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The water resistance of waterborne all-acrylic and styrene acrylic dispersions is investigated at different T_gs. The performance of films obtained from latexes stabilized using conventional surfactants (SLS and Surf 1) is compared to that of latexes stabilized using polymerizable surfactants (PolySurf 1 and 2). The effect of the surfactant concentration and surfactant chemistry on the water whitening and water uptake of the latex films is studied. The surfactant chemistry and concentration, as well as the pH of the final latex have a significant influence on the water resistance results. The water whitening phenomenon is directly linked to the latex colloidal stability during drying and the excess of surfactant in the continuous water phase. Atomic Force Microscopy (AFM) images revealed that labile surfactants can migrate within the film during drying and form hydrophilic pathways or pockets, making the film more susceptible to water at higher concentration of surfactants. Proton nuclear magnetic resonance (^{1}H-NMR) analyses, combined with AFM imaging, showed that when polymerizable surfactant is used, due to its incorporation into the polymer backbone, the residual amount of surfactant in the continuous phase is low, resulting in films with superior water resistance. Moreover, the controlled distribution of the polymerizable surfactant on the latex particles results in a more homogeneous distribution of the surfactant in the latex film lowering the water sensitivity of the films. Overall, for T_gs between -5 °C and 10 °C in acrylic latexes, the PolySurf2 exhibits superior water whitening and water intake performances as compared to conventional surfactants. PolySurf2 is designed to provide superior water resistance performances in clearcoats.

Introduction

Clearcoats are widely used in coatings markets such as industrial and architectural paints as an invisible top layer to protect the underlying paint coats from UV rays, dirt, and water. Indeed, paints in direct contact with rain or a high-humidity environment require extra protection against water penetration. Because of additional environmental regulations and recent market trends toward more sustainable technologies, solvent-based formulations that provide excellent water resistance are under scrutiny, and waterborne clearcoats have become more desirable.

Waterborne polymers used in clearcoats are environmentally friendly, easy to handle, relatively low in cost, and can be made with high-solids content through emulsion polymerization. Although surfactants and hydrophilic monomers are necessary during the latex synthesis to provide steric and/or electrostatic stabilization to the particles formed, their distribution during drying can impede the water resistance of the polymer films. The phenomenon of water whitening in polymer films has been mainly attributed to water molecules "clustering" near the polar constituents of the films, such as the surfactants and the hydrophilic monomers.[1-4] Moreover, during the film formation, surfactants can migrate toward interfaces, forming hydrophilic pockets within the polymer film or concentrate near the surface of the particles to create

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Water Resistance Properties of Acrylic Polymer Films Using Polymerizable Surfactants

hydrophilic pathways throughout the film.[1-5] The water-swollen pockets scatter light and make the film appear cloudy or white.[6,7] To reduce the negative effects of conventional ionic surfactants on the water sensitivity of the latex films, polymerizable surfactants are used. These reactive surfactants polymerize with the monomers and are incorporated into the backbone of the polymer chains of the latex.

Polymerizable surfactants are then locked on the latex particles, and a better control of their distribution within the polymer film is achieved during drying because of the lack of both desorption from the latex particles and migration in the polymer film.[8-10] Although the mechanisms of water sensitivity of polymer films have been extensively studied before, to the best of our knowledge, a broad analysis of the water whitening and the water uptake of clear latex films as a function of T_g has not been reported to this date.

The effect of the latex pH on the water whitening resistance of the final films was also studied. In addition, the effect of surfactant concentration on the latex films' water-resistance properties was investigated. Finally, it was demonstrated that the polymerizable surfactants used in this study are almost fully converted during latex syntheses leaving very little unreacted surfactant in the dried polymer films, which enhances the water-resistance properties of thus films.

Materials and Methods

Materials

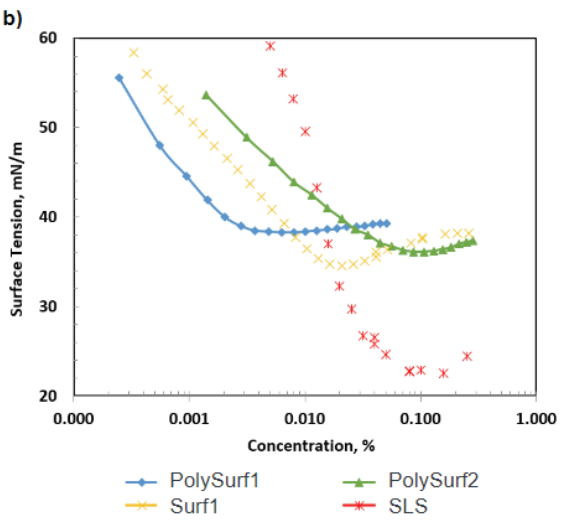
Methyl methacrylate (MMA), butyl acrylate (BA), and methacrylic acid (MAA) (99%, Sigma-Aldrich) were used as is. Surf1 (Syensqo), SLS (Syensqo), PolySurf1 (Syensqo), and PolySurf2 (Syensqo) were used as emulsifiers in the latex syntheses. Sodium bicarbonate (99.7%, Sigma-Aldrich) was used as a buffer in the preparation of the latex surfactant control. Ammonium

FIGURE 1
(a) Surfactants' physico-chemical properties; (b) concentrations.

a)

Surfactants & Properties	CMC (%)	ST @ CMC (mN/m)	Solids (%)
SLS	0.04	23	29.5
Surf1	0.016	35	30.5
PolySurf1	0.002	40	26.4
PolySurf2	0.087	36	26.4

b)



persulfate (99.8%, Sigma) was used as an initiator in all latex synthesis. Deionized (DI) water was used throughout the work. **Figure 1** presents the main characteristics of the surfactants used throughout this study.

Methods

Latex Synthesis. The latex was synthesized by emulsion polymerization in a 2-liter glass reactor from methyl methacrylate, butyl acrylate and methacrylic acid as monomers; ammonium persulfate as the initiator, one surfactant, and two chaser solutions: t-BHP and isoascorbic acid. First, the glass reactor was charged with a solution of water containing the surfactant and heated to 82 °C. While the solution was heating, the monomer emulsion was prepared by mixing water and surfactant and then slowly pipetting each monomer into the solution under shear. Once the solution in the glass reactor reached the target temperature, a monomer seed, which is 5% of the previously prepared monomer emulsion, and an initiator seed were added concomitantly to the reactor. The seeds were left to polymerize for 15 minutes. The rest of the monomer emulsion and the initiator feed solution were fed over 3 h. After the feed was complete, the reaction was held at 82 °C for 30 minutes. Then, the temperature was decreased to 65 °C to add the two chaser solutions simultaneously. The reaction was held for another 30 minutes. After holding, the solid content and particle size were measured, and then the reactor was cooled to room temperature. Finally, the latex was discharged from the glass reactor and filtered through a 150-micron filter into a storage container. The pH of the latex was adjusted to 8.5-9.0 using 28% ammonium hydroxide.

Particle Size. The particle size of the latex samples was measured with the Zetasizer Nano Particle Sizer Analyzer. The sample was diluted up to an almost clear solution and placed into a polystyrene cuvette. The average particle size and PDI of 3 sequences of 12 intensity measurements were recorded.

Solid content. A moisture balance analyzer (OHAUS MB120) was used to determine the solid content of the latex dispersions (1 g of latex was dried at 120 °C for 5-10 min).

Viscosity. The viscosity of emulsions was determined by Brookfield Viscometer (DV2T Model) at room temperature.

Minimum Film Formation Temperature. The minimum film formation temperature (MFFT) was measured with the "MFFT bar 90." The latex was applied using a 75-micron cube applicator from the warm end to the cold end. The visual MFFT was directly read where the dried films started to crack. The mechanical MFFT was visually assessed by pulling the tape at a 90° angle and recording the temperature at which the film started to crack.

Surface tension measurements. An Attension tensiometer from Biolin Scientific with a Du Nouy ring was used to measure the surface tension of surfactant solutions and latex dispersions. All surfactant solutions were prepared at 1 wt % in DI water and subsequently diluted to obtain the CMC curves. The surface tension measurements of latex dispersions were performed as is (no dilution). All surface tension measurements were obtained at room temperature. The precision of the surface tension values obtained for the latex dispersions was +/- 0.5 mN/m.

^{1}H-NMR. All latex samples were prepared in THF-d8 and analyzed by ^{1}H-NMR on a Bruker Avance 500 MHz spectrometer, equipped with a PABBO BB/19F-1H/D 5 mm multinuclear probe, using standard conditions. NS was increased to 1024 scans for each experiment to be able to lower the limit of detection of the unreacted polymerizable surfactants in the latex-based formulations.

Atomic Force Microscopy. Atomic Force Microscopy was used to image the latex particles. The latex particles were diluted and dried overnight. Imaging was performed on a Bruker AFM in ScanAsyst-air mode (**Figure 1**) and in tapping mode for imaging of the surfactant in between the particles (**Figure 10**). For each sample, several areas of the film formed from latex particles were analyzed. Regarding the surfactant imaging in the interparticle spaces, AFM tips of both 8 and 2 nm showed similar patterns. The observed surfactant features remained at the same position upon change of the scan direction and rotation of the image.

Water whitening. The latex films were cast on previously cleaned glass panels using a 6 mil drawdown bar. The films

were dried at 22 °C and 50% room humidity for 24 hours. The dry films were then immersed in a water bath at room temperature for 24 hours. After one day, the film appearance was recorded (blue tint, white opaque, blisters, etc.) and pictures of the films were taken.

Water uptake. The latex films were drawn down on hydrophobic black Leneta scrub charts using a 6 mil square bar. The films were dried at 22 °C and 50% room humidity for 24 hours. After drying, films and substrates were cut into 1 in. x 1 in. squares (triplicates). The initial weight of each square was reported. The squares were submerged in water for 24 hours. After one day, the films were padded dry using KimWipes and were weighted. The percentage of water intake in the films was reported over the course of 7 days. Finally, the average value of the triplicates was calculated.

Results and Discussion

Latex Syntheses and Characterizations

In this work, the factors impacting the water resistance of poly(butyl acrylate-co-methyl methacrylate-co-methacrylic acid) and of poly(butyl acrylate-co-styrene-co-acrylic acid) latex films were studied. To enhance the colloidal stability of the latexes, 2% BOTM methacrylic acid or acrylic acid was used. Different ratios of MMA/BA or Sty/BA were used to adjust the T_g of the final polymer. The 45 wt % acrylic latexes stabilized with different surfactants were synthesized by seeded semi-batch emulsion polymerization (details are given in the materials and methods section). Briefly, the emulsion polymerizations were carried out at 82 °C by loading a small amount of monomer and initiator in the reactor (seeding stage) and then feeding a monomer pre-emulsion and additional initiator over 3 h. Two different latex recipes were studied: all acrylic and styrene acrylic. For each recipe, several T_gs and four surfactants were investigated. The amount of surfactant used in the seed stage was slightly adjusted to obtain a similar particle size for all the surfactants tested. The surfactant concentration, expressed as a percentage of the total monomer weight (%BOTM), was kept constant across all surfactants. As the molecular weight of the different surfactants studied were different from one another and because the amount of surfactant was considered as solids content in the latex recipe; the amount of water used was slightly varied in each reaction in order to adjust the final solids content to 45 wt %.

The main characteristics of the four surfactants studied are presented in **Figure 1**. Sodium lauryl sulfate (SLS) is commonly used as an emulsifier. Surf1 is a proprietary aliphatic ethoxylated sulfate surfactant. PolySurf1 and PolySurf2 are proprietary ethoxylated sulfate polymerizable surfactants that have different hydrophobicities. Each polymerizable surfactant molecule contains on average more than one polymerizable unit. PolySurf1 and Surf1 have a close chemical structure. As can be seen on the graph in **Figure 1b**, the most hydrophilic surfactant is the PolySurf2 (highest CMC) whereas the most hydrophobic surfactant is the PolySurf1 (lowest CMC).

Characterizations of the different latex dispersions are presented in **Figure 2**. For most of the latexes, the conversion was about 100% and the coagulum was low. The only latex with a significant amount of coagulum (about 1%) was the one made with 0.5% BOTM of PolySurf2. The viscosity of styrene acrylic latex is overall 5 to 10 times

FIGURE 2
Latex characterizations.

Latex composition	Description	T_g (°C)	Dz(nm)	Solids(%)	Conversion(%)	Viscosity(cP)	Coagulum(%)	MFFT (°C) (Visual/Mechanical)
All acrylic (MMA/BA/MAA)	1.5%BOTM PolySurf1	-20.3	116	44.9	99.9	58	<0.01	Out of range
	1.5%BOTM PolySurf2		127	45.2	100.0	44	<0.01	Out of range
	1.5%BOTM SLS		116	45.4	100.0	103	<0.01	Out of range
	1.5%BOTM Surf1		117	45.6	100.0	104	<0.01	Out of range
	0.5%BOTM PolySurf2	-4.7	156	45.2	100.0	29	1	-1 / 3
	0.5%BOTM SLS		145	45.2	100.0	41	<0.01	0 / 6
	1.5%BOTM PolySurf1		131	45.4	100.0	50	0.02	-1 / 5
	1.5%BOTM PolySurf2		127	45.6	100.0	42	<0.01	-1 / 4
	1.5%BOTM SLS		117	44.9	99.7	79	<0.01	-1 / 2
	1.5%BOTM Surf1		126	45.4	100.0	48	<0.01	0 / 3
	3%BOTM PolySurf1		137	45.3	100.0	62	0.134	-1 / 8
	3%BOTM PolySurf2		117	44.8	99.2	40	0.2	-1 / 4
	3%BOTM SLS		109	45.8	100.0	90	<0.01	-1 / 2
	3%BOTM Surf1		114	44.7	99.9	50	<0.01	-1 / 3
	1.5%BOTM PolySurf1	10.4	143	45.2	100.0	33	0.01	15 / >18
	1.5%BOTM PolySurf2		124	45.1	99.4	44	0.02	13 / 17
	1.5%BOTM SLS		114	45.2	99.9	60	<0.01	13 / 14
	1.5%BOTM Surf1		135	45.1	100.0	32	<0.01	13 / 13
	1.5%BOTM PolySurf2	24.4	137	45.3	100.0	24.0	<0.01	33 / 33
	1.5%BOTM SLS		120	45.3	100.0	35.0	<0.01	28 / 29
	1.5%BOTM Surf1		134	45.3	100.0	24.6	0.026	28 / 28
Styrene acrylic (Sty/BA/AA)	1.5%BOTM PolySurf1	-20.6	108	44.6	98.9	404	0.04	-5 / -1
	1.5%BOTM PolySurf2		112	45.3	100.0	412	<0.01	-3 / -1
	1.5%BOTM SLS		99	45.8	100.0	640	0.02	-3 / -1
	1.5%BOTM Surf1		114	45.2	100.0	155	0.01	-3 / -1
	1.5%BOTM PolySurf1	0	107	45.1	100.0	577	0.13	12 / 16
	1.5%BOTM PolySurf2		108	45.2	100.0	268	0.03	11 / 12
	1.5%BOTM SLS		99	45.2	100.0	493	<0.01	13 / 15
	1.5%BOTM Surf1		117	44.6	99.0	102	<0.01	13 / 14

higher than the viscosity of the all-acrylic latex. This observation can be explained by the smaller particle sizes of styrene acrylic latexes as compared to the particle sizes of all-acrylic latexes. Indeed, for the all-acrylic latexes made with 1.5% BOTM surfactant, the particle sizes are in the range 114-143 nm. For styrene acrylic latexes made with 1.5% BOTM surfactant, the particle sizes are in the range 93-117 nm. No significant impact of the T_g was observed on the latex particle size for the four surfactants studied. A surfactant concentration ladder study was carried out for latexes at T_g -5C. At equal total %BOTM of surfactant, the %BOTM of SLS and Surf1 used in the seed stage was adjusted to match the particle size obtained with the polymerizable surfactants. The largest particle size was obtained with 0.5% BOTM of PolySurf2 in the all-acrylic latex because the amount of surfactant used in the seed stage was divided by half as compared to the 1.5% BOTM PolySurf2 all-acrylic recipe. No significant difference in particle size was observed when polymerizable surfactants were used at 3% BOTM (the amount of surfactant was doubled both in the seed and feed stages).

AFM Imaging

AFM height images of the selected acrylic latexes with T_g approximately 20 °C show that particles obtained with SLS and Surf1 are spherical and have a low size dispersity as evidenced by the crystalline organization of the particles on **Figures 3a** and **3b.** The presence of multiple reactive groups on each reactive surfactant molecule is proposed to be the reason behind the lobed shape of the particles made with the polymerizable surfactants (**Figure 3c)**. Indeed, if all polymerizable units present on one single molecule of surfactant are incorporated in polymer chains, it is likely that the polymerizable surfactant molecules also act as crosslinkers that are known to impact the sphericity of latex particles. To achieve homogeneous and more resistant polymer films, tight compaction of the latex particles during drying is important. This is typically achieved with monodisperse particles. However, Burel et al.[11] have reported that for a similar average diameter, particle dispersions with some polydispersity can lead to superior volume packing fraction. At equivalent average particle diameter, the volume packing fraction of latex made with polymerizable surfactants should be at least as good, if not better than the volume packing fraction of latex made with regular surfactants.

Water Intake of Latex Films

Water intake results of polymer films made from the latexes at T_g -20 °C to 10 °C with 1.5%BOTM of surfactants are presented in **Figure 4**. For all-acrylic latexes at T_g -20 °C **(Figure 4a)**, no significant differences are observed between the four different surfactants studied. At low T_g, the resistance of the polymer matrix to deformation is much lower and more water can penetrate the films. Using a polymerizable surfactant in the low T_g latexes cannot counteract this phenomenon and the water resistance of the films is not improved.[6] At T_g -5 °C, the films containing labile surfactants SLS and Surf1 adsorbed about twice the amount of water as compared to films with polymerizable surfactants. At T_g 10 °C, the films containing SLS lead to superior water intake, followed by the Surf1 which also results in significant water adsorption. The use of polymerizable surfactants significantly decreases the water intake at that T_g. For styrene acrylic latex, at T_g -20 °C, films with SLS and Surf1 showed larger water intake than PolySurf2. Surprisingly, PolySurf1 showed the largest water intake. Because the particle size of the latex made using PolySurf1 is not significantly larger than the ones made with PolySurf2 or Surf1, it is hard to rationalize the result obtained. At T_g 0 °C, the water intake of films containing conventional surfactants SLS and Surf1 was higher than the ones with polymerizable surfactants. Overall, from T_g -5 °C to 10 °C, for both latex recipes, films made of latex with polymerizable surfactants showed less adsorption of water.

Water Whitening of Latex Films

The 24-hour water whitening results are presented in **Figure 5** for the different surfactants used at 1.5% BOTM in the latexes with T_gs -20 °C to 10 °C. All-acrylic latex results are shown in **Figure 5a** and styrene acrylic latex results in **Figure 5b**. Similarly to the water uptake results of all-acrylic latex at T_g -20 °C, one can observe that the water whitening of these latexes are very poor for Surf1, PolySurf1, and PolySurf2. At T_g -5 °C and 10 °C, PolySurf2 shows clearer film blue tints as compared to regular surfactants SLS and Surf1. This observation also correlates with the water intake results previously discussed. Regarding styrene acrylic latex, the water whitening images of latex at T_g -20 °C, with PolySurf1 and Surf1 are much worse than the water whitening obtained with PolySurf2 and SLS. At T_g 0°C, the water whitening results obtained with PolySurfs 1 and 2 are better than with Surf 1 but worse than with SLS. At T_g 0 °C, the water whitening results of the styrene acrylic latexes are not fully aligned with the water intake results. The particle size of the SLS styrene acrylic latexes are 10-15 nm smaller than the other latexes at the same T_g. This could be a reason for the differences observed. Overall, PolySurf2 shows the lowest water whitening and water intake.

FIGURE 3
AFM height images of acrylic latexes. (a) 1.5% BOTM SLS, T_g 15 °C; (b) 1.5% BOTM Surf1, T_g 25 °C, and (c) 1.5% BOTM PolySurf2, T_g 25 °C.

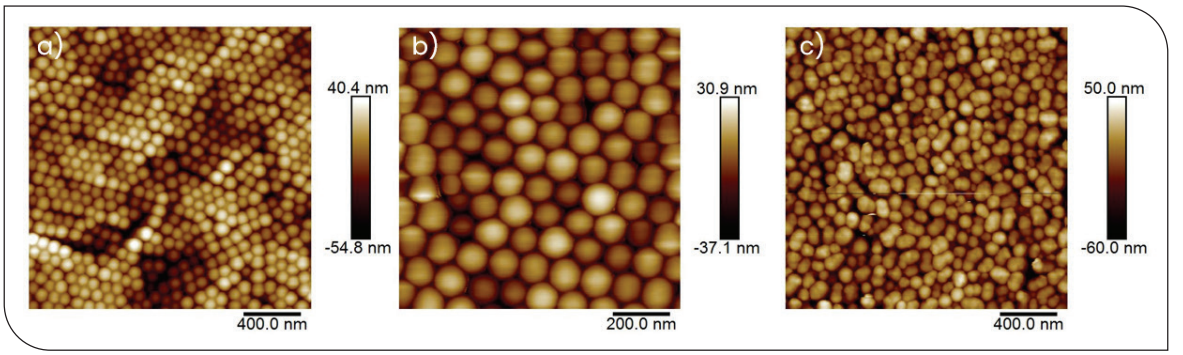


FIGURE 4
Water intake of films for the all-acrylic latex made with 1.5% BOTM surfactant at (a) T_g = -20 °C, (b) T_g = -5 °C, and (c) T_g = 10 °C; and for the styrene acrylic latex at (d) T_g = -20 °C and (e) T_g = 0 °C.

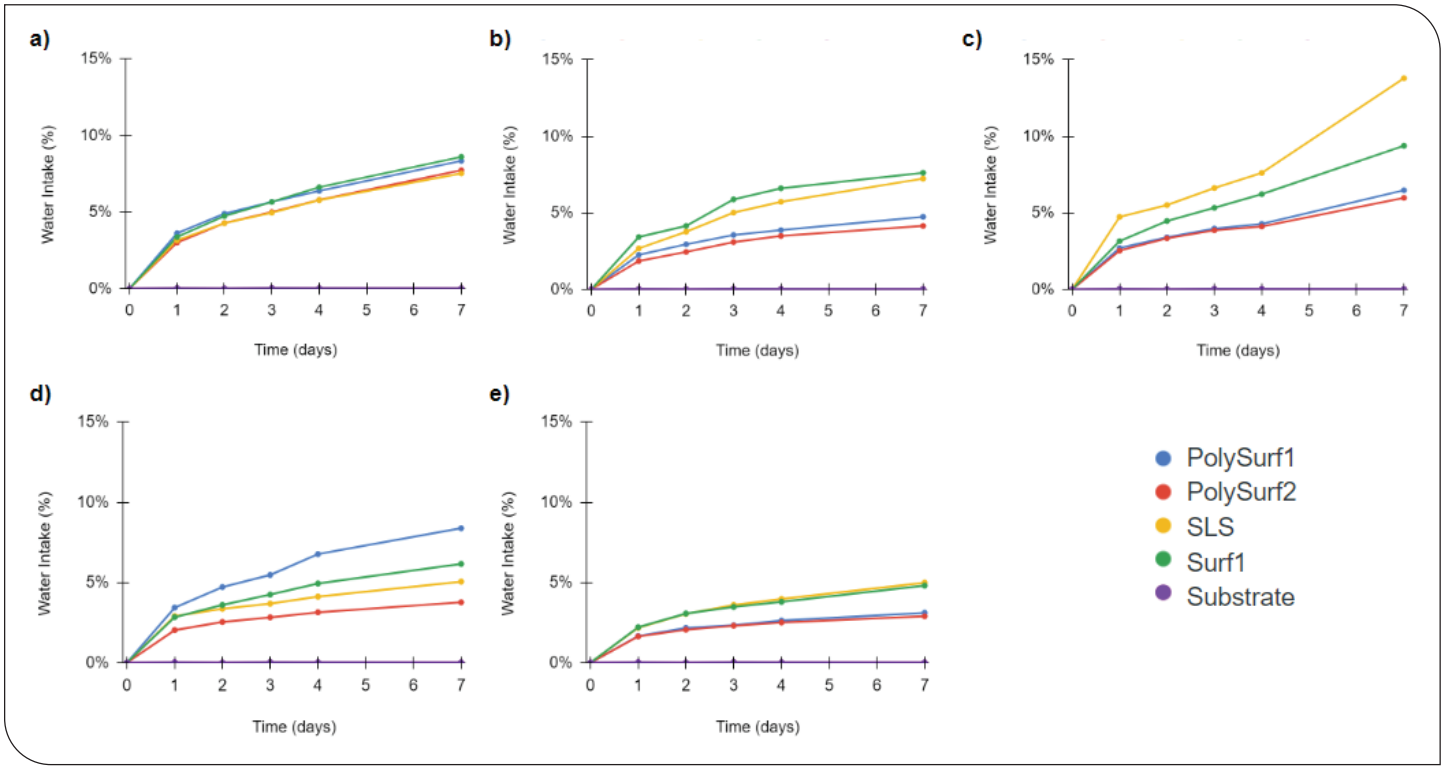
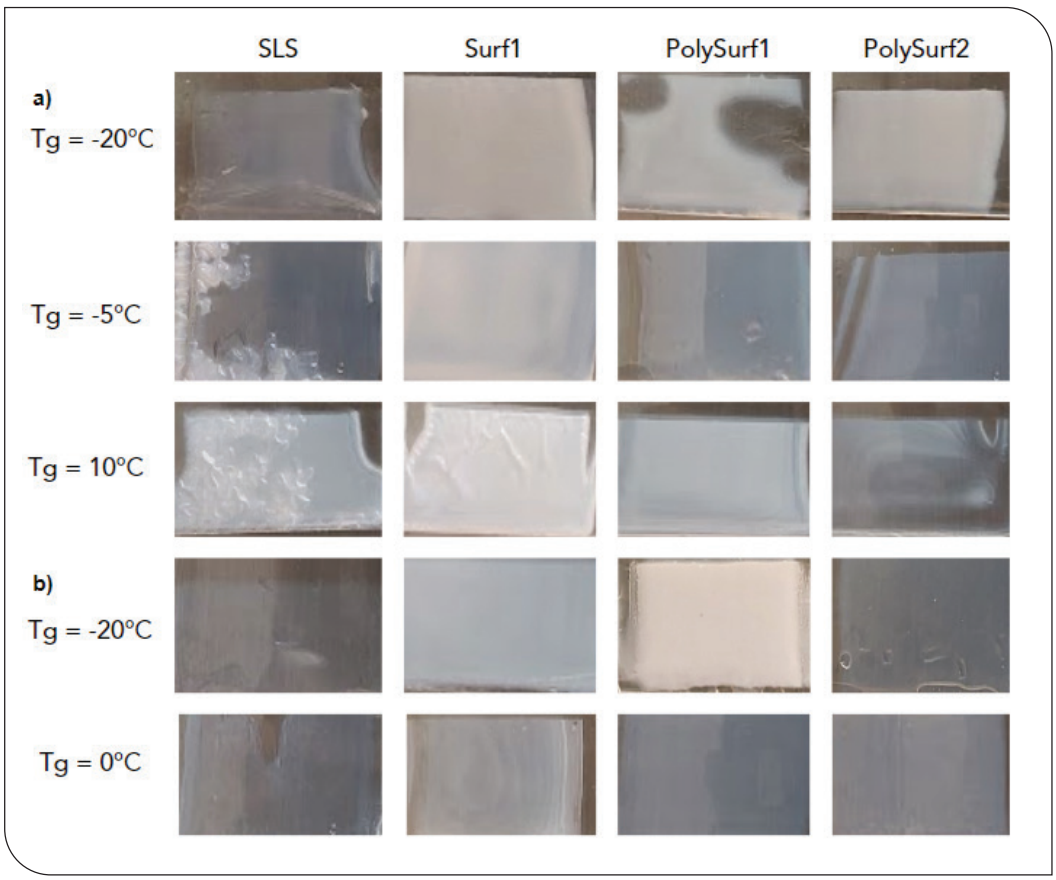


FIGURE 5
24 hours water whitening of films for (a) all-acrylic latex at different T_gs and (b) styrene acrylic latex at different T_gs. All latexes were made with 1.5% BOTM surfactant.



Effect of Latex Ionization on the Water

Whitening of Latex Film

To better understand the importance of the colloidal stabilization of the latex particles during film formation and its impact on the water resistance properties of the films, the water whitening of latex films formed from a latex made at T_g -5 °C with 1.5% BOTM SLS is studied at low and high pH. Images presented in **Figure 6** show that the water whitening of the polymer film formed from unneutralized latex (pH 2) is much worse than the one obtained with neutralized latex (pH 8.9). This illustrates the significant role that charged MAA plays in the colloidal stability of latex particles during the drying process.[12] Indeed, poor electrostatic stabilization of the latex particles during drying can lead to poor particle packing and particle aggregation which would favor the formation of surfactant pockets and film defects in fine worsening the water whitening of the polymer film.[7,13] Feng and Winnik found a similar effect of neutralization for poly(n-butyl methacrylate) latices made with MAA.[14]

Surfactant Concentration Effect on the Water Whitening of Latex Films

The effect of the surfactant concentration on the water whitening of latex films was studied for SLS and PolySurf2 at T_g -5 °C. Results presented in **Figure 7** show that as the surfactant concentration is increased, the water whitening of the latex films containing SLS worsen—the film becomes cloudier and blisters form—whereas the water whitening of the latex film containing PolySurf2 slightly improves. These observations confirm previous findings by the group of J. R. Leiza et al.[7] The incorporation of the surfactant/stabilizer in the polymer backbone suppresses the migration of the surfactants within the latex film; surfactant-rich pockets are not formed, and the water whitening is improved. Indeed, analyzing AFM imaging of the cross-section of latex films, Z. Aguirreurreta et al. have shown that, at high surfactant concentration, surfactant aggregation occurs within the film only when conventional surfactant is used.[7] Since increasing the amount of polymerizable surfactant slightly improves the water whitening of the latex film, one might consider that increasing the surfactant concentration also leads to a more homogeneous film structure arising from better particles packing due to stronger repulsive interactions or particle size dispersity.

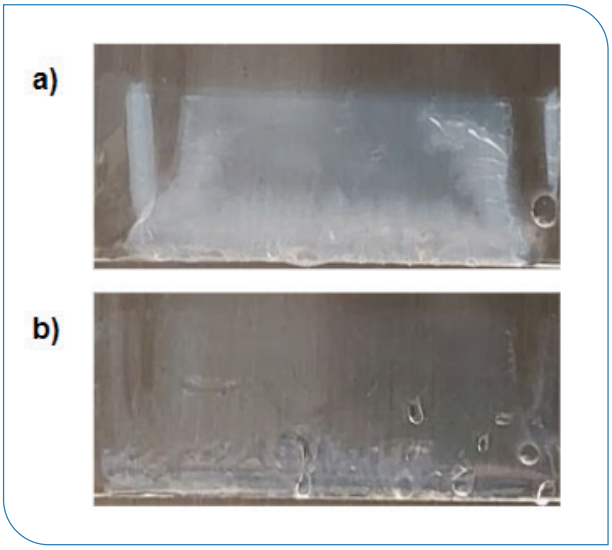


FIGURE 6
Water whitening of latex films made with 1.5% BOTM SLS (a) before and (b) after latex neutralization with ammonia. Films were immersed in water for 1 hour.

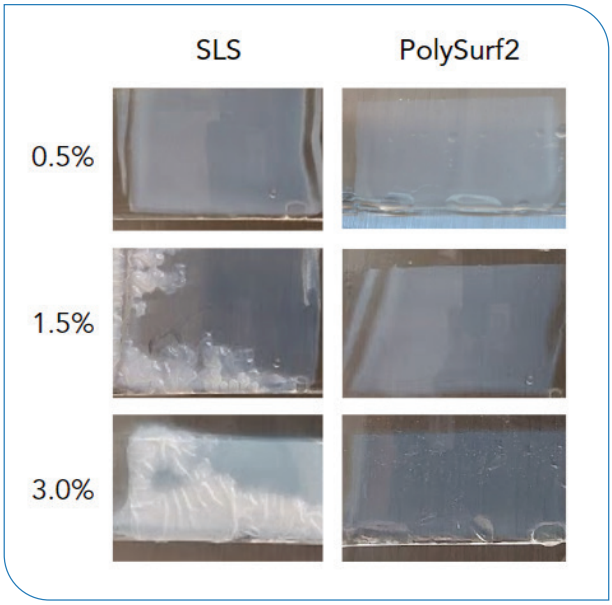


FIGURE 7
24 hours water whitening of SLS and PolySurf2 latex films at different surfactant concentrations. The latexes used have a T_g of -5 °C.

Quantification and Imaging of Unreacted Surfactants in Latexes:

Surface tension measurements were performed on all-acrylic latexes (T_g -5 °C) were synthesized with SLS, Surf1, PolySurf1, and PolySurf2. For each surfactant, two concentrations were studied: 1.5% BOTM and 3% BOTM. **Figure 8** shows the results. The surface tension of the latexes containing 1.5% BOTM of SLS (41.3 mN/m) or 1.5% BOTM or Surf1 (43.5 mN/m) was lower than the surface tension of the latexes made with 1.5% BOTM of PolySurf1 and 1.5% BOTM of PolySurf2 (46.9 and 47.8 mN/m, respectively). As the concentrations of the surfactants used in the latex synthesis is increased to 3%, the surface tension of the latexes made with SLS and Surf1 is significantly decreased to 34.5 mN/m and 39.8 mN/m, whereas the surface tension of the latexes made with PolySurf 1 and PolySurf2 remains unchanged (45.5 and 46.6 mN/m, respectively). The surface tension of latexes at 3% BOTM of SLS or 3% BOTM of Surf1 is then significantly lower than the surface tension of the latex at 3% BOTM PolySurf 1 or PolySurf2. As more non-polymerizable surfactant is added, the particle surface starts to get saturated by the surfactant molecules and the surface tension decreases due to an increased number of free surfactant molecules in the water phase. On the contrary, with a polymerizable surfactant, an unchanged surface

tension value shows that the free surfactant concentration in the water phase remains constant. Knowing that Surf1 is a close chemical match to PolySurf1, the differences in surface tension observed for these two surfactants used at 3% can then be mainly attributed to the fact that PolySurf1 is polymerized onto the particles. Simple correlation of the surface tension measurement with the CMC curves presented in **Figure 1** show that for all surfactants, more than 95% of the surfactant is present on the latex particle surface.

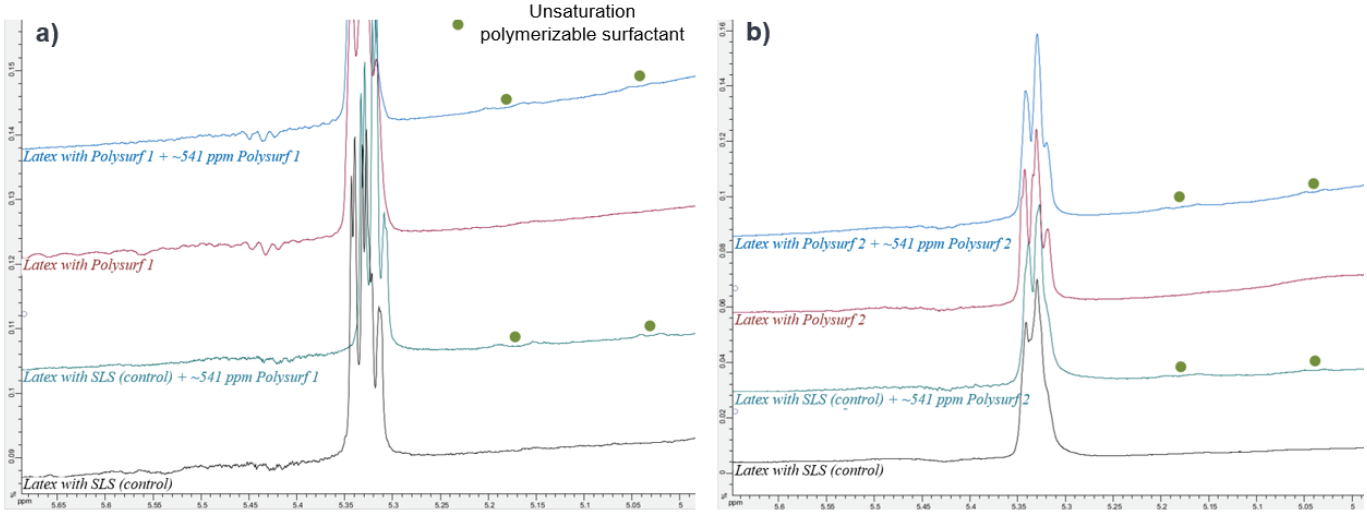
Quantification of residual unpolymerized reactive surfactants PolySurf1 and PolySurf 2 are performed by ^{1}H-NMR for all-acrylic and sty-acrylic latexes (**Figure 9**). The syntheses of the latexes used for this study are slightly different than previously. The 50 wt % all-acrylic latexes at T_g 6 °C (49% BOTM MMA / 49% BOTM BA/ 2% BOTM AA) are made by seeded semi-batch emulsion polymerization using 2.2% BOTM SLS, PolySurf1 or PolySurf2. The 45 wt % styrene acrylic latexes at T_g 16 °C (43% BOTM BA / 20% BOTM Sty / 35% BOTM MMA / 2% BOTM MAA) are made by seeded semi-batch emulsion polymerization using 2.2% BOTM SLS, PolySurf1, or PolySurf2.

First, the limit of detection of PolySurf1 and PolySurf2 is estimated by spiking the 2.2% BOTM SLS controls with known amounts of polymerizable surfactants. To that purpose, quantification of the signals detected at about 5.03 and 5.17ppm, accounting for the unreacted unsaturation protons of the polymerizable surfactants, is investigated. The limit of detection is found to be approximately 550 ppm for both reactive surfactants in all-acrylic and styrene acrylic latexes. Then, the ^{1}H-NMR spectra of latexes made with PolySurf1 and PolySurf2 are obtained and reveal that

FIGURE 8
Quantification of residual unreacted polymerizable surfactant by 1H-NMR in the all-acrylic latex at T_g = 6 °C (49% BOTM MMA / 49% BOTM BA / 2% BOTM AA) made with (a) 2.2% BOTM PolySurf1 and (b) 2.2% BOTM PolySurf2. Latexes were prepared at 50% solids. The green dots correspond to the unreacted unsaturation protons of the polymerizable surfactants. (c) The table shows the % incorporation of the polymerizable surfactants in the latexes.

Surfactant	[Surfactant] (%BOTM)	Dz (nm)	ST (mN/m)
SLS	1.5	102	41.3
	3	109	34.5
Surf1	1.5	126	43.5
	3	114	39.8
PolySurf1	1.5	131	46.9
	3	137	45.5
PolySurf2	1.5	127	47.8
	3	117	46.6

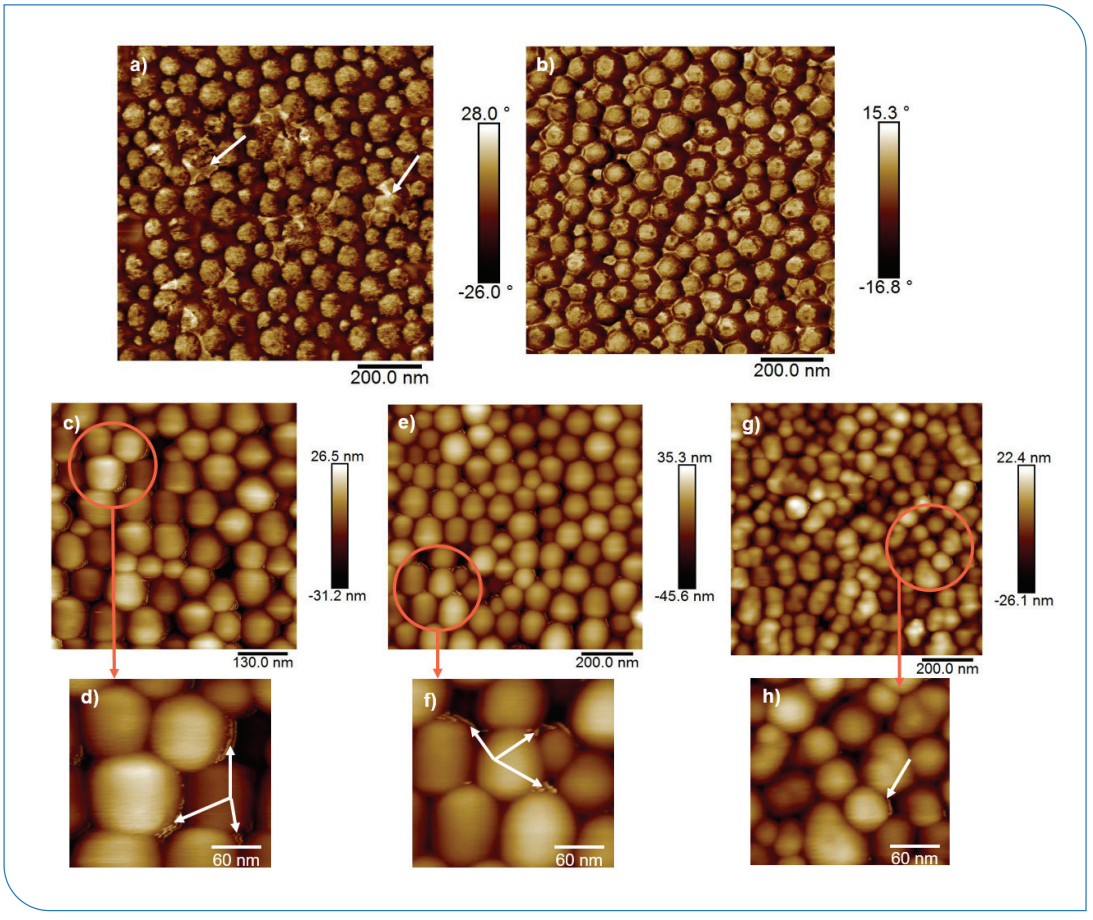
FIGURE 9
Quantification of residual unreacted polymerizable surfactant by 1H-NMR in the all-acrylic latex at T_g = 6 °C (49% BOTM MMA / 49% BOTM BA / 2% BOTM AA) made with (a) 2.2% BOTM PolySurf1 and (b) 2.2% BOTM PolySurf2. Latexes were prepared at 50% solids. The green dots correspond to the unreacted unsaturation protons of the polymerizable surfactants. (c) The table shows the % incorporation of the polymerizable surfactants in the latexes.



c)

Latex	Surfactant (2.2 %BOTM)	Surfactant conversion obtained by ^{1}H-NMR (%)
All acrylic Tg 6°C	PolySurf1	> 95.1
	PolySurf2	> 95.1
Styrene-acrylic Tg 16°C	PolySurf1	> 94.3
	PolySurf2	> 90.0

FIGURE 10
AFM phase images of the air-film surface of latex particles synthesized with 3% BOTM SLS: (a) before and (b) after water rinsing. AFM height images show the distribution of surfactant in between the particles for 1.5% BOTM SLS (c, d); 1.5% BOTM Surf1 (e, f), and 1.5% BOTM PolySurf2 (g, h). Images (d), (f), and (h) are zoomed-in views of (c), (e), and (g), respectively. Imaging was carried out on latex particles with a T_g 25 °C.



the residual amount of both reactive surfactants is below the detection limit for all acrylic and styrene acrylic latexes. **Figures 9a and 9b** show the typical ^{1}H-NMR spectra obtained with all-acrylic latexes made with SLS or polymerizable surfactants before and after spiking. Similar spectra—not disclosed here—are obtained for the styrene acrylic latexes. A rough estimation of the polymerizable surfactant conversion during latex synthesis could then be achieved and shows that more than 90% of PolySurf1 and PolySurf2 are incorporated in the latex particles during emulsion polymerization for both all acrylic and styrene acrylic recipes at T_g 6 °C and 16 °C, respectively (**Figure 9 c**). The experiment was not carried at other T_gs but an impact of the T_g on the conversion of the reactive surfactant is not expected.

AFM height and phase images of latex particles synthesized with regular and polymerizable surfactants are presented in **Figure 10**. Latex particles were prepared at T_g 25 °C to minimize the interaction of the AFM tip with the latex particle surface. First, AFM phase images of the air-film surface of 3% BOTM SLS latex particles were performed before (**Figure 10a**) and after rinsing (**Figure 10b**) the dry film with water. One can see that water-soluble species—indicated by the white arrows—found on the surface of the film are removed by water rinsing. These water-soluble domains are most likely composed of surfactant molecules migrating towards the top surface of latex film during drying.[6-7] Precision imaging of the interstitial spaces of 1.5% BOTM SLS latex particles also reveal species which can be washed away upon water rinsing (**Figure 10c**). These water-soluble species are present in almost each gap in between the particles. White arrows indicate their localization in the zoomed image **Figure 10d**. The same observations can be made for latex particles made with the non-reactive surfactant Surf1 (**Figure 10e**). The white arrows on image of **Figure 10f** indicate the water-soluble species. Images of **Figures 10g and 10h** display latex particles made with PolySurf2. Very little water-soluble species can be observed in the interparticle spaces. Because the polymerizations were run in the same experimental conditions (low pH and same monomers), the amount of water-soluble oligomers (if any) present in latexes made with regular surfactants should be similar to the one contained in latex prepared with polymerizable surfactant. Therefore, the observed water-soluble species most likely correspond to the free-unpolymerized surfactant molecules. This confirms the surface tension and ^{1}H-NMR measurements carried out previously. Most of the polymerizable surfactant molecules are incorporated in the latex particles during synthesis which leads to a latex dispersion with a higher surface tension and to a low amount of free surfactant in between the latex particles.

Conclusions

Water whitening and water intake of latex films are studied at different T_gs for four different surfactants. Overall, at a low T_g (-20°C), both water resistance tests show that the use of polymerizable surfactants is not enough to compensate for the loss of resistance to deformation of the softer polymer matrix. At a T_g between -5 °C and 10 °C for both the acrylic and styrene acrylic latexes, both the water intake and the water whitening results are improved using polymerizable surfactants. Overall, using PolySurf2 results in slightly better water resistance than PolySurf1. The water whitening phenomena is not only affected by the T_g of the latex films but also by the surfactant chemistry and the surfactant concentration. Indeed, for conventional surfactants, a sufficient amount of the surfactant is needed to enable particle stabilization during drying, but not too much to prevent hydrophilic pathways in the film and limit the water whitening. On the contrary, increasing the amount of polymerizable surfactant improves the water whitening resistance because the polymerizable surfactants cannot migrate within the film during drying. Moreover, it was demonstrated that the pH of the latex has a strong impact on the water whitening resistance of the resulting films. The best performance is obtained when the latex is neutralized to a pH approximately 8–9 because it provides a better electrostatic stabilization to the particles during drying, leading to a more homogeneous film structure. Finally, ^{1}H-NMR combined with AFM imaging showed that PolySurf 1 and 2 have a high incorporation in the latex particles leading to a higher surface tension of the latex dispersion. The amount of unpolymerized double bonds is below the detection limit of the ^{1}H-NMR and very little unreacted polymerizable surfactant is observed in between the latex particles by AFM. The high conversion of the reactive surfactants justifies the improved water resistance of polymer films made from latex prepared with PolySurf1 and PolySurf2.

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