture was cooled to 25 °C.

Droplet and Particle Size Distribution Determination

Droplet and particle diameters were obtained using a Dynamic Light Scattering (DLS) instrument (Malvern NanoS Zetasizer) with a scattering angle of 173°. A drop of the latex was diluted in DDI H_2O and placed in a 4 mL cuvette. The reported diameter is an intensity-weighted average particle size, a.k.a. z-average, made of 3 measurements that were analyzed in 10 runs of 30 s each.

Polymer Property Characterization

Molecular weight distributions were determined using Gel Permeation Chromatography (GPC). 0.1 g of dried polymer was placed in a vial with 5 mL of tetrahydrofuran. The vial was closed and placed in a wrist-action shaker for 24 h. The solution was filtered using a 0.45 μm syringe filter with polytetrafluoroethylene membrane (Pall Corporation). The samples were analyzed with a Waters GPC instrument equipped with a Differential Refractive Index detector, a manual injector and three Waters Styragel columns (HR6, HR4 and HR3) in series. The flow rate was set at 0.3 mL/min and with an internal temperature of 37 °C. The data was analyzed using Empower 2 software (Waters). The calibration curve included a set of 12 standards (EasiCal from Polymer Laboratories) with a range of 162 to 6,035,000 g/mol. The values of K and alpha used for EHA were 1.24×10^{-4} dL/g and 0.67 while those for MMA were 1.28×10^{-4} dL/g and 0.69[21,22], respectively.

Tack, peel strength and shear strength were measured using Pressure Sensitive Tape Council standards PSTC-6, PSTC-1 and PSTC-7, respectively. The latex was filtered using glass wool and cast onto a 50 μm Mylar® sheet. The cast film was dried at room temperature and conditioned for 24 h at standard conditions of temperature and humidity (23 ± 2 °C and 50% ± 2 Relative Humidity). A Universal Instron tester was used to evaluate loop tack and peel strength. In the case of loop tack, a strip of 25.4 mm × 177.8 mm was cut from the film and used to form a loop with the adhesive side facing outward. Approximately 25.4 mm at both ends of the strip was masked with tape and inserted into the upper grip. The instrument moved the upper grip downward at a speed of 300 m/min until an area of 25.4 mm^2 came into contact with the stainless steel substrate mounted into the lower grip. Next, the tester moved the upper grip upwards at the same speed while recording the force needed to debond the loop from the substrate. The maximum force per surface area necessary to remove the adhesive was reported as loop tack.

PSTC 1 Test Method A evaluates peel strength at a peel angle of 180°. A specimen of 25.4 mm × 304.8 mm was cut. The strip was laminated onto a stainless steel substrate with the help of a 2040 g roll coater. The roll coater was passed through the film front to back twice (i.e., along the length of the film). The dwell time did not exceed one minute. The substrate and the strip were inserted into the grips and the upper grip was set to move upward at a speed of 300 mm/min. The average force per m required to peel the strip from the substrate was recorded and reported as peel strength.

Lastly, PSTC 7 was used to measure shear strength. A specimen of 25.4 mm × 152.4 mm of the film was cut. The strip was laminated onto a stainless steel substrate and then placed in a home-built shear tester using a C-clamp. A 500 g weight was suspended at the end of the strip. The time to failure was recorded automatically using Labview software.

Results and Discussion

In order to create nanocompartments that can be exploited for applications such as coatings and PSAs, the copolymer EHA/VAc was prepared using different stabilization systems, i.e., a combination of surfac-

Table 1.
Miniemulsion polymerization of EHA/VAc/MAA using the stabilization system SDS/Triton X-405/ODA

Run	EHA/VAc	SDS	Triton-X405	D_p	N_d	N_p	N_p/N_d
	(wt.-%)	(phm[b])	(phm)	(nm)	($\times 10^{17}$)	($\times 10^{17}$)	
201	70/30	0.35	4.85	161	0.34	1.50	4.46
202	60/40	0.35	4.85	162	0.55	1.51	2.66
203	70/30	0.35	3.75	214	0.78[c]	0.67	(see [c])
204[a]	70/30	0.35	3.75	221	1.01[c]	0.62	(see [c])
205	70/30	0.40	4.00	127	0.33	1.54	4.93
206	70/30	0.35	3.50	207	0.36[c]	1.22	(see [c])

[a] [Ammonium persulfate] = 0.6 phm
[b] phm = parts per hundred parts monomer
[c] Bimodal DSD observed in the Dynamic Light Scattering measurements

tants and hydrophobe that effectively protect monomer droplets against diffusional degradation, were investigated. This particular copolymer involves two challenges that must be dealt with. The first one is the elevated water solubility of VAc monomer of 250 mM[23],which might enhance secondary nucleation at the beginning of the polymerization and/or prevent complete polymerization. The second challenge is the large difference in their reactivity ratios ($r_{EHA} = 7.5$ and $r_{VAc} = 0.04$[24]), which consequently leads to compositional drift. In this work, the reactions were carried out as batch polymerizations and there is little that can be done to circumvent compositional drift under these conditions.

Stabilization System SDS/Triton X-405

Table 1 shows the formulations and the results of the miniemulsion-based latexes polymerized using the stabilization system SDS/Triton X-405 together with ODA as the hydrophobe. The concentrations of ODA and initiator, which in this case was the water-soluble APS, were kept constant at 2.6 and 0.35 phm, respectively, unless otherwise indicated. The ratio between N_p and the initial N_d is also included in Table 1 and can be used as a measure of the success of miniemulsion compartmentalization. Ideally, a properly-stabilized miniemulsion would maintain a N_p/N_d ratio close to unity[13].

Table 1 shows that most of the runs carried out using SDS/Triton X-405 resulted in large deviations from the initial N_d. Figure 1(a) shows the DSD of runs 201, 203, 205 and 206. These formulations were prepared using the same copolymer composition but with different surfactant concentrations. Two of these formulations (runs 203 and 206) displayed a second peak of large droplets, an indication that these miniemulsions were not stabilized properly and it is likely that soon

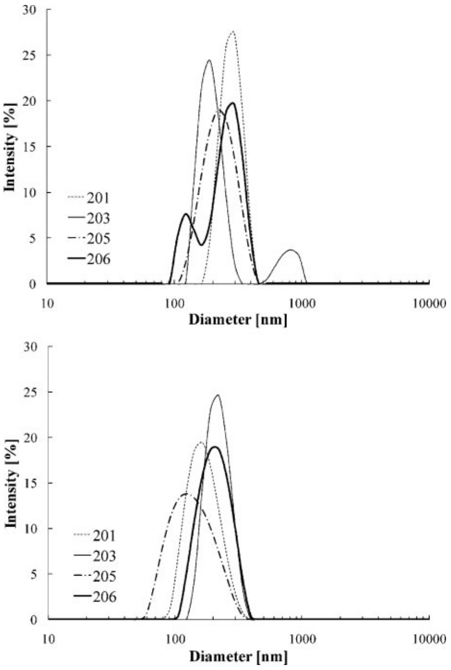

Figure 1.
a) DSD and b) PSD of miniemulsion runs with different concentrations of surfactant.

after the sonication, the smaller droplets started to diffuse into the larger ones and that the amount of surfactant used in the formulation was not enough to stabilize these miniemulsions. Increasing the surfactant concentration to 4.0 and 4.85 phm (runs 205 and 201, respectively) gave a monomodal DSD; however, as can be observed in Figure 1(b), the final PSDs are broader than the initial DSDs with the presence of smaller particles. This is likely the result of secondary nucleation and the ratio N_p/N_d also supports this idea with values of ~5.

Figure 2 shows the influence of the VAc amount on the DSD and PSD. It is known that surfactant adsorption is determined by the monomer concentration[25] and thus, it was necessary to verify if a change in the monomer composition in this case could lead to a different DSD. Figure 2a shows that larger concentrations of VAc in the formulation (Run 202) led to smaller average D_d. However, it is questionable whether this change is significant or not. It is plausible that with the same surfactant concentration, the droplets with higher VAc amounts need less surface charge density to be stabilized, which could explain the lower D_d. It is also possible that changing the VAc amount poses no effect on the DSD if it is considered that VAc resides on the outermost part of the droplet, thus a change in the VAc amount in the formulation does not really change the nature of the surface. Nevertheless, the reaction did not proceed under droplet nucleation conditions since the final N_p in both runs (201 and 202) was the same, which suggests that it was likely a function of the surfactant and initiator concentrations and proceeded as a conventional emulsion polymerization. It was also observed that the maximum in the rate of polymerization (R_p) was higher for the run with the lower VAc amount, which was expected due to the lower reactivity of VAc.

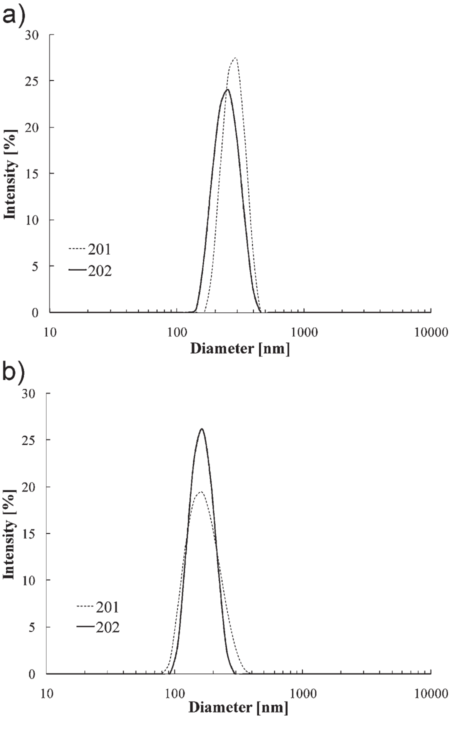

Figure 2.
a) DSD and b) PSD of miniemulsion runs with different copolymer composition.

Figure 3 shows the influence of increasing the initiator concentration from 0.35 to 0.6 phm. As can be observed in Figure 3b, no effect was observed in the final PSD, although there was an increase in the maxima of the R_p, as expected. The change in initiator concentration was carried out using one of the recipes that had given a bimodal DSD in an attempt to verify whether a portion of the droplets would get nucleated or if the bimodality would serve to enhance a mixed nucleation mechanism. The results showed that doubling the initiator concentration and thus, increasing the radical flux did not have an impact in the final D_p. The lowest APS concentration yielded 214 nm particles while the highest APS concentration resulted in 221 nm particles, which is within the experimental error of the technique. Moreover, the D_p are not much smaller than the D_d in both cases, which suggests that they did not proceed completely as a conventional emulsion polymerization. The final N_p was 0.67×10^{17} and 0.62×10^{17} par-particle/L for APS concentration of 0.35

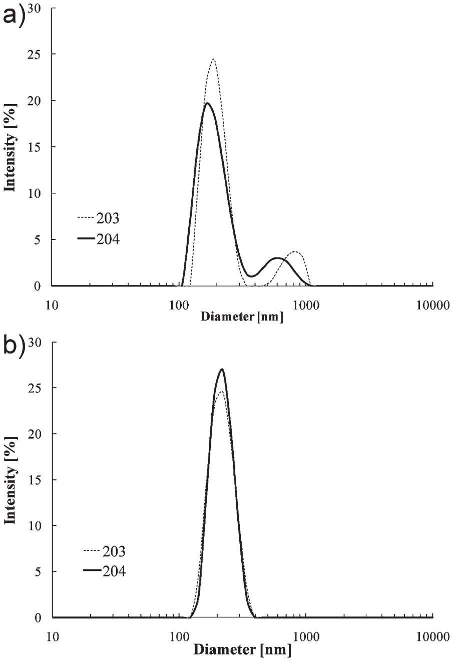

Figure 3.
a) DSD and b) PSD of miniemulsion runs with different initiator concentration.

and 0.6 phm, respectively. It is interesting to note that doubling APS concentration did not increase the final N_p but it remained almost the same.

The results found using the stabilization system SDS/Triton X-405 suggest that only part of the original monomer droplets nucleated while the rest likely served as monomer reservoirs. The main purpose of this study was to find an appropriate stabilization system that could generate nanocompartments that could be tailored for specific applications. The fact that we were unable to achieve compartmentalization with SDS/Triton X-405 even though the P_O was adjusted slightly above the P_L, suggests that this type of surfactant mixture is not the most appropriate for the EHA/VAc co-monomer system. Graillat and Guyot[20] were able to produce stable poly(VAc) miniemulsion-based latexes using a combination of SDS and Triton X-405 but it is likely that in this work, the inclusion of a highly hydrophobic monomer (i.e., EHA) was responsible for not achieving stable miniemulsions with this non-ionic surfactant. Triton X-405 has a high hydrophilic-lipophilic balance of ~18[26] and it is perhaps more adequate to stabilize miniemulsions of only poly(VAc)[27]. However, it must be mentioned that some of the PSD of miniemulsions prepared with this surfactant mixture were as narrow as those usually associated with conventional emulsion polymerization.

Stabilization System SDS/Disponil A3065

The non-ionic surfactant Triton X-405 was substituted for Disponil A3065 to evaluate if an adequate stability of EHA/VAc miniemulsions could be obtained using this particular non-ionic surfactant. Disponil A3065 is a mixture of ethoxylated linear fatty alcohols that do not contain a phenyl group as does Triton X-405. Do Amaral et al.[3] used a combination of Disponil A3065 and an anionic surfactant to stabilize EHA/methyl methacrylate (MMA) miniemulsions. According to their results, the miniemulsions were visually stable for up to a week, although no DSD were reported.

It was also considered that the ODA concentration used in the initial series of runs was not enough to provide a P_O that could prevent or delay Ostwald ripening. In this case, ODA concentration was increased to 4.5 phm in an attempt to increase P_O. Table 2 shows the formulations together with the results of the DSD and PSD using the stabilization system SDS/Disponil A3065. The temperature was kept constant at 60 °C for all runs in this series.

Runs 301 and 303 were prepared using solely SDS as surfactant while runs 302 and 304 were prepared using Disponil A3065 in order to evaluate how each of these two surfactants was influencing the DSD. Runs 301 and 303 contain the same SDS concentration but they were polymerized using two different initiator concentrations (c.f. Table 2). Similarly, runs 302 and 304 had the same Disponil A3065 concentration but were polymerized using the same two initiator concentrations as with SDS.

Table 2.
Miniemulsion polymerization of EHA/VAc/MAA using the stabilization system SDS/Disponil A3065/ODA

Run	[SDS]	[Disponil A3065]	[Initiator[b]]	D_p	N_d	N_p	N_p/N_d
	(phm)	(phm[a])	Phm	(nm)	(× 10^{17})	(x 10^{17}]	
301	1.0	0.0	0.30 (A)	124	0.69	1.37	2.00
302	0.0	2.30	0.30 (A)	280	0.15	0.13	0.86
303	1.0	0.0	0.15 (A)	113	0.36	2.02	5.60
304	0.0	2.30	0.15 (A)	230	0.28	0.23	0.82
305	0.22	3.00	0.15 (A)	165	0.48	0.68	1.42
306	0.11	3.30	0.15 (A)	180	0.48	0.56	1.16
307	0.11	3.30	0.15 (B)	208	0.53	0.38	0.72
308	0.11	3.30	0.60 (B)	257	0.40	0.22	0.55
309[c]	0.11	3.30	0.15 (A)	201	0.61	0.65	1.06

[a] phm = parts per hundred parts monomer
[b] A = Ammonium persulfate; B = benzoyl peroxide
Solids content was 43% for run 309 and for runs 301 to 308 was 30%.

As can be observed in Figures 4a and 4b, the measured DSD of both SDS- and Disponil-based miniemulsions were monomodal in nature. However, the formulation prepared with ionic surfactant gave a narrower DSD (run 301) compared to that prepared with the non-ionic surfactant (run 302). Miniemulsions produced with SDS resulted in large increases in the N_p with N_p/N_d values of 2 and 5. It is interesting to note that at the higher APS concentration, (i.e., at 0.35 phm) N_p/N_d was closer to unity which could be due to more droplets being nucleated at the beginning of the reaction due to higher concentrations of initiator radicals and less new particles generated. However, it is clear that the miniemulsions were not properly stabilized and compartmentalization was not achieved.

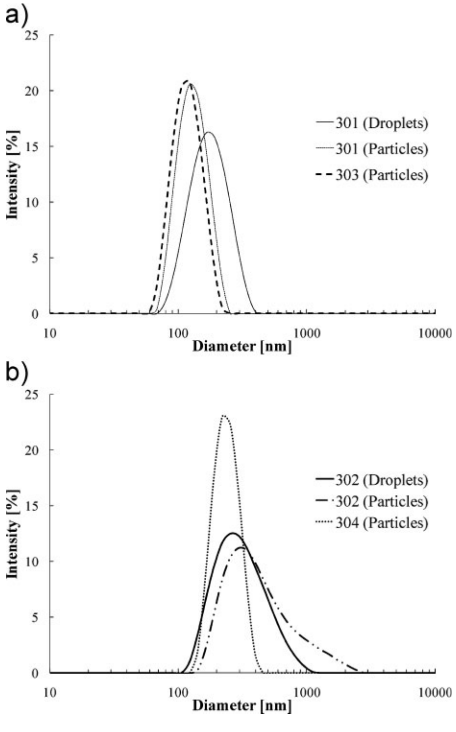

Figure 4.
a) DSD and PSD of runs 301 and 303 prepared using SDS as the sole stabilizer and b) DSD and PSD of runs 302 and 304 prepared using Disponil A3065 as the sole stabilizer.

Runs 305 and 306 were prepared using a mixture of ionic and non-ionic surfactants in a 80/20 and 90/10 mole ratio of Disponil A3065/SDS. These ratios were chosen since formulations with SDS led to large values of N_p/N_d while formulations with Disponil gave N_p/N_d ratios below 1, an indication that in the first case, generation of new particles occurred and in the second case, particles coalesced. It was hypothesized that a stabilization system with a higher amount of Disponil A3065 could avoid the generation of new particles while the presence of SDS could stabilize the recipe against coalescence. Figure 5 shows the results of runs 305 and 306. One can see that a mixture of Disponil A3065/SDS led to narrower DSD compared to the previous run prepared where only one surfactant was used. However, there was not a significant difference when the

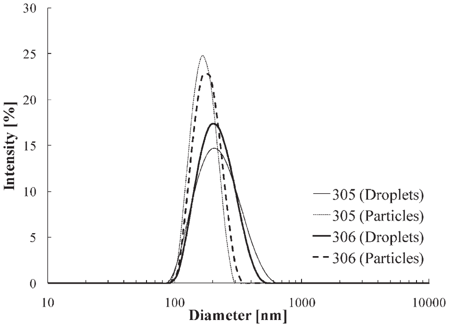

Figure 5.
DSD and PSD of runs 305 and 306 using a mixture of 80/20 mol.-% and 90/10 mol.-% Disponil/SDS, respectively.

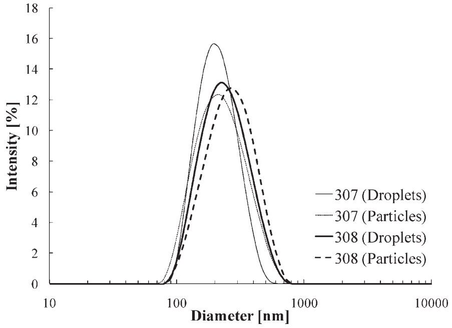

Figure 7.
DSD and PSD of runs 307 and 308 polymerized using 0.15 and 0.60 phm of BPO as initiator.

Disponil A3065/SDS ratio was changed from a molar ratio of 80/20 to 90/10.

Although the miniemulsions gave N_p/N_d values closer to unity, they were not behaving as compartmentalized systems. Figure 6 shows the evolution of N_p/N_d throughout the reaction. It can be observed that in run 306, which gave a value of N_p/N_d closest to unity at the end of the polymerization (c.f. Table 2), the N_p actually increased $\sim$80% after the initiator was injected (this sample was taken after 4 min). This result suggests a combined nucleation mechanism where new particles were generated at the beginning of the reaction as well as the nucleation of a portion of the initial droplets. However, there was not enough surfactant to stabilize the newly generated polymer particles causing some of those particles to coalesce and thus, the average D_p increased again to a value very close to the initial D_d.

Figure 7 shows the DSD and PSD for runs 307 and 308, which were polymerized using the oil-soluble initiator BPO. BPO, a water-insoluble compound (water solubility of $\sim$0.012 mM) is also thought to act as a hydrophobe improving miniemulsion stability. As a matter of fact, there was an increase of $\sim$4% and $\sim$12% in the P_O. As can be observed in Figure 7, the final PSD of run 307 is reasonably close to its initial DSD and although N_p/N_d is below 1, it does not fluctuate as much as previous runs (c.f. Figure 6). However, the maximum conversion attained in run 307 was $\sim$57 wt.-% after 3 h. Therefore, it was decided to carry out run 308 with a higher initiator concentration and longer reaction time. The DSD and PSD of run 308 are also shown in Figure 7 and as can be seen, they are reasonably close to each other. The maximum conversion in run 308 after 7 h was $\sim$67 wt.-%. The conversion profile (not shown here) displayed a plateau at 67 wt.-% after 4 h of reaction without appreciable change afterwards. An analysis of the copolymer composition by ^{1}H-NMR spectroscopy showed that most of the polymer in the particles was EHA homopolymer. This is consistent with the reactivity ratios (discussed earlier) which favour EHA homopolymer production and the relatively high water solubility of VAc.

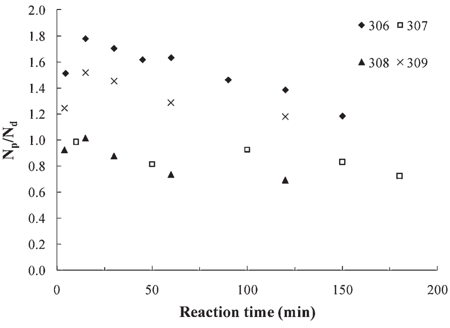

Figure 6.
Evolution of N_p/N_d for runs 306 to 309.

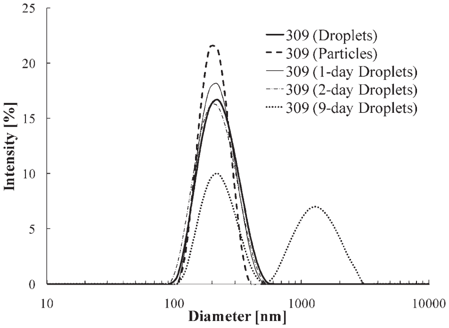

Figure 8.
DSD and PSD of run 309 using a mixture of 96/4 wt.-% of Disponil/SDS and with 43% solids content.

The miniemulsion prepared for run 306 was the most stable miniemulsion prepared up to this point with a conversion above 95%. However, the formulation contained 30 wt.-% solids, which is a relatively low solids content. Run 309 was prepared with a solids content of 43 wt.-% in order to test the stability of the miniemulsion. Figure 8 shows the DSD of run 309 immediately after sonication as well as after 1, 2 and 9 days. It also shows the final PSD of the latex, which was polymerized using the miniemulsion right after sonication. Figure 8 shows that the DSD did not change significantly after 2 days, which strongly suggest that the miniemulsion was stable and that the higher solids content did not impede the preparation of a kinetically-stable miniemulsion. It was also observed that the measurement taken after 9 days showed two peaks, where one of them had approximately the same diameter as that initially reported. The second peak (large particles) is evidently the result of degradation processes.

Influence of Comonomer, Surfactant and DDM Concentration

Once a set of conditions that gave a kinetically-stable miniemulsion was found, a 2^3 factorial design was carried out to evaluate the influence of the copolymer, surfactant and DDM concentration on D_d, D_p, N_p/N_d and afterwards, their influence on the three main PSA properties: tack, peel strength and shear strength[28]. The statistical analysis was carried out using an alpha value of 0.05 for statistical significance. Table 3 shows the levels for each factor as well as the results of D_p, N_p/N_d, the maximum conversion (X_{max}) attained and the maximum deviation observed from an ideal N_p/N_d of 1 (be it at any point during the reaction).

The statistical analysis showed that D_d was strongly influenced by the monomer and surfactant concentrations with p-values of 0.007 and 0.01, respectively. It was expected that the surfactant concentration would play a role in determining D_d; however, it was not anticipated that the monomer composition would have a significant influence. It was then noticed that the N_d was larger for those recipes containing a monomer composition of 65/35 wt.-% of EHA/VAc, i.e., higher levels of VAc, which in turn decreased D_d.

Table 3.
2^3 factorial design of the miniemulsion polymerization of EHA/VAc/MAA

Run	MC	[S]	[DDM]	D_p	X_{max}	N_p/N_d	Max.dev.^{b} (%)	M_w
	(wt.-%)	(phm)	(phm)	(nm)	(wt.-%)			(g mol^{-1})
401	85/15	3.5	1.0	217	86	0.99	13	58,800
402	85/15	4.5	0.5	188	88	1.09	11	120,600
403	65/35	4.5	0.5	184	93	0.86	11	200,000
404	65/35	4.5	1.0	169	75	1.21	30	37,000
405	65/35	3.5	0.5	189	76	1.07	16	63,200
406	85/15	4.5	1.0	191	92	1.16	31	64,000
407	85/15	3.5	0.5	215	91	1.07	17	112,600
408	65/35	3.5	1.0	199	77	0.97	3	47,200

MC = Monomer composition as EHA/VAc; S = Surfactant; DDM = Dodecyl mercaptan
Maximum deviation of N_p/N_d from 1.0

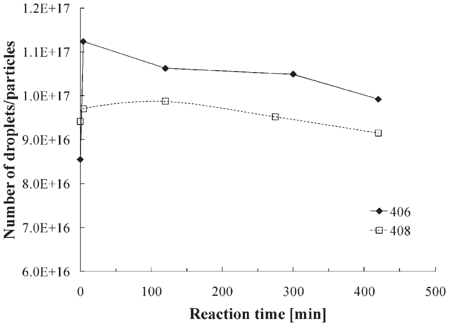

Figure 9.
Initial N_d and evolution of the N_p for miniemulsion-based runs 406 and 408.

There were a number of runs that did not reach full conversion (c.f. Table 3) and it was observed that the maximum conversion was strongly correlated to the VAc content, which is likely due to the low reactivity of this monomer. This raised the question on how much the lower values of conversion influenced miniemulsion compartmentalization. The evolution of N_p/N_d throughout the reaction in each one of the reactions was analyzed and the largest deviation observed was recorded (also shown in Table 3). It was noted that the largest deviations were not correlated with the VAc nor were DDM concentrations significant in obtaining lower deviation values. It was initially thought that a higher DDM concentration would build up P_O and in turn, have an influence on stability. However, the surfactant concentration was the only statistically significant factor. Figure 9 shows the initial N_d and the evolution of N_p for runs 406 and 408. Run 406 presented the largest deviation from an ideal N_p/N_d of 1, with a change of ~30% with respect to N_d while run 408 presented the lowest deviation of ~3%. It must be mentioned that a deviation of 3% at the beginning of the reaction can represent a miniemulsion that is compartmentalized properly.

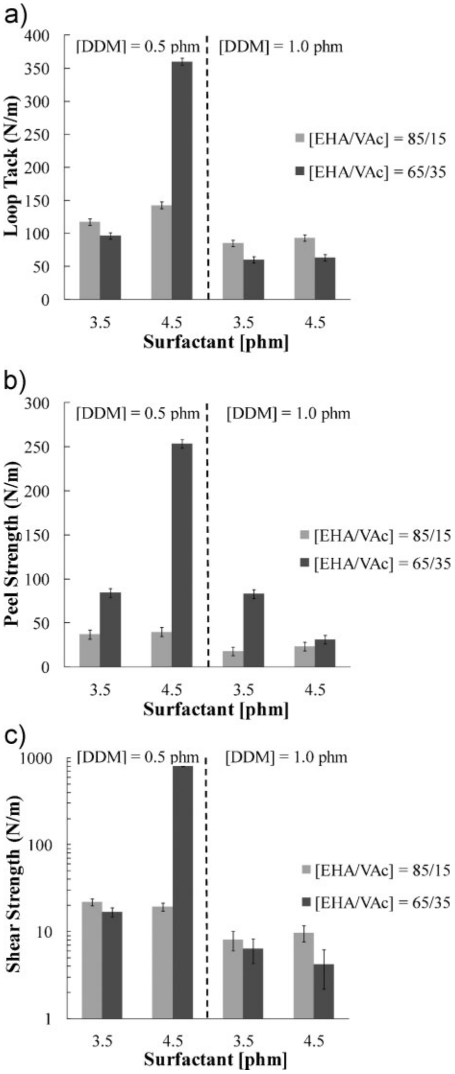

Figure 10.
Influence of EHA/VAc polymer composition, surfactant and DDM concentration on a) loop tack, b) peel strength and c) shear strength (log scale).

Pressure-Sensitive Adhesive Properties

Figure 10 shows the results of loop tack, peel strength and shear strength obtained in the factorial design. However, it was difficult to assess the influence of the copolymer composition on the PSA properties due to the fact that a number of the runs did not reach full conversion and the polymer particles were mostly comprised of homopolymer of EHA. Nevertheless, it was observed that those latexes prepared with a monomer mixture of EHA/VAc of 85/15 wt.% gave higher values of loop tack and lower values of peel strength. Con-

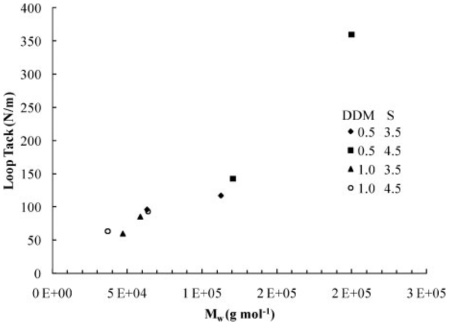

Figure 11.
Loop tack versus M_w (S = Surfactant; DDM = Dodecyl mercaptan).

versely, shear strength did not seem to be affected by the copolymer composition.

On the other hand, DDM concentration had a strong influence on the determination of the three PSA properties. At the levels of M_w produced within the range of experimental conditions, loop tack, peel and shear strength increased with a decrease of DDM concentration. Figure 11 shows how loop tack was strongly correlated to M_w with a linear increase towards larger loop tack values with higher molecular weights. A similar trend was observed for peel and shear strength (not shown here). One can see that highest loop tack values were attained at a M_w above 1×10^5 g mol^{-1}, which observed an adhesive failure, while those below this M_w limit displayed cohesive failure. It is likely that at this M_w, fibrils started forming, which have been suggested to be responsible for adequate levels of tack in PSAs[29].

Conclusion

The preparation of stable miniemulsion-based latexes of poly(EHA/VAc) was studied. Two surfactant mixtures were investigated: SDS/Triton X-405 and SDS/Disponil A3065. The first mixture contained Triton X-405, a non-ionic surfactant with a high content of water soluble groups. The results showed that SDS/Triton X-405 was not able to adequately stabilize the miniemulsions to ensure compartmentalization, even though the ODA concentration had been adjusted to give a P_O slightly higher than the P_L. The second surfactant mixture contained Disponil A3065, an ethoxylated linear fatty alcohol surfactant with a lower amount of water soluble groups compared to Triton X-405. Through the screening experiments, we found that a 10/90 mol.-% ratio of SDS/Disponil A3065 with an ODA concentration of 4.5 phm were able to adequately stabilize the miniemulsion resulting in 43% solids-content latexes. The final N_p/N_d obtained in the most stable recipe was 1.06 with a maximum deviation in the N_p at the beginning of the polymerization of ~3%.

Once a stable range of conditions was identified, a 2^3 factorial design was carried out to understand the influence of changes in co-monomer, surfactant and DDM concentration on the DSD and PSD and later, in the PSA properties (loop tack, peel strength and shear strength). The analysis showed that the DSD was strongly influenced by the co-monomer and surfactant concentrations. It was also noted that the change in DDM concentration did not contribute to the miniemulsion stability in the range studied in this work nor did it represent a significant factor in determining the DSD and PSD. However, the statistical analysis was unable to identify the influence of the co-monomer concentration on the final PSD due to the fact that 5 out of 8 runs in the factorial design did not reach full conversion (conversions between 71 and 91 wt.-%). This was likely due to the water solubility of VAc monomer combined with its low reactivity compared to EHA. This is typical of VAc-containing systems and it continues to represent a significant challenge for industrial applications. Typically, semi-continuous monomer feed strategies are employed to counteract this effect; however, as mentioned by Schork et al.[2], the semi-continuous monomer feed in miniemulsion polymerization would not differ from that obtained in conventional emulsion polymerization.

The DDM concentration did not affect DSD or PSD but it played a strong role in the determination of M_w. Within the range of DDM and surfactant concentrations studied in this work, the M_w varied from 40,000 to 200,000 g mol^{-1}. As a consequence, DDM concentration had a strong influence on loop tack, peel strength and shear strength. A linear relationship between tack and M_w was observed, i.e., higher M_w resulted in higher loop tack. Similar trends were observed for peel and shear strength.

Nomenclature

APS	Ammonium persulfate
BMA	Butyl methacrylate
BPO	Benzoyl peroxide
D_d	Droplet diameter
DDI H_2O	Distilled deionized water
DDM	1-dodecanethiol
DLS	Dynamic light scattering
D_p	Particle diameter
DSD	Droplet size distribution
EHA	2-ethyl hexyl acrylate
GPC	Gel permeation chromatography
H-NMR	Proton nuclear magnetic resonance
KPS	Potassium persulfate
LPO	Lauroyl peroxide
MAA	Methacrylic acid
MMA	Methyl methacrylate
N_d	Number of droplets
N_p	Number of particles
ODA	Octadecyl acrylate
P_L	Laplace pressure
P_O	Osmotic pressure
PSA	Pressure-sensitive adhesive
PSD	Particle size distribution
PVOH	Polyvinyl alcohol
R_p	Rate of polymerization
SA	Stearyl acrylate
SDS	Sodium dodecyl sulfate
STY	Styrene
VAc	Vinyl acetate

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