

Synthesis and Characterization of Colloidally Stable Self-crosslinking Water-based Anticorrosive Polymer at Room Temperature

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ABSTRACT

The emulsion polymerization of butyl acrylate (BuA), styrene (St), and 3-isopropenyl- α,α -dimethylbenzyl isocyanate (IPMBI) is presented in this work. Obtain colloidally stable latexes for the poly (BuA/St/IPMBI) system during polymerization and storage for use in a water-based coating formulation. A series of semicontinuous polymerizations were also performed to investigate the effect of comonomer composition (w/w) in the feed (BuA/St) on conversion. The particle diameter (Dp), particle number (Np), hydrolysis of the IPMBI's isocyanate groups, stability and storage properties. Films were created in which the effect of comonomer composition was also investigated, the glass transition temperature (Tg) was determined, the gel content was selected, and the mechanical properties and capacity as a barrier to water vapour and oxygen were assessed. Another series of reactions, on the other hand, was carried out in which the effect of the IPMBI content (1.5, 3.5, and 5.5%) was studied using a constant composition BuA/St=60/40. The studies conducted are the same as those mentioned for the effect of comonomer composition in feed. With increasing IPMBI percentage, slight differences in conversion, Dp, and Np were observed; the latexes undergo hydrolysis during polymerization and storage. Colloidal stability, on the other hand, was preserved. The mechanical properties of the films improved as the percentage of IPMBI increased, while the boundary characteristics to moisture and oxygen improved when compared to the white film (0% of IPMBI). Finally, the formulation of a self-crosslinking water-based coating at room temperature using the previously obtained latex as a binder is reported; the coating demonstrated excellent adhesion, scratch hardness, and gloss regardless of the type of latex used.

Keywords: Anticorrosive polymer, Self-crosslinking polymer, Synthesis, Characterization, Application.

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INTRODUCTION

Water-based corrosion control coatings have gained popularity due to strict environmental regulations on volatile organic compound emissions from solvent-based coatings.¹ Binders (polymeric resin), pigments, fillers, additives, and solvents make up a water-based coating (usually just water). The resin is so vital that it is named after it. Emulsion polymerization is used to create resin or latex, a polymer-water mixture. Emulsion polymerization is a heterogeneous process that involves free radicals polymerizing monomers in a colloidal dispersion. Choosing a monomer combination based on the application's glass transition temperature (Tg) is critical. Due to the Tg that the respective homopolymers present, the BuA/St copolymers can be obtained in a wide range of Tg. If the latex is used in the coating formulation, it must have a Tg below.² IPMBI is a bifunctional monomer that contains both a >C=C double bond and an aliphatic isocyanate group, allowing them to react independently. Because the resulting

polymers can crosslink at room temperature, they improve the film formed when latex is applied to a substrate, enhancing mechanical, chemical and oxygen permeability properties. These results show that anionic sulfosuccinate surfactants can semi-continuously polymerize the BuA/St/IPMBI system. The effects of monomer addition were studied twice. The effect of the feed monomer composition (BuA/St) was then investigated, while the IPMBI content was kept constant. For the last two effects, various latexes and films were investigated. Finally, a coating was made using the previously obtained latex as the main component. According to the literature,^{3,4} the following issues persist when trying to obtain IPMBI functionalized binder resins for use in water-based coatings for metal protection. This research aims to create latexes that crosslink at room temperature and stay stable during polymerization and storage. Obtaining latex with a solids content close to 50% is difficult because the intended applications of latexes require a high solids content (>40%), unlike most previous reports

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(20%). These surfactants have been used in polymerizations with IPMBI as a monomer but not with aerosol polysorbate-80, SDS, or SDBS. Mono ester sulfosuccinate is an anionic sulfosuccinate surfactant. Botelho and Bittencourt⁴¹ used this surfactant instead of ethoxylated alkylphenol surfactants to make paintable latex. This study's primary goal is to create colloidally stable poly(BuA/St/IPMBI) latexes for use in water-based coating formulations during polymerization and storage.

MATERIAL AND METHODS

Reagents and Materials

The origin, purity and type of purification (when applicable) of the compounds used are The butyl acrylate (Aldrich 99%) and styrene (Aldrich 99%) monomers were washed with a 5% by weight solution of sodium hydroxide (NaOH) in order to remove the inhibitor, dried with calcium chloride and subsequently distilled vacuum and stored at 7°C before use other reagents, chemicals and solutions purchased from sigma Aldrich with 98–99% purity, solutions prepared with double distilled water (pH 7.02).

Polymerizations and Characterizing of Latexes

The polymerizations took place in a 0.5 L transparent Jacketed glass reactor with five ports, including a central port for mechanical agitation via an arrow and three stainless steel propellers, a port for injecting initiators, and a port for nitrogen flow. Another for the monomers, a third for a condenser and cooling system, and a fourth for sampling. A poly science recirculating bath connected to the reactor jacket maintained a temperature of 40°C for the reaction. As initiators, potassium persulfate (oxidant) and potassium metabisulfite (reductant) were used (reducer). As a surfactant, Aerosol EF-800 or Aerosol Polysorbate- 80 was used. All experiments used distilled water. The polymerizations were carried out with 99% purity under nitrogen flow. The micellar solution was formed by adding the surfactant to the reactor with most of the water and stirring the mixture at 300 rpm. The remaining water went into making the initiator solutions. The micellar solution was bubbled with nitrogen for 30 minutes while the reactor was heated by circulating water at 40°C through the reactor jacket. After this time, 5% of the total monomer mixture was added, followed by 33% of the initiators, and the reaction was allowed to proceed in a batch process for 30 minutes. After that, the semicontinuous addition of the remaining monomer mixture and initiators began, which was done with KD Scientific infusion pumps. A double infusion pump and two 25 mL plastic syringes were used to add the initiators; a simple pump and 60 mL syringes were used to add the monomers, which were exchanged when the content of each one was finished until the total addition of monomers was completed. The monomer was added in t hours and the initiator in h hours to achieve the highest possible conversion.

Determination of Conversion by Gravimetry

During the reaction,⁵ samples were taken before, during, and after each syringe of monomer and initiator addition. In 2 mL

samples were taken with a 5 mL plastic syringe. The samples were placed in vials with 0.5 g of a 3.5 % hydroquinone solution and covered with wool to stop polymerization. The samples were then lyophilized at 387×10^{-3} millibars vacuum for 15 hours to remove water and residual monomer. Gravimetry was used to obtain the conversion percentage.

Determination of Particle Size

To determine the evolution of particle size during polymerization, 1-mL of the sample was separated into another vial containing 3 mL of deionized water/filtered. Then, a drop of the sample from the vial was placed in a disposable cell, diluted with 2 mL of deionized/filtered water. QLS measurements (3p/sample) were made at 25°C using a Zetasizer Nano S-90 light scatterer with an argon laser. D_z is the average intensity diameter.

Determination of the Number of Particles

The number of particles was determined from the following equation: 42

$$N_p = \left(\frac{6M_o x}{\pi \rho_p D_v^3} \right) (Eq \dots 2.1)$$

Where: M_o = monomer concentration, x = conversion, ρ_p = polymer density and D_v = volume average diameter.

The density of the terpolymer (BuA/St/IPMBI) is obtained by averaging the homopolymers' densities related to each polymer's weight fraction. The density values for this system were PBuA43= 1.08 g/cm³ and PSt2=1.05 g/cm³, while the contribution of IPMBI is neglected due to its low percentage about the other two monomers.

Determination of IPMBI Content, Viscosity, Adhesion and Molecular Weight in Latexes

The latexes' IPMBI content was determined by flowing the ASTM D2572-87 according to Xu *et al.*⁶ latex viscosity determined by Brookfield model DV-11 viscometer and the molecular weight by the soluble polymer fraction's molecular weights (M_n and M_w) and GPC determined molecular weight distribution. The equipment used was a Waters IR detector with a polystyrene calibration curve and adhesion tests used steel specimens 5 cm long and 5 cm wide using the method developed.⁷

Film Formation from Poly(BuA/St/IPMBI) Latex

The films were made the next day. The latex is poured onto a wooden plate covered with Teflon film and separated by 1-mm thick glass slides (22 x 32 cm). The latex is spread evenly across the plate using a glass rod. The films were dried for 3 days at room temperature in an unvented vacuum oven. After this, the films were removed from the plate and dried for a minimum of 7 days at 23°C and 50% humidity before evaluation.

Film Thickness

The film thickness was measured with a Mitutoyo DI-C1121BT digital micrometer. Measurements were taken at various points to get an average.

Gel Content and Swelling Index

To determine the gel content and swelling index, a 1 x 2 cm piece of film was cut, its weight (P1) was recorded, and placed in a 20 mL vial. In 10 mL acetone, the vial was sealed for 24 hours. The acetone was removed, the vial with the swollen film sample (P2) was weighed, and acetone was immediately added to completely remove the soluble polymer. In the end, the vial was baked at 40°C for an hour to dry out the insoluble polymer (P3). Each sample's gel content and swelling index were measured in triplicate and averaged.

Mechanical Tests

The tensile properties of the latex films were determined using ASTM D882-12. Straight specimens of each film were obtained using a metal die and a die press. The evaluation machine used a 24 pound load cell, a 50 mm pneumatic jaw separation, an extensometer to track the specimen's deformation, and a 500 mm/min speed. The modulus and maximum stress were determined. Each study required a minimum of 5 specimens to determine an average.

Permeability to Water Vapor

The ASTM E96-00 standard was used for the water vapor permeability tests.

Oxygen Permeability

The oxygen permeability of the films was determined using the ASTM D3985-02 method in a MOCON OX-TRAN model 2/21 module. The sample size was 100 cm². Work was done at 23°C, 640 mm Hg barometric pressure, and 0% relative humidity. Each film was tested twice, with an average obtained.

Formulation of Coatings

Materials

To formulate the water-based coatings, previously synthesized poly (BuA/St/IPMBI) latexes were used, which function as a binder (resin). Since the correct selection of all the formula ingredients is required, a selection of the possible materials to be used was made, shown in Tables 1 and 2.

Characterization of Coatings

Determination of viscosity

A Brookfield model DV-11 viscometer was used to measure the viscosity of the coatings. Spindle number 2 was used at a speed of 30 rpm. Before carrying out the measurements, the samples were conditioned at 25°C for 1-hour.

Table 1: Possible components used for the formulation of the coating

Component	Chemical name
binder (resin)	Poly(BuA/St/IPMBI) latex
defoamer	silicone oil
Burden	Calcium carbonate
Burden	Rutile type titanium dioxide
Surfactant	Variable*
Pigment	Organic Blue

*See Table 2.

Adhesion tests

Steel specimens were used to carry out the adhesion tests. Said specimens were cleaned with acetone and toluene to eliminate dust residue and impurities. Once the specimens were clean, the coating was applied using a fine bristle brush. Qualitative adhesion tests were made after 24 hours of drying. The measurements were made based on the WHO standard, which is applied to evaluate coatings, paints, varnishes and related products. Two repetitions of each measurement were made and an average was obtained.

Gloss analysis

The gloss of the coating applied to the steel specimens was measured with the help of a 60° micro-gloss gloss meter. Measurements were made after 24 hours of drying, 5 measurements were made and an average was obtained.

Hardness tests

To determine the resistance of the coating to the effects of scratching on the surface, a scratch hardness test was carried out. For this, the method based on the ASTM D3363-92 standard was used, allowing the use of known hardness pencils that are moved over the coating at an angle and fixed pressure to perform the test. A range of pencils are used, each being harder than the last. The result is given by the hardness of the last pencil that does not scratch the surface of the coating.

RESULTS AND DISCUSSION

Effect of the Type and Concentration of Surfactant and Time of Addition of the Monomer

The polymerizations were carried out to study these effects using 2 anionic surfactants of the sodium sulfosuccinate type and Polysorbate- 80 with a value of CMC= 0.03% by weight. Two semicontinuous monomer addition times were handled 6 hand. Table 3 shows the reaction variables. A series of experiments were carried out where a total of 8 reactions were carried out. In this study, the weight ratio of the 49/49/1.5 monomers (BuA/St/IPMBI) was kept fixed and the effect of the type and concentration of surfactant used on the conversion (X), particle size (Dp) and several particles (Np).

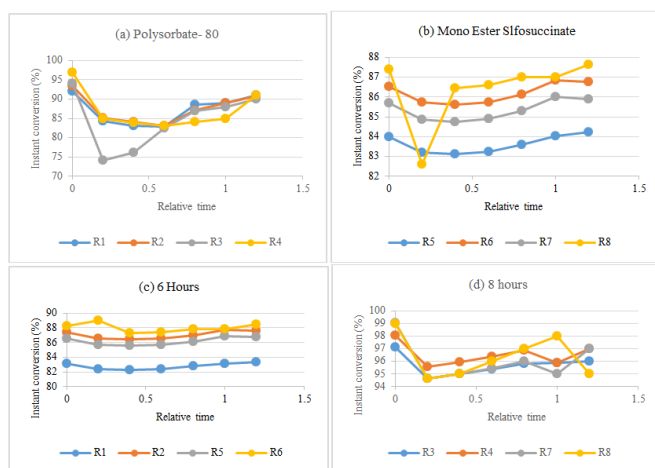
Figure 1 shows the instantaneous conversion vs relative time curves for each emulsion polymerization for the BuA/St/IPMBI (49/49/1.5) system. Relative time is defined as the ratio of sampling time to total monomer addition time. Instantaneous

Table 2: Possible surfactants that can be used in the formulation of the coating

HLB (Hydrophile Lipophile Balance)	Surfactant Chemical name
15	Sorbitan monooleate POE (20)
8.9	Nonyl Phenol POE (4)
12.8	Lauric Alcohol POE (9)
7.3	Lauric Alcohol POE (3)
4.3	polysorbates-80 (MA-80) (polyoxyethylene (20) sorbitan monooleate)
14.1	Hydrogenated Castor Oil POE(40)

Table 3: Variables were studied in the different reactions

	Surfactant	Surfactant (% weight)	Monomer feed time (h)	Monomer addition rate		
				(g/min)	X (%)	Dp _{final} (nm)
R1	Polysorbate 80	1.5	5.5	0.6597	95.4	96.4
R2	Polysorbate 80	2.5	5.5		93.9	80.5
R3	Polysorbate 80	1.5	7.5		91.9	94.4
R4	Polysorbate 80	2.5	7.5		92.9	74.3
R5	Mono ester sulfosuccinate	1.5	5.5	0.4947	85.7	117
R6	Mono ester sulfosuccinate	2.5	5.5		88.1	106.1
R7	Mono ester sulfosuccinate	1.5	7.5		91.1	120.6
R8	Mono ester sulfosuccinate	2.5	7.5		93.4	91.9


Figure 1: Evolution of the instantaneous conversion with relative time for semicontinuous polymerization of BuA/St/IPMBI, varying the type and concentration of surfactant, and the time of addition of monomers

conversion at a given time is defined as the fraction of monomer converted to polymer relative to monomer added to the system up to that given time.

As shown in Figure 1a, increasing the surfactant concentration has little effect on the instantaneous conversion, as the difference between the maximum and minimum response values at 0.5 is less than 5.5%. In this case, using concentrations of Polysorbate-80 surfactant higher than the critical micellar concentration (1.5 and 3%) and adding at the rates used, no significant differences were observed in the BuA/St/IPMBI instantaneous conversion. Increasing the concentration of the mono ester Sulfosuccinate (Aerosol EF-800) surfactant (R5 vs R6 and R7 vs R8 in Figure 1b) increased the instantaneous conversion (Figure 1b). A similar effect⁸ occurs when Polysorbate-80 is used and is better appreciated in a monomer addition time of 6h (Figure 1c) than in 8h (Figure 1d). Figure 1b shows that the instantaneous conversion increases as the addition rate decreases (R5 vs R7 and R6 vs R8). The rate of monomer addition has been shown to directly affect conversion,⁹ with lower rates of addition increasing conversion.

The evolution of particle size (Dp) between 74 and 120 nm at the end of polymerization. The type of surfactant and concentration are used to determine particle size. Using the same surfactant concentrations (2 and 3%), the differences in

Dp between surfactants may be related to their different values of critical micellar concentration (CMCMA-80=1.5.5% weight and CMCEF-800=0.03% weight). Limited coagulation refers to the growth of particles from unstable primary particles until the particles are stable and their growth is mainly propagative. The decrease in monomer addition rate has been linked to a reduction in particle size due to a decrease in monomer concentration in the particles or a preference for nucleation overgrowth semicontinuous emulsion polymerization with monomer avidity. Using equation 2.1, the particle number was calculated as¹⁰ found that inverse behavior to Dp.

In some cases, after polymerization, Np decreased, indicating a coalescence process due to limited coagulation of particles that lack sufficient surfactant to stabilize, resulting in fewer particles with larger diameters. Increasing the surfactant concentration causes a more significant number of particles, which occurs at both times of monomer addition. A lack of batch process control can be attributed to the behavior observed when comparing R6 and R8.

Latices must be colloidal stable during polymerization and storage for various applications. Dp was monitored for 5 and 6 months for both surfactants, but those formulated with Mono ester sulfosuccinate for up to 9 months. Those latexes formulated with Polysorbate-80 surfactant show problems with colloidal stability over time; Dp values increase gradually, reaching up to six times their original value. On the other hand, the mono ester sulfosuccinate surfactant produces colloidal stable latexes with minimal particle size variation over time (9 months). Different factors may cause differences in colloidal stability.

Effect of Monomer Composition in Feed

If you want to use BuA/St/IPMBI terpolymers in a water-based coating, you must select the monomers based on their glass transition temperature. While allowing particle coalescence during film formation, Tg must be high enough to ensure hardness. To obtain polymers with Tg values between 5 and 20°C, the BuA/St ratio was adjusted to obtain polymers with Tg values between 5 and 20°C. Table 4 shows three different BuA/St monomer compositions (45/50, 50/50, and 60/40). The monoester sulfosuccinate surfactant was used at a concentration of 1.5%, chosen for the largest particle size

Table 4: Formulations used in the polymerizations with different BuA/St compositions, keeping the IPMBI content constant (1.5%)

Component	40/60	50/50	60/40
	Quantity (g)	Quantity (g)	Quantity (g)
butyl acrylate	110.25	122.5	134.75
styrene	134.75	122.5	110.25
IPMBI	5	5	5
Mono ester sulfosuccinate Spray*	5	5	5
K ₂ S ₂ O ₈	1.50	1.50	1.50
K ₂ S ₂ O ₅	1.50	1.50	1.50
H ₂ O	250	250	250

*Surfactant, solid content 50%

obtained; a monomer addition time of 8 hours and an initiator addition time of 9 hours. To increase final conversion and thus decrease residual monomer in the latexes, the polymerizations were allowed to react for one hour after addition and then stopped after ten hours.

Conversion

The conversion behaviour of BuA/St/IPMBI polymerization reactions using semicontinuous polymerization. Similar behaviour was observed for the three comonomer ratios, achieving final conversions of around 94%. The polymerization rate increases with BuA concentration and decreases with St Concentration in BuA/St copolymerization, but not in intermediate concentration ratios (40:60 and 60:40). The study's findings (40/60, 50/50, and 60/40 compositions) did not. It should affect conversion because in this concentration range, with similar polymerization, surfactant, and monomer addition rates, the reactivity should be unaffected by the feed monomer ratio.

Diameters and particle number at the end of the polymerization

Given that the particle size decreases and the number of particles increases with increasing butyl acrylate content in the feed composition, the particle size and number are related to the hydrophobicity of the monomers (1.5%). This behavior can be seen in the evolution of particle diameter during polymerizations with varying BuA/St ratios. The final particle diameters for the 40/60, 50/50, and 60/40 polymerization ratios were 103.6, 90.3, and 86.8 nm. The more hydrophobic the monomers are, the more particle nucleation is favored. Many smaller particles were expected because styrene is less soluble than butyl acrylate (0.2 g BuA/100g H₂O)². However,

as St (composition 40/60) increased, the number of particles decreased. The three BuA/St compositions used here are not sufficient to explain this behavior because their differences are 5 and 10%.

Colloidal storage stability

Latexes formulated with monoester sulfosuccinate surfactant exhibited significant stability. A change in the comonomer composition did not affect the particle diameter of latexes stored at room temperature. For 40 days, the D_p/D_{p0} ratio did not change significantly, indicating that the latexes obtained are stable.

Hydrolysis of IPMBI during polymerization and storage of latexes.

Intraparticle crosslinking occurs when NCO groups are hydrolyzed during polymerization or storage, reducing film strength.³⁷ Despite its stability, IPMBI's isocyanate group, can be hydrolyzed. The isocyanate group content varies throughout the polymerization. Titration (ASTM D2572-87) was used to calculate IPMBI. Table 5 shows the results. With BuA/St ratios of 40/60, 50/50, and 60/40, the remaining IPMBI after polymerization is lost by 10.55, 19.15, and 16.63%, respectively. That is, hydrolysis ate the NCO groups. Throughout the polymerization process, styrene-rich latexes (BuA/St ratio = 40/60) were more resistant to hydrolysis than butyl acrylate-rich latexes (BuA/St ratio = 40/60). Increased hydrolysis may be due to smaller lattice particle sizes.

According to He *et al.*,¹⁹ semicontinuous emulsion polymerization consumes 10 to 20% of isocyanate groups. Due to the uniform distribution of IPMBI units in latex particles, semicontinuous work exposes more groups at the particle/water interface. A long-term study was carried out to assess NCO group stability. IPMBI content varies during room temperature storage (Figure 2). After 30 days, IPMBI loss ranged from 16 to 19% (relative to the polymerization content), with similar behaviour in all three monomer ratios. Ramirez *et al.*,²⁰ found that after 30 days of storage, IPMBI content decreased from 85 to 50%. Batch polymerization at 40°C yields (1.5%) IPMBI. Acetate groups in polymer chains hydrolyze to form CH₃COOH.

Effect of Feed Monomer Composition on Film Properties

The latexes with the three BuA/St compositions studied (40/60, 50/50, and 60/40) produced films with a constant IPMBI content of 1.5%. The films formed from the 40/60 latexes were brittle at 23°C, so tensile tests and oxygen and water vapor permeability tests could not be performed. They were 50/50 and 60/40. The

Table 5: Determination of the % of IPMBI present in the latexes

Sample	% IPMBI in monomers	% IPMBI in monomers	% IPMBI in the polymer *	% IPMBI at the end of polymerization**
40/60	2	0.5252	1.79	89.45
50/50	2	0.5052	1.62	80.85
60/40	2	0.5696	1.67	83.37

*% IPMBI in the polymer = ((B-V)N0.2013)/(g polymer)100, where B is the volume (mL) of HCl consumed by the blank; V is the volume of HCl consumed by the sample; N is normal HCl (Eq/L); 0.2013 are the milliequivalents in weight of the IPMBI; g polymer is the weight of the polymer sample used in the titration. ** (% IPMBI in polymer/% IPMBI in monomers)100

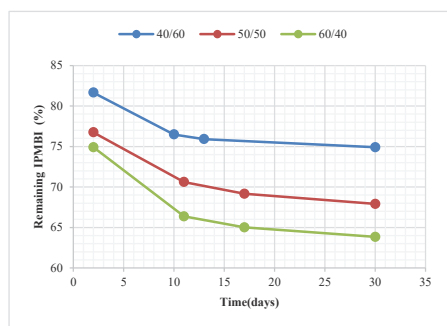


Figure 2: IPMBI (%) remaining latex content stored at room temperature, in which the BuA/St composition was varied and the IPMBI content (1.5%) was kept constant.

three films' gel content and glass transition temperature were also determined.

The experimental values are higher than expected (Figure 3). These discrepancies can be attributed to the absence of the IPMBI in the theoretical calculations, partial conversion of monomers to polymers, and/or crosslinking generated by the hydrolysis of NCO groups. Similarly, Bakhshi *et al.*²¹ observed differences between theoretical and experimental Tg in their BuA/MMA/GMA emulsion polymerization study. Thus, partially crosslinked latices during film formation reduce free volume, limiting chain mobility and increasing Tg. The gel contains crosslinked polymers. As shown in Figure 3, latex films with higher styrene content (40/60) dissolved in the solvent (acetone) required centrifugation to separate the non-soluble fraction. Butyl acrylate increases in monomer composition for two reasons. This reduces particle deformation resistance during film formation and promotes interdiffusion of polymer chains and thus, crosslinking.

Mechanical tests

The formed films were mechanically tested. Straight specimens were cut to ASTM D882-12 and the universal machine was set up to this standard. Figure 3 shows the stress-strain curves for the 50/50 and 60/40 ratios (b). The stiffest phase causes an elastic deformation until yielding. The 50/50 film has a greater (Figure 4) Young's modulus (E) and yield stress, while the 60/40 film has a greater elongation at break. The film becomes more elastomeric with more butyl acrylate, reaching nearly 900% elongation before rupture. These findings align with Tg, which decreases as BuA content increases.

Permeability to water vapor and oxygen

The latex film formed by an anticorrosive coating must have low water vapor and oxygen permeability. This can affect its function as a protector against corrosion of metallic parts, resulting in film degradation or direct substrate damage. Permeability is the water vapor transmission rate through a material of a certain thickness when two surfaces are at different temperatures and humidity. Films with BuA/St ratio of 50/50 and 60/40 showed 0.0348 cm²/day mm Hg water vapour permeability, which had a barrier property similar to Devona and Essigmann¹¹ films. The results here match those of Kim *et al.*,¹² A higher butyl acrylate content promotes water

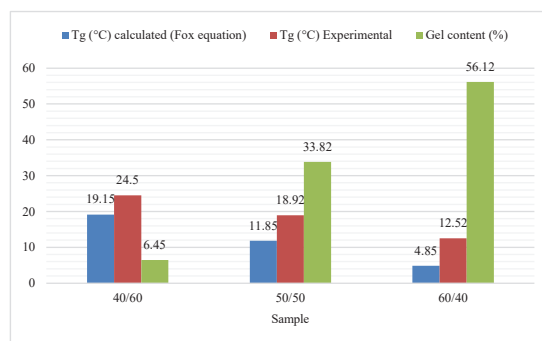


Figure 3: Tg values in latex and Gel content of films (evaluated over 20 days) with different BuA/St ratios and with a constant content of 1.5% IPMBI

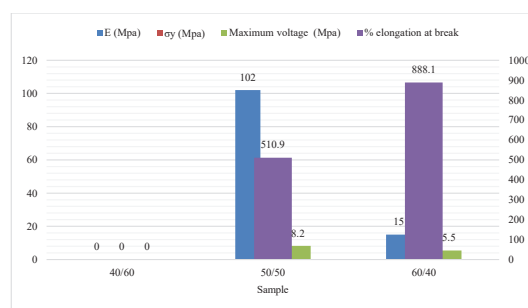


Figure 4: Mechanical properties of films prepared from poly(BuA/St/IPMBI) latex, varying the BuA/St composition and constant IPMBI content

vapour permeability in the film, while hydrophobic polymers are less porous.¹³ The average oxygen transmission rate of the 50/50 film was 347.59 cm³/m²/day, while the 60/40 film was 327.61 cm³/m²/day. Mirzataheri¹⁴ reported similar values. Pa (BuA/St ratio=50/50) and 2.39x10⁻¹³ cm³/cm² s Pa (BuA/St ratio=60/4) agree with the literature.¹⁵

Effect of IPMBI Content

To assess the impact of IPMBI content on latex and film properties, a constant BuA/St composition and three IPMBI concentrations were used (Table 6). According to the literature, low concentrations of IPMBI produce similar properties to higher concentrations (10 and 20%), so it was worked at 1.5, 3.5, and 5.5 % IPMBI content. adjusting the amounts of both monomers

Conversion

A decrease in the conversion is expected if the concentration of IPMBI is increased. The experiment with a higher concentration of IPMBI (5.5%) shows lower conversions, possibly due to a lower polymerization rate, which is consistent with the literature.⁹ This behaviour has been linked to IPMBI's structure, which is similar to -methyl styrene.

Particle diameter (Dp) and the number of particles (Np)

However, the differences in particle size 3.5 and 5.5% are small. A similar number of particles increases until 20% conversion, then stays constant. Np and Dp were expected to behave similarly under the same reaction conditions (same monomer addition time, initiator and surfactant concentration).

Table 6: Formulations used in the polymerizations keeping the BuA/St= 60/40 ratio constant and varying the IPMBI content

Component	0%	1.5%	3.5%	5.5%
	Quantity (g)	Quantity (g)	Quantity (g)	Quantity (g)
butyl acrylate	137.5	134.75	132	129.25
styrene	112.5	110.25	108	105.75
IPMBI	0	5	10	15
Mono Ester Sifosuccinate* surfactant	5	5	5	5
K ₂ S ₂ O ₈	1.5	1.5	1.5	1.5
K ₂ S ₂ O ₅	1.5	1.5	1.5	1.5
H ₂ O	250	250	250	250

*Surfactant at 50% by weight in water

Colloidal storage stability

As stated previously, the colloidal stability of latex is critical for its applications. Because latexes are used in the coating formulation, the particle diameter was monitored during storage at room temperature. The latexes were stable for 60 days regardless of IPMBI content.

Hydrolysis of IPMBI during polymerization and storage of latexes

The degree of isocyanate hydrolysis was studied at the end of polymerization and during storage at room temperature for three concentrations IPMBI 1.5, 3.5, and 5.5%. Table 7 shows the IPMBI percentage after polymerization. The IPMBI hydrolysis was similar for all three latexes, regardless of IPMBI concentration. Lovell and Yoon²⁰ found that the rate of isocyanate group loss is unaffected by the IPMBI concentration (2 and 5%) used in a batch process.

Molecular weights and molecular weight distribution

(Mn) and (Mw) of latexes with varying IPMBI contents are shown in Figure 5. After dialysis and lyophilization, the IPMBI NCO groups crosslinked the latexes. Thus, the values shown here are for the soluble fraction. As the percentage of IPMBI increases, the molecular weight decreases, possibly due to increased crosslinking in the polymer (0% IPMBI).

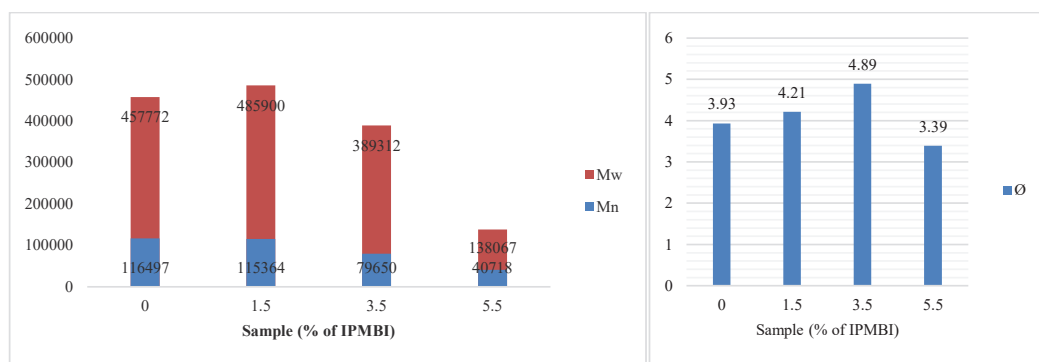

Figure 5: Values of Mn, Mw and dispersity (\emptyset) of the soluble fraction of polymers with constant composition BuA/St= 60/40 and variation of the IPMBI content

Table 7: Determination of the percentage of IPMBI presents in the latexes at the end of the polymerization, varying the content of IPMBI and keeping the BuA/St=60/40 composition constant.

% IPMBI in monomers	g of polymer in titration	% IPMBI in the polymer	% IPMBI at the end of the polymerization
1.5	0.5696	1.67	83.37
3.5	0.5323	3.44	85.98
5.5	0.5353	4.97	82.85

Adhesion tests

A latex system (BuA/St/IPMBI) with varying IPMBI content and a constant composition BuA/St=60/40 was tested for adhesion. The measurements were made on steel specimens according to WHO standards; the results are shown in Figure 6. The ordinate axis shows each latex's adhesion level at various drying times. 0 means the film was completely removed, while 5 means it fully adhered.

The IPMBI stiffens the polymer, preventing adhesion to the specimen. However, even with IPMBI, adhesion was good, and it appears that adhesion improves with IPMBI content. These results indicate latex adhesion capacity. Using these latexes in a water-based coating formulation is feasible.

Mechanical tests

Crosslinking increases the stiffness and tensile strength of films with higher IPMBI content. Crosslinking makes the polymer more rigid (higher Young's modulus), making the film less flexible. According to Mohamed *et al.*¹⁶ the amount of IPMBI used is not harmful. Stress vs strain results show that films with higher IPMBI content have better mechanical properties. The maximum stress increases, but the break elongation decreases. This is consistent with the literature. Figure 7 shows Young's modulus, maximum stress, yield stress, and elongation percentage (%).

Permeability to Water Vapor and Oxygen

The water vapour permeability (WVP) was higher in the film made from latex without IPMBI and decreased with IPMBI concentration from 1.5 to 3.5%, but not with 3.5 to 5.5%. This is because the polymer has reached a similar crosslinking and thus a similar barrier capacity at the last two concentrations.

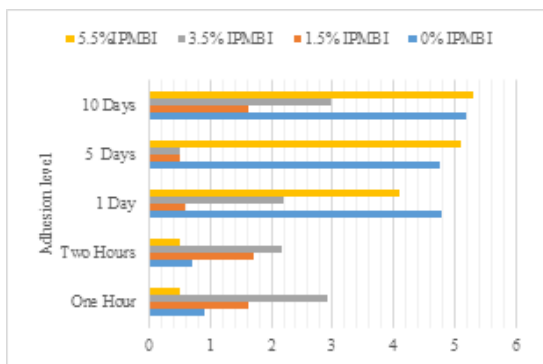


Figure 6: The effect of IPMBI content on latex adhesion to steel specimens keeps the BuA/St= 60/40 composition constant

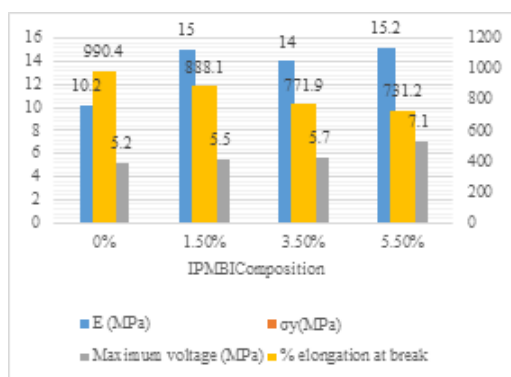


Figure 7: Mechanical properties of films prepared from latex with different IPMBI content and a constant composition BuA/St=60/40

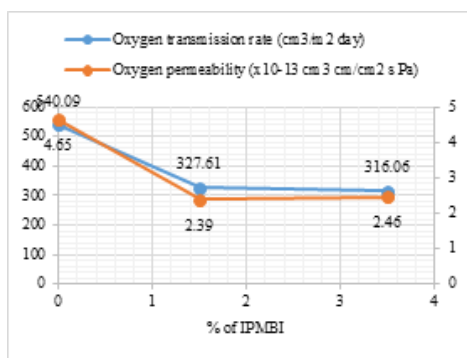


Figure 8: Oxygen transmission rate (OTR) and oxygen permeability in films obtained from poly(BuA/St/IPMBI) latex varying the IPMBI content, with a constant composition of BuA/St=60/40

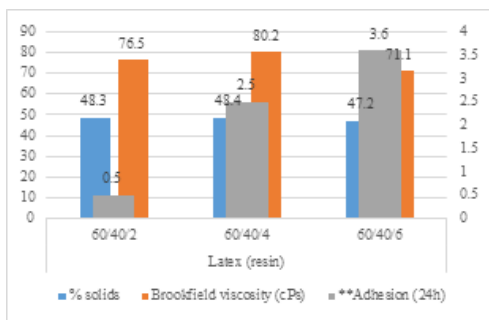


Figure 9: Properties of polymeric resins ** 0 = poor adhesion, 5 = excellent adhesion

Table 8: Compatibility of commercial surfactants with polymeric resins, fillers and pigment

#	Surfactant	Resin			Carga		Pigmento
		1.5%	3.5%	5.5%	TiO ₂	CaCO ₃	
1	Canarcel TW-80	+	+	+	+	+/-	+
2	Canasol NF-400	-	-	-	-	-	-
3	Canasol BJ 309	+	+	+	+/-	+/-	+/-
4	Canasol BJ 303	+/-	+/-	+/-	+/-	-	-
5	Canarcel 80	+/-	+/-	+/-	+/-	-	-
6	Canasol R400H	+	+	+	+	+/-	+

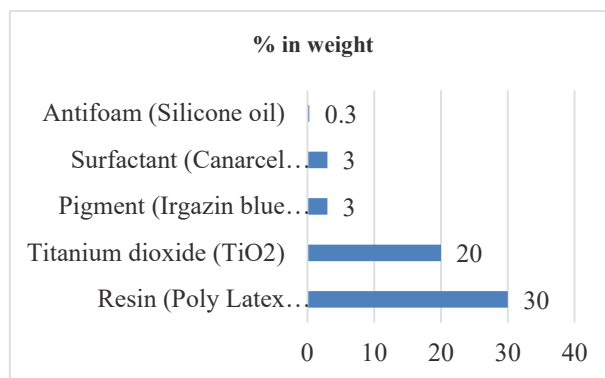


Figure 10: The formulation for obtaining a water-based coating from self-crosslinking latex at room temperature

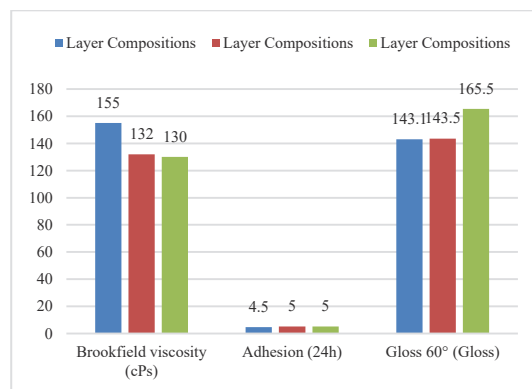


Figure 11: Properties of water-based coatings formulated with poly (BuA/St/IPMBI) latex

To compare the average oxygen transmission rate (OTR) and oxygen permeability of films with 0, 1.5, and 3.5% IPMBI, see Figure 8. The permeability values match Pauly's¹⁵ polymer permeability range. Crosslinking improves the oxygen barrier property of IPMBI films over Bu/St copolymer alone.

Formulation of Water-based Coatings

The previously obtained poly(BuA/St/IPMBI) latexes were used as polymeric resin, formulated with a constant BuA/St=60/40 and different IPMBI content (1.5, 3.5 and 5.5%). Figure 9 shows some of its properties.

Before coating formulation, proper component selection and dispersion were required. As a result, the compatibility of commercial surfactants with resin, filler, and pigment was evaluated (Table 8). Positive (+) surfactant-latex compatibility

results indicate a homogeneous dispersion free of gel and/or coagulum. The (+/-) indicates a partially homogeneous dispersion, gel or foam formation. The result marked (-) indicates latex instability and thus clot formation. The surfactant-filler compatibility was classified as excellent (+), fair (+/-), and poor dispersion.

Figure 10 shows the water-based coating formulation. The components were concentrated based on reports from the literature.¹⁷ After several tests, the procedure was determined to produce coatings with good mixing and homogeneity. Figure 11 shows the coating properties, showing excellent adhesion after 24 hours of drying. The coatings on the specimens had a gloss of 140-165, which is higher than the values reported by Khan *et al.*¹² in poly(St/BuA) coatings, Gloss 60°= 8.8 and 9.9. The three coatings had a scratch hardness H, which agrees with Badran *et al.*¹⁸ hardness reports (H and 2H). Finally, the coatings' viscosity is higher than the original latexes' due to the higher solids content.

Using the results obtained, the pigment was tested for compatibility with the surfactants TW-80, BJ 309, and R-400H. Testing revealed TW-80 as the surfactant and titanium dioxide (TiO₂) as the filler. It also had Irgazil blue pigment and silicone oil as an antifoam.

CONCLUSION

Semicontinuous emulsion polymerization produced stable latexes for the poly (BuA/St/IPMBI) system. Monoester succinate produces larger particles (90–120 nm) than Polysorbate 80 (74–96 nm). Larger Dps may indicate poor coagulation. Longer addition times increased instantaneous conversion in experiments with a BuA/St/IPMBI monomer ratio of 49/49/1.5. Over nine months, monoester sulfosuccinate surfactant was more colloidal stable than Polysorbate 80 Dp values and surfactant structure differ. Dp and Np appear to be hydrophobicity dependent. The smaller particle size (50/50 and 60/40 compositions) may have reduced IPMBI hydrolysis in latexes with this composition (40/60). Films from latexes with ratios of (45/50, 50/50, and 60/40) were obtained (24°C). Young's modulus and yield stress were higher than in the 60/40 ratio film. Similar to commercial latexes, both films were water and oxygen barriers. The IPMBI concentrations (1.5, 3.5, and 5.5%) produced stable latexes with a solid content close to 50%. It did not affect conversions, particle diameters, or the number of colloidal latex particles (60 days). Uncontrollable seed causes Dp and Np deviations. The hydrolysis of isocyanate groups did not affect the colloidal stability of latexes when IPMBI concentration was varied. The soluble latex molecular weight increased with IPMBI concentration. Crosslinking reduces the molecular weight of the soluble fraction. After 90 days, the gel content in these latex films increased to 90% for 1.5, 3.5, and 5.5 IPMBI. The films' mechanical properties improved as IPMBI content increased, while water vapour and oxygen barrier properties improved (0% of IPMBI). All three latexes tested had good adhesion to steel, indicating that any of them could be used in the coating formulation—the best formula for mixing and homogeneity. The described formula

produced three water-based coatings with excellent adhesion to steel and scratch hardness.

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