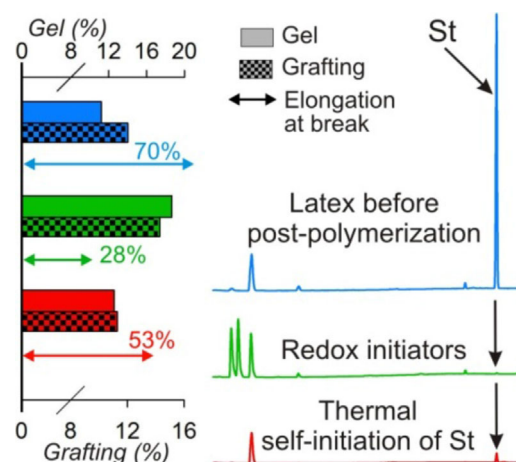


Hybrid Polystyrene/Polybutadiene Latexes With Low Environmental Impact

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The polybutadiene incorporation in waterborne polystyrene nanoparticles by miniemulsion polymerization improves the toughness of the final product. Unfortunately, the polymerization does not proceed to completion, remaining a high level of unreacted monomer. This work addresses the implementation of two post-treatment methods to efficiently remove the residual styrene from polybutadiene/polystyrene latexes with 50% of solid content: i) post-polymerization with redox initiators; and ii) post-polymerization by thermal initiation of styrene at high temperature ($\geq 120^\circ\text{C}$). The mechanisms responsible of the effects of both post-treatments on the properties of hybrid materials are here discussed.



1. Introduction

Due to the growing global regulations about pollutants emission, the synthesis of a product with low content of volatile organic compounds (VOCs) is a fundamental aspect of its development. In the case of polymeric materials, the unreacted monomer is normally present as a VOC.

Miniemulsion polymerization represents an alternative for the synthesis of hybrid latexes; and enables the incorporation of hydrophobic components into the polymer particles, without requiring their diffusion through the aqueous phase. The incorporation of polybutadiene (PB) into waterborne polystyrene (PS) nanoparticles by miniemulsion polymerization was recently studied to positively combine the properties of both materials, improving the toughness of the final product.^[1] This strategy of synthesis represents an alternative more environmentally friendly than the bulk/solution process normally used for producing

this kind of materials, and enables the synthesis of nanostructured and toughened polystyrenes, with mechanical properties similar to those of a commercial High Impact Polystyrene. Unfortunately, the miniemulsion polymerization of styrene (St) in the presence of PB does not proceed to completion, and a high level of unreacted monomer remains in the produced latex,^[1] similarly to that reported for other hybrid latexes synthesized by miniemulsion polymerization.^[2,3]

Both post-polymerization^[3–11] and devolatilization^[9–13] are used to reduce the residual monomer content in polymer latexes. Post-polymerization is usually preferred because it is carried out in the polymerization reactor, without requiring additional equipment; and consists of adding, after the end of the main polymerization process, fresh initiators to polymerize the residual monomer. Water soluble redox initiators are commonly employed in post-polymerizations, due to they generate a high radical flow, reducing the post-polymerization times respect to thermal initiators.^[10,11] Ilundain et al.^[5] investigated different water-soluble redox initiators to post-polymerize acrylic latexes observing that the higher the hydrophobicity of the radicals formed, the higher the residual monomer removal

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efficiency. Moore and Feast^[6] studied the reduction of residual St from different latexes (PS, St-butadiene copolymers, and St-butadiene-acrylonitrile polymers) using a redox initiation system composed by an oil soluble oxidizing component (e.g., cumene hydroperoxide) and a water soluble activator (e.g., diethylene triamine), reaching residual St contents of 0.01% (with respect to the latex).

As the authors are aware, post-polymerization processes without requiring additional initiator were not previously studied for latexes. Considering that St can be thermally self-initiated at high temperature ($>120\text{ }^{\circ}\text{C}$) forming spontaneously radicals, this alternative of initiation could be adopted in post-polymerizations of St-containing latexes. The mechanism of St thermal initiation involves the formation of a Diels–Alder dimer, and the transfer of a proton from the dimer to other St molecule, giving two different radicals.^[14] Thermal initiation was studied in the St miniemulsion polymerization by Katzer et al.^[15] The employment of a mathematical model allowed to explain the acceleration of the polymerization rate, with respect to that observed during the St bulk polymerization. This effect was attributed to the desorption of monomeric radicals from the polymer particles to the aqueous phase, resulting in a compartmentalized system where the rate of termination is three to four orders of magnitude lower than in a bulk polymerization system.

Additionally to residual monomer reduction, the post-polymerization process could be an alternative to tune the polymer microstructure, which in turn could affect the particle morphology and the material properties. In this sense, Ilundain et al.^[16] investigated different redox initiators to post-polymerize acrylic latexes, evaluating the effect on the microstructure. They observed: (i) an increment of the gel content of butyl acrylate-rich copolymers during the post-polymerization, with the initiators tert-butyl hydroperoxide (TBHP) or tert-butyl perbenzoate, and ascorbic acid (AsAc) as reducing agent; and (ii) a reduction of molecular weights of vinyl acetate-rich copolymers when tert-butyl hydroperoxide/AsAc was employed. Also, important changes in polymer microstructure were observed during the post-polymerization with redox initiators of acrylic/alkyd hybrid latexes. This affected the particle morphology, resulting in a more compatibilized system with homogeneous acrylic/alkyd particles, without phase separation, when increased the fraction of grafted copolymer.^[3]

In this work, the performance of two different strategies of post-polymerization was studied with the aim of removing the residual St in high solids (50%) PB/PS hybrid latexes synthesized by miniemulsion polymerization. The investigated post-treatment strategies involved: (i) post-polymerization with redox initiators; and (ii) post-polymerization by thermal self-initiation of St at high temperature ($\geq 120\text{ }^{\circ}\text{C}$), which at first have the advantage of avoiding the employment of additional initiator. Both post-

polymerization methods were applied on several hybrid latexes synthesized with different initiators and varied PB content, and their effects on the molecular microstructure, particle morphology and mechanical properties of the final materials were investigated.

2. Experimental Section

2.1. Materials

Demineralized water was used throughout the work. The following reagents were employed as received. Potassium persulfate (KPS) from Mallinckrodt (99% purity), benzoyl peroxide (BPO) from AkzoNobel (Perkadox L-W75, with 25% water), TBHP from Aldrich, and AsAc from Cicarelli were used as initiators. Hexadecane (HD) from Aldrich ($\geq 99\%$ purity) was the costabilizer; Dowfax 2EP from Dow (45% purity) was the surfactant; and hydroquinone from Fluka AG ($>99\%$ purity) was the polymerization inhibitor. St was first washed with an aqueous solution of KOH (to remove polymerization inhibitors), and then with demineralized water until reaching the pH of the washing water. PB (Buna CB 55 GPT) was supplied by Lanxes. A set of 9 (Shodex) narrow PS standards ($10^3\text{--}10^6\text{ g}\cdot\text{mol}^{-1}$) was used to calibrate the liquid chromatograph. Tetrahydrofuran (HPLC Solvent, J.T. Baker) was the eluent of the size exclusion chromatography (SEC) runs. Methyl-ethyl ketone (MEK, Anedra, 99% purity) was employed as a selective solvent for determining the degree of grafting. Cyclopentane (CP) from Fluka ($>99\%$ purity) was used as standard for the residual St characterization.

2.2. Synthesis of the Latexes

Table 1 summarizes the latexes used in this work. The 50% solid content latexes were produced by miniemulsion polymerization as follows. First, the organic phase was prepared by dissolution of 5–10% wbp (weight based on organic phase) of PB and 4% wbm (weight based on monomer) of HD into the St. Then, the aqueous solution of 3% wbp of surfactant and 0.2% wbp of NaHCO_3 was poured into the organic phase under magnetic stirring (15 min at 1000 rpm) to create an emulsion. The resulting emulsion was sonicated during 45 min in a Sonics VC 750 (power 750 watts) at

Table 1. Summary of the basic characteristics of the employed latexes.

Exp.	T_r [$^{\circ}\text{C}$]	x [%]	\bar{d}_p [nm]
PB ₅ K _{0.75}	70	94	109
PB ₁₀ K _{0.75}	70	96	108
PB ₅ B _{2.1}	90	94	223
PB ₁₀ B _{0.75}	90	96	213
PB ₁₀ B _{2.1}	90	96	221

100% of amplitude, in cycles of 20 s on and 5 s off. Polymerizations were carried out with 0.75–2.1% wbm of BPO or 0.75% wbm of KPS in a 0.2 L batch glass reactor equipped with a reflux condenser, a stirrer, a sampling device, and a nitrogen inlet. The reaction temperature ($T_r = 70$ or 90 °C) was adjusted by manipulating the reactor jacket temperature, in turn controlled by a water bath. The miniemulsion was loaded into the reactor, and the system was kept under stirring and nitrogen bubbling until the desired reaction temperature was reached. While KPS was previously dissolved in water and injected into the reactor as a shot to initiate the polymerization, BPO was dissolved in the organic phase before preparing of the miniemulsion. The total polymerization times were 2 h for reactions with KPS, and 3 h for reactions with BPO. The experiment codes contain: (a) the abbreviation “PB” with a subscript indicating the PB content in % wbm; and (b) the initiator used in the synthesis, KPS (K) or BPO (B) with a subscript indicating its concentration in % wbm. At the end of polymerizations, the latexes were filtrated with an $85\ \mu\text{m}$ nylon mesh to collect the coagulum formed during the polymerization. Therefore, latexes employed for post-polymerizations were free of coagulum. The final particle diameter (\bar{d}_p) determined by dynamic light scattering (DLS) and the monomer conversion (x) measured by gravimetry are also indicated in Table 1. The final x was 94–96%, resulting the residual St content between 26 000 and 16 600 ppm (part per million). Details about the kinetics involved in the synthesis of those latexes can be found elsewhere.^[1]

2.3. Post-Polymerizations

Two different initiation strategies were employed in the post-polymerizations: (i) the redox initiation with the TBHP/AsAc system, and (ii) the thermal initiation of St at high temperature. Post-polymerizations with TBHP/AsAc were carried out at 70 °C in the same reactor employed for the miniemulsion polymerizations. Three different molar ratios of residual St/TBHP/AsAc were employed, 100/45/22.5, 100/25/12.25, and 100/15/7.5. The feeding time was 60 min in post-polymerizations with molar ratios of 100/45/22.5 and 100/25/12.25, which were called “R1” and “R2,” respectively; and 20 min when the molar ratio 100/15/7.5 was employed, calling this experiment “R3.” The aqueous solutions of the oxidant and the reductant were separately fed into the reactor. After feeding the initiator, the reactor temperature was held at 70 °C for 30 min more. Post-polymerizations with thermal initiation of St were performed at 120 or 130 °C during 3 h in a 0.3 L minireactor from Parr Instruments, which is a hermetic reactor with a maximum operation pressure of 3000 psi. These post-polymerizations were codified as “T1” or “T2,” indicating the post-treatment temperatures of 120 or 130 °C, respectively.

2.4. Characterization

Residual St was measured by headspace gas chromatography (GC) using the full evaporation technique in a Perkin Elmer Clarus 600 GC system equipped with DB-5ms ($50\ \text{m} \times 0.25\ \text{mm} \times 0.25\ \mu\text{m}$) column and a flame-ionization detector. CP was used as internal standard.

The gel content in the vacuum-dried polymer samples was determined by Soxhlet extraction under THF reflux along 24 h. For

some samples not all the gel was retained by the paper filter during the Soxhlet extraction, and this fraction was isolated from the THF solution containing the extracted soluble polymer by centrifugation at 6000 rpm during 2.5 h. The total gel was reported as the sum of the gel fraction retained in the paper filter and that separated by centrifugation.

The grafting efficiency (E_g) is defined as the mass of grafted St with respect to the total mass of polymerized St. The mass of grafted PS onto the PB was determined by solvent extraction, by dissolution of the free PS in MEK; while the PB (including the grafted polymer) remained insoluble.^[17] To this effect, a procedure of multiple sample dispersion in MEK and centrifugation was applied to separate the free PS, obtaining E_g from the sample content of PS and PB, and the mass of free PS.^[18]

The molecular weight distribution (MWD) and its averages (\bar{M}_n and \bar{M}_w) for the free PS were determined by SEC. The measurements were carried out with a Waters 1515 chromatograph fitted with HR 4E and HR 5E columns from Waters Corp., of nominal fractionation range of 10^3 – $10^7\ \text{g} \cdot \text{mol}^{-1}$; and a differential refractometer (DR, Waters 2414).

Particle morphology was determined by TEM, in a JEOL 100 CX (100 kV). Samples of diluted latex were stained in liquid phase with a 2 wt% aqueous solution of osmium tetroxide for 2 h. OsO_4 reacts with the butadiene double bonds, and shows the rubber phase in a dark color. Then, a drop of the stained and diluted latex was placed on copper grids covered with polyvinyl formal (Formvar by Fluka), and dried at room temperature. Micrographs were taken at different magnifications, depending on the particle size.

To obtain the final dry polymers, 1 wt% of antioxidant was added onto the latexes, and then they were coagulated with isopropyl alcohol. The obtained bulk polymer was washed with demineralized water to eliminate the emulsifier through several cycles of centrifugation/redispersion, until the surface tension of the supernatant reached the surface tension of the washing water. Then, the wet polymer was dried under vacuum at room temperature. For the tensile tests, dumbbell-shaped specimens were obtained by compression molding at 180 °C for 25 min. The elongation section dimensions were: length 9.53 mm, and cross-section $3.18 \times 1\ \text{mm}^2$. ASTM D 638 tests were carried out in a universal testing machine (INSTRON 3344), at 23 °C, 50% relative humidity, and $0.5\ \text{mm} \cdot \text{min}^{-1}$ elongation rate. At least five specimens of each sample were tested.

3. Results and Discussion

3.1. Post-Polymerization Kinetics

The results obtained during post-polymerization of different PS/PB latexes with TBHP/AsAc as initiator were presented in Table 2 and Figure 1. This Figure shows that after 20 min of the post-polymerization R1 (residual St/TBHP/AsAc ratio 100/45/22.5) of the latex $\text{PB}_{5\text{B}_{2.1}}$, the residual St was practically reduced up to the final values (<50 ppm, Table 2). This fast St reduction evidenced an excess of redox initiators. On the other hand, when post-polymerizations were carried out with the St/TBHP/AsAc molar ratio of 100/22.5/12.25 (R2), the residual St was

Table 2. Post-polymerization with the redox initiator TBHP/AsAc. Residual St, percentage of coagulum, and final pH.

Latex	Post-polymerization system (molar ratio St/TBHP/AsAc)	Residual St [ppm]	Coagulum [%] ^{a)}	Final pH
PB ₅ B _{2.1}	R1 (100/45/22.5)	26 000	Absence	5.0
	R2 (100/22.5/12.25)	<50	0.8	2.9
	R3 (100/15/7.5)	230	Absence	3.3
	R3 (100/15/7.5)	62	Absence	3.2
PB ₁₀ B _{2.1}	R2 (100/22.5/12.25)	16 600	Absence	4.4
	R2 (100/22.5/12.25)	<50	0.4	3.3
PB ₁₀ B _{0.75}	R2 (100/22.5/12.25)	16 600	Absence	4.7
	R2 (100/22.5/12.25)	158	0.6	2.3
PB ₅ K _{0.75}	R2 (100/22.5/12.25)	26 000	Absence	5.7
	R2 (100/22.5/12.25)	167	0.6	1.9
PB ₁₀ K _{0.75}	R2 (100/22.5/12.25)	16 600	Absence	4.7
	R2 (100/22.5/12.25)	97	0.3	2.0

^{a)}% Weight based on total latex.

continuously reduced during the feeding period (60 min) up to values below 230 ppm in all latexes; giving place to a more efficient use of the initiator system. Also, the redox post-polymerization of latex PB₅B_{2.1} with the system R3 (residual St/TBHP/AsAc ratio 100/15/7.5) allowed a fast reduction of residual St up to 63 ppm, feeding one third of the amount of initiator employed in R1 and reducing the feeding time to 20 min.

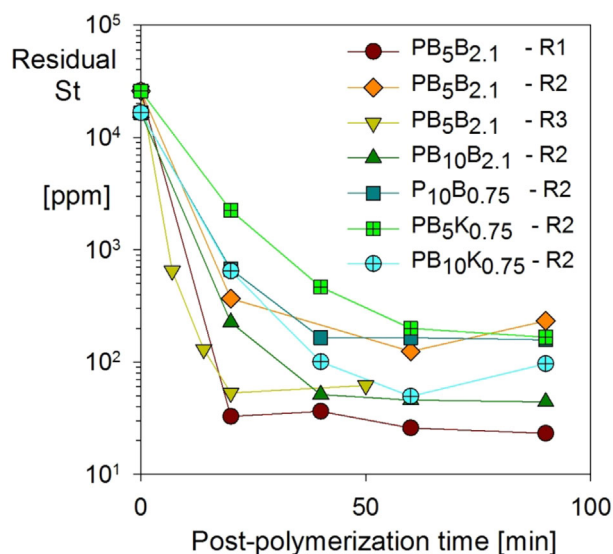


Figure 1. Evolution of the residual St concentration during post-polymerizations with TBHP/AsAc.

The results of residual St obtained when applying post-polymerization by thermal self-initiation of St (T1 and T2) on different PS/PB latexes are presented in Table 3. Figure 2 shows the evolution of residual St during post-polymerizations T1 and T2 of PS/PB latexes synthesized with BPO. It could be observed that, during the post-polymerizations T1 and T2 of latexes synthesized with BPO, the residual St concentration was reduced faster in the first 30 min than in rest of the post-treatment. This could be due to the decomposition of remnant BPO from the main polymerization. Approximately, 17% of the loaded BPO remains in latexes after 3 h at 90 °C ($k_d = 1.65 \times 10^{-4} \cdot s^{-1}$).^[19] Note that in post-polymerization at 130 °C of PB10B0.75 the residual St was reduced almost constantly during the post-treatment, without an abrupt St decrease in the first 30 min. This is an indication that the low concentration of remnant BPO in PB10B0.75 (this latex was synthesized with lower BPO concentration, 0.75% wbm) did not significantly contribute to the initiation process (i.e., almost pure thermal initiation of St was present), in contrast to that observed in post-polymerizations of latexes synthesized with higher BPO concentration.

It is observed in Table 3 and Figure 2 that post-polymerization of PB₅B_{2.1} at 120 °C (T1), was not efficient to reduce the residual St. At 120 °C, the residual St was only reduced in the first 30 min of post-treatment (Figure 2), due to the decomposition of the remnant BPO, but then no additional St consumption was detected. This result is an indication that radical generation by thermal self-initiation of St at 120 °C was not efficient to reduce the residual St.

Table 3. Post-polymerization by thermal self-initiation of St. Residual St, percentage of coagulum, and final pH.

Latex	Post-polymerization system (Temp.)	Residual St [ppm]	Coagulum [%] ^{a)}	Final pH
PB ₅ B _{2.1}		26 000	Absence	5.0
	T1 (120 °C)	3500	1.5	4.8
	T2 (130 °C)	330	0.2	5.2
PB ₁₀ B _{2.1}		16 600	Absence	4.4
	T2 (130 °C)	167	1.9	4.7
PB ₁₀ B _{0.75}		16 600	Absence	4.7
	T2 (130 °C)	843	2.0	5.0
PB ₅ K _{0.75}		26 000	Absence	5.7
	T2 (130 °C)	145	≈6.0	2.4
PB ₁₀ K _{0.75}		16 600	Absence	4.7
	T2 (130 °C) ^{b)}	123	1.5	2.1
	T2 (130 °C) ^{b)}	139	2.0	2.2

^{a)}% Weight based on total latex; ^{b)}latexes diluted at 40% of solids content before post-polymerization.

However, when post-polymerizations were carried out at 130 °C, the St concentration was progressively reduced during 3 h, indicating that St thermal initiation occurred at this temperature. From Table 3, it is observed that post-polymerization at 130 °C was efficient for reducing the residual St, with final monomer concentrations comparable to those obtained with the redox post-polymerizations, except for the latex PB₁₀B_{0.75}, (residual St ≈ 850 ppm). In this last case, the St concentration exhibited a constant reduction (Figure 2) during post-polymerization at 130 °C,

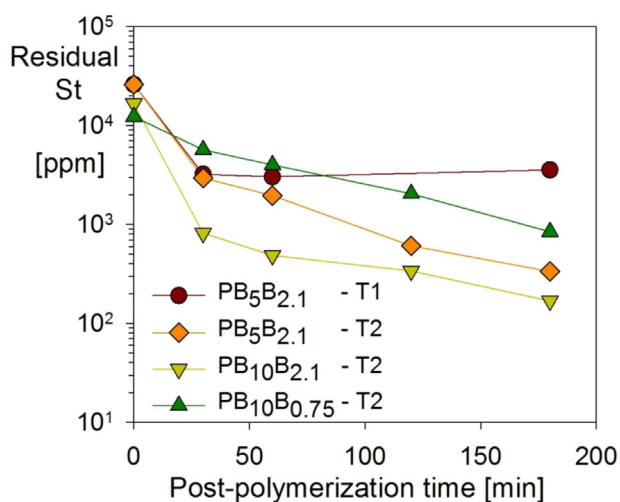


Figure 2. Evolution of the residual St concentration during post-polymerizations by thermal initiation of St of latexes produced with BPO.

and it would be expected a further St reduction by extending the post-polymerization time.

Note that, with both redox and thermal post-polymerizations it was possible to obtain final concentrations of residual styrene similar to those suggested for commercial HIPS (300–600 ppm) by the Association of Plastic Manufacturers in Europe (APME).^[20]

Figure 3 presents the GC chromatograms corresponding to the latex PB₅B_{2.1} before post-polymerization (Figure 3a), and after being post-polymerized with TBHP/AsAc (R1, Figure 3b) and by thermal self-initiation of St at 130 °C (T2, Figure 3c). Despite TBHP/AsAc was the most efficient system to reduce the residual St, the formation of new VOCs was detected, such as acetone (AC) and tert-butanol (t-BuOH). These new VOCs were formed due to two parallel reactions that tert-butoxyl radicals suffer in addition to the polymerization reaction: (i) a β scission reaction which produces AC, and (ii) an H abstraction (from monomer, polymer or impurities) that generates t-BuOH.^[4] On the other hand, the post-polymerizations by thermal initiation of St did not employ additional initiator, and therefore they did not form other VOCs, as it can be observed in the practically clean GC chromatogram (Figure 3c).

In most post-polymerization experiments coagulum was formed (Table 2 and 3), mainly adhered to reactor wall, stirring paddles, temperature sensor, and sampling tube. In most experiments, coagulum contents quantified after post-polymerization, were similar to those obtained in the latexes synthesis.^[1] A higher amount of coagulum was formed during the thermal post-polymerization. It was expected due to the high post-polymerization temperature, higher than the PS glass transition temperature ($T_g = 96$ °C),

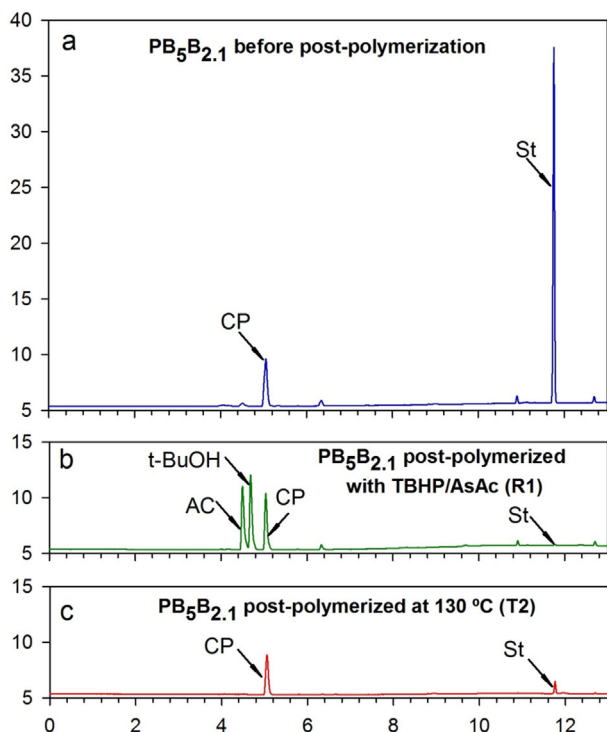


Figure 3. GC chromatograms for the latex PB₅B_{2.1}: (a) before post-polymerization; (b) after post-polymerization with TBHP/AsAc (R1); and (c) after post-polymerization by thermal initiation of St at 130 °C (T2).

that increases the particle kinetic energy, favoring coagulum formation during collisions of soft particles. In the particular case of post-polymerization at 130 °C of the latex PB₅K_{0.75}, synthesized with KPS, the residual St was significantly reduced but an important amount of coagulum was formed on reactor wall and inserts, resulting in a post-polymerized latex of 38% solid content (Table 3).

In latexes electrostatically stabilized, particles are surrounded by an electric double layer formed by the surface charge from the initiator and surfactant, and the atmosphere of counterions.^[21] These colloidal systems are very sensitive to changes in pH and ionic strength. Note that, post-polymerization at high temperature of PB₅K_{0.75} produced a pH latex reduction from 5.7 to 2.4, while pH of latexes synthesized with BPO remained practically constant (pH ≈ 5) during the thermal post-treatment (Table 3). It is a consequence of that under the post-polymerization condition (130 °C) remnant KPS from latex synthesis was completely decomposed and, as it is well known, persulfates could form H₂SO₄ by other routes than the thermal decomposition.^[22] On the other hand, a similar pH reduction was also obtained in latexes post-polymerized with TBHP/AsAc at 70 °C, as consequence of the AsAc addition, but without the formation of a high amount of coagulum (Table 2). In spite of both the pH reduction and the ionic

strength increment that favor the coagulum formation, the results of post-polymerization with TBHP/AsAc indicate that they are not the main causes of latex destabilization.

Therefore, it is thought that destabilization of the latex PB₅K_{0.75}, during the post-treatment at 130 °C, could be a consequence of the combination of the following factors: (i) the pH reduction that affects the electric double layer; (ii) the high solids content (50%), with small polymer particles ($\bar{d}_p = 108$ nm, Table 1), that reduces both the separation between particles and the fraction of particle surface covered by the emulsifier, compared with that of latexes synthesized with BPO ($\bar{d}_p > 200$ nm, Table 1); and (iii) the high post-polymerization temperature (above the PS T_g), that increase the particle kinetic energy favoring the collisions of soften nanoparticles.

In order to reduce the coagulum formation during post-polymerization at 130 °C, additional surfactant (Dowfax 2EP) was added to latex PB₅K_{0.75} to obtain a particle area covered by surfactant ($\bar{d}_p = 109$ nm) equal to the latex PB₅B_{2.1}, synthesized with BPO ($\bar{d}_p = 223$ nm), which was stable during the thermal post-treatment. However, this experiment did not improve the latex stability probably due to the surfactant addition increased the ionic strength without reducing the separation between particles. Then, the solid contents of latexes PB₅K_{0.75} and PB₁₀K_{0.75} were reduced up to 40% before post-treatment. Under this condition, it was observed that post-polymerization at 130 °C was efficient, reducing the St concentration below 140 ppm, and significantly improving the latex stability (Table 3). The final pHs of these latexes were as low as those obtained in the thermal post-polymerization of latexes without dilution (Table 3). For this reason, it seems that the solid content reduction increased the distance between particles, reducing their collisions, and thus the coagulum formation.

3.2. Effect of Post-Polymerizations Methods on Polymer Microstructure and Particle Morphology

Table 4 presents the effect of post-polymerizations of PS/PB latexes on total gel contents, E_g , and average molecular weights of the free PS (isolated by MEK extraction). It is observed that post-polymerization processes importantly increased gel content and E_g . Due to latexes contain a residual St of 4–6% ($x = 94$ –96%) before post-treatment, the E_g increment indicates that most PS formed during post-polymerization was grafted onto PB. This effect was smaller in the post-polymerization by thermal initiation of St, mainly because of the low transfer capacity of styryl radicals with respect to the oxygen centered ones of tert-butoxyl radicals (post-polymerization R2).^[3] Therefore, gel content was increased as a consequence of the formation of new grafted copolymer and of PB cross-linking. The higher increase in gel content observed in latex post-polymerized with TBHP/AsAc, even when the lowest content of redox

Table 4. Microstructural characteristics of the polymers before and after different post-polymerizations.

Latex	Post-polym. system	Gel [%]	E_g [%]	\bar{M}_{nPS} [$g \cdot mol^{-1}$]	\bar{M}_{wPS} [$g \cdot mol^{-1}$]
PB ₅ B _{2.1}		15.7	12.0	15 400	35 500
	R1	18.7	14.4	15 100	34 000
	R2	17.9	15.2	15 300	40 100
	R3	17.9	14.7	16 600	41 100
	T2	16.8	13.6	15 100	36 100
PB ₁₀ B _{2.1}		17.9	17.2	13 300	47 000
	R2	23.1	23.3	13 000	44 800
	T2	18.3	19.9	14 800	50 000
PB ₁₀ B _{0.75}		15.6	22.7	31 900	177 600
	R2	20.2	26.8	23 200	168 400
	T2	16.8	25.5	28 900	173 200
PB ₅ K _{0.75}		2.0	6.7	134 900	1 300 100
	R2	17.2	13.8	163 600	1 366 100
	T2 ^{a)}	9.3	7.7	139 300	1 623 600
PB ₁₀ K _{0.75}		11.2	12.0	154 400	1 663 400
	R2	18.7	14.3	156 200	1 335 700
	T2 ^{a)}	12.6	11.3	179 100	1 543 500

^{a)} latex diluted at 40% solids content before the thermal post-polymerization.

initiator was employed (experiment PB₅B_{2.1}-R3), indicates that the important flux of tert-butoxyl radicals with high transfer capacity could generate high levels of cross-linking in the rubbery phase, by abstraction of the allylic hydrogens from the PB chains or propagation on PB double bonds. These cross-linking reactions became more important at low St concentration in polymer particles, as in the case of post-polymerizations. The generation of a moderate degree of cross-linking in PB could be required to maintain the rubbery phase shape during the material processing, and therefore improve the mechanical properties. However, with a high cross-linking degree, the PB phase is hardened thus reducing the material toughness.^[23] Due to most of the PS produced during the post-polymerization was grafted, average molecular weights of free PS were not significantly modified after post-treatments (Table 4).

Particle morphology observed by TEM of latexes PB₁₀B_{2.1} and PB₅K_{0.75} before and after post-polymerizations are showed in Figure 4 and 5, respectively. In both latexes, the particle morphology was not modified during the different post-polymerizations (redox or thermal), even working at a temperature above the PS T_g during the thermal post-treatment. This was expected, because the final St conversions during the latex synthesis were high ($x \geq 94\%$), and therefore the PS produced in the post-polymerization should not importantly modify the particle morphology previously generated in the main

polymerization.^[1] Also, the presence of a moderate amount of grafted copolymer, generated in the main polymerization, helps to compatibilize both phases,^[24] avoiding morphology changes, which were observed for other hybrid polymer particles subjected to thermal aging at temperatures above the polymer T_g .^[25]

In the latex PB₁₀B_{2.1} synthesized with BPO (Figure 4), most of the particles exhibit an internal rubbery phase with multiple PS occlusions before and after post-polymerizations. In the latex PB₁₀K_{0.75} synthesized with KPS (Figure 5), most of the particles are homogeneous, while hybrid particles exhibit “core-shell” morphologies, and this is also observed before and after post-polymerization.

3.3. Effect of Post-Polymerization on Mechanical Properties of Final Materials

Bulk materials were obtained by compression molding at 180 °C for 25 min. Materials morphologies were characterized by AFM of cross-sectional cuts of final materials. Morphologies obtained before post-polymerization were published elsewhere.^[1] Materials synthesized with KPS showed a hard matrix composed by PS melted with some soft PB particles. This phase distribution is related with the morphology observed for the particles, where PS particles melt together in the continuous phase and the PB core of the hybrid particles become the

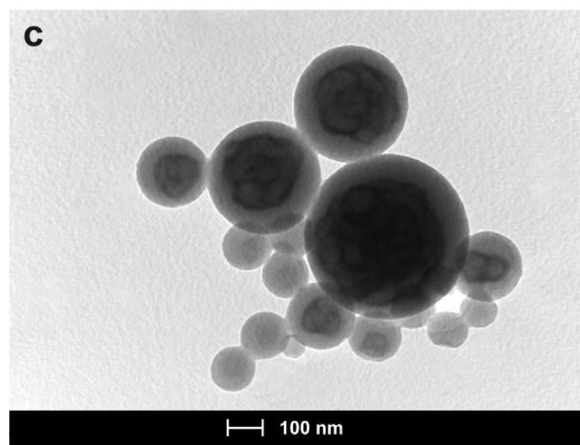
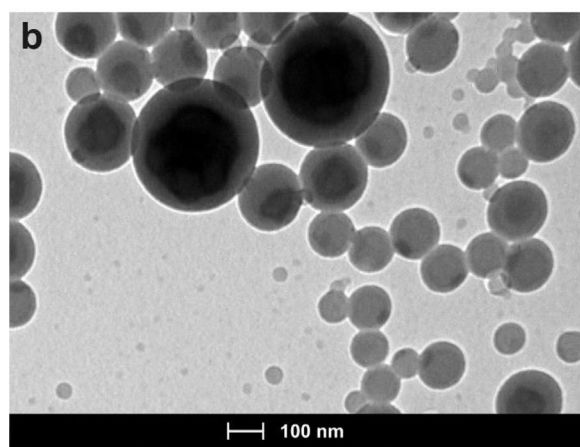
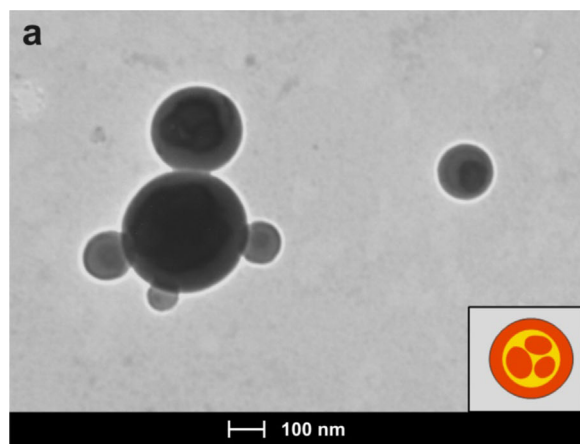


Figure 4. TEM micrographs of the final hybrid particles of the latex $PB_{10}B_{2.1}$: (a) before post-polymerization; (b) after post-polymerization with TBHP/AsAc (R2); and (c) after post-polymerization by thermal self-initiation of St at $130\text{ }^{\circ}\text{C}$ (T2).

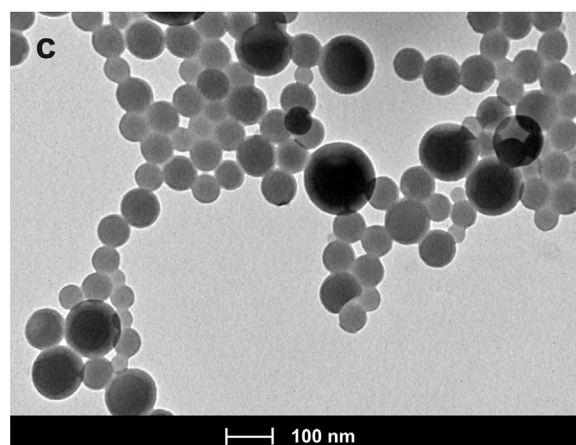
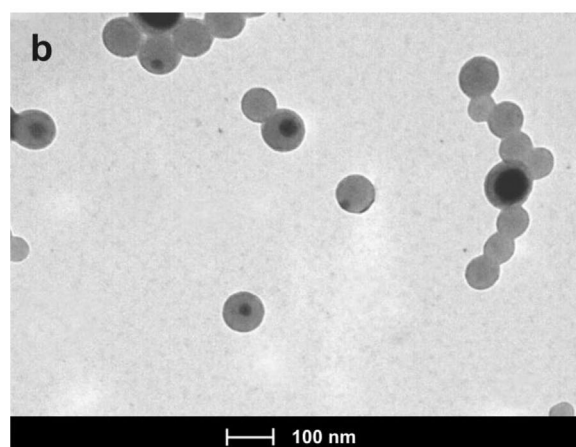
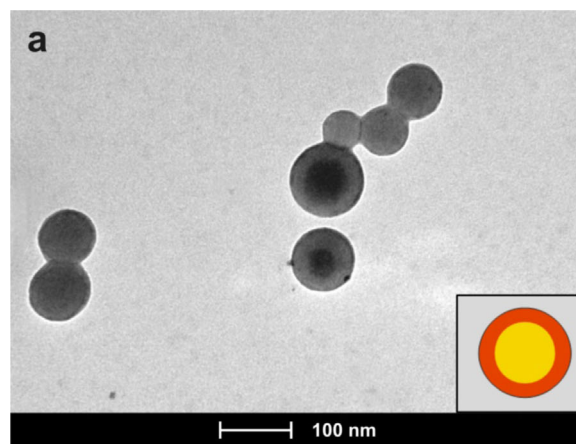


Figure 5. TEM micrographs of the final hybrid particles of the latex $PB_{10}K_{0.75}$: (a) before post-polymerization; (b) after post-polymerization with TBHP/AsAc (R2); and (c) after post-polymerization by thermal self-initiation of St at $130\text{ }^{\circ}\text{C}$ (T2).

discrete soft phase. On the other hand, the material produced with BPO does not evidence a continuous PS phase and presents an internal morphology with two types of zones: a hard PS phase with irregular form and size; and a phase constituted by very small PS particles surrounded by the soft

PB. This morphology is a consequence of agglomeration of particles with multiple PS occlusions, giving rise to the heterogeneous zones, while the PS which is ungrafted and outside of the occlusions, form the irregular PS phases. Even though not shown for brevity reason, and in agreement with

TEM observations, materials morphologies were not modified by post-polymerization.

The effect of the post-polymerization process on the stress–strain curves and the corresponding global mechanical properties of the final materials are presented in Figure 6 and Table 5, respectively. Materials corresponding to latexes synthesized with high BPO concentration (2.1% wbm, PB₅B_{2.1} and PB₁₀B_{2.1}) were not analyzed due to they were too brittle, with low tensile strength and elongation at

break.^[1] The differences observed in tensile properties of materials before post-polymerization depend on the initiator employed in the latex synthesis and in turn on the polymer microstructure and material morphology, according to results published elsewhere.^[1]

Most post-polymerized materials exhibited an increase in Young modulus and tensile strength, likely due to the generation of cross-linking in the rubbery phase.^[23] In the case of materials post-polymerized with TBHP/AsAc, elongation at break was significantly reduced compared to those without post-treatment. In this case, materials resulted with lower toughness. This is consistent with the increased gel content of PS/PB nanoparticles, and therefore a high cross-linking in the PB phase (that hardens the rubbery phase), associated to the high transfer capacity of tert-butoxyl radicals. When comparing samples post-polymerized with TBHP/AsAc with those post-treated at 130 °C, it is evident that the thermal post-polymerization had a lower effect on materials toughness. This is related with the lower capability of styryl radicals, generated by thermal initiation of St, to abstract hydrogen from PB chains and to form cross-linking in the rubbery phase; producing post-polymerization T2 a minor increase in gel content (Table 4). Finally, it can be observed a slight improvement in the material toughness for the sample PB₁₀B_{0.75} post-polymerized by thermal self-initiation of St at 130 °C, with respect to the same material without post-treatment.

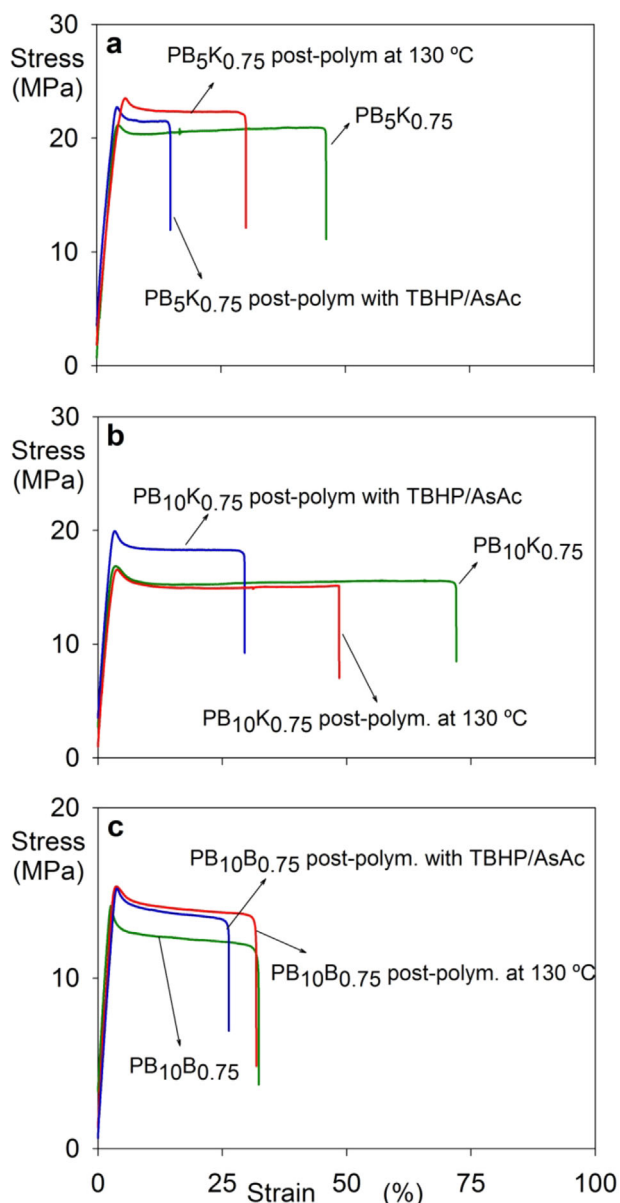


Figure 6. Tensile stress–strain curves of the final dry toughened PS materials corresponding to the latexes: PB₅K_{0.75} (a), PB₁₀K_{0.75} (b), and PB₁₀B_{0.75} (c), before post-polymerization, after post-polymerization with TBHP/AsAc (R2), and after post-polymerization by St thermal initiation at 130 °C (T2).

4. Conclusion

In order to reduce the residual St present in high solid content (50%) PB/PS hybrid latexes, synthesized by mini-emulsion polymerization, two post-polymerization strategies were investigated. When the post-polymerization was carried out by dosing the redox initiator system TBHP/AsAc, the residual St was significantly reduced below 250 ppm. Unfortunately, with this strategy new VOCs, as acetone and tert-butanol, were formed. On the other hand, the post-polymerization by thermal self-initiation of St at 130 °C considerably reduced the residual St below 330 ppm in most latexes and this alternative resulted more eco-friendly because it avoided both the use of additional initiators and the formation of new VOCs. However, the thermal post-treatment at 130 °C generated a high coagulum formation in the latexes synthesized with KPS, requiring a reduction in the latex solid content from 50 to 40% to avoid their destabilization.

Post-polymerization increased the grafted PS and gel content without altering the morphology of latex nanoparticles and final materials. The increase in the gel content, which was more important in post-polymerization with TBHP/AsAc, is attributed to the new grafted copolymer formation and the radicals attack on PB, generating cross-linking in the rubbery phase.

Table 5. Effect of post-polymerization on tensile properties of the final dry toughened PS materials.

Final dry material of experiment	Young modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]	Toughness [$\text{J} \cdot \text{m}^{-3} \times 10^2$]
PB ₅ K _{0.75}	765 ± 31	21.0 ± 0.4	47.1 ± 4.8	931 ± 106
PB ₅ K _{0.75} post-polym. R2	785 ± 22	22.7 ± 1.0	16.4 ± 4.0	316 ± 74
PB ₅ K _{0.75} post-polym. T2 ^{a)}	799 ± 47	23.7 ± 0.3	33.3 ± 4.7	688 ± 63
PB ₁₀ K _{0.75}	710 ± 26	16.9 ± 0.5	69.1 ± 10.4	1046 ± 178
PB ₁₀ K _{0.75} post-polym. R2	730 ± 45	20.0 ± 0.9	27.8 ± 4.2	489 ± 65
PB ₁₀ K _{0.75} post-polym. T2 ^{a)}	716 ± 39	16.2 ± 0.6	52.7 ± 7.4	786 ± 110
PB ₁₀ B _{0.75}	582 ± 15	13.9 ± 0.5	32.7 ± 4.8	393 ± 62
PB ₁₀ B _{0.75} post-polym. R2	565 ± 21	14.8 ± 0.7	24.4 ± 3.3	324 ± 57
PB ₁₀ B _{0.75} post-polym. T2	621 ± 35	14.9 ± 0.5	31.6 ± 2.0	429 ± 20

^{a)} latex diluted at 40% solids content before the thermal post-polymerization.

The modification on polymer microstructure also affected the mechanical performance of post-treated materials. Most post-polymerized toughened PS was hardened, with increased Young modulus and tensile strength. Also, the toughness of post-polymerized materials with TBHP/AsAc was importantly reduced as consequence of a high cross-linking of the rubbery phase. Finally, this effect was less pronounced in materials obtained with the more eco-friendly alternative of thermal self-initiation of St, because lower PB cross-linking was produced.

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