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Post-polymerization of waterborne alkyd/acrylics. Effect on polymer architecture and particle morphology

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ABSTRACT

The limiting conversion commonly attained in the synthesis of waterborne alkyd/acrylic hybrid latexes hinders their industrialization. In this work, the mechanisms causing the limiting conversion were studied and post-polymerization conditions to efficiently remove the residual monomer determined. Further, it was observed that both the polymer architecture and the particle morphology were modified during post-polymerization. The mechanisms involved in the modification were investigated.

1. Introduction

Waterborne alkyd/acrylic coatings are interesting materials as they combine the positive properties of the alkyd resins (e.g. autoxidative curing, high gloss and penetration in wood) with the fast drying and color retention of acrylic latexes. It is expected that properties will improve with the intimate contact between the components of the hybrid system. Miniemulsion polymerization offers the possibility to achieve this intimate contact using a solution of the alkyd resin in the acrylic monomer as disperse phase [1]. Unfortunately, miniemulsion polymerization of monomer/resin system often shows a limiting monomer conversion which results in an unacceptable high concentration of residual monomer [1–3]. This is a serious problem that hinders the commercialization of these products.

Although several hypotheses have been proposed to explain the limiting conversion in waterborne polymer–polymer latexes (impurities within the resin [1,4], retardative chain transfer [1,5], retardative addition [6] and segregation of the resin within the polymer particle [5]), the actual reason is still an open question. (Meth)acrylate radicals may either abstract a hydrogen from the resin or propagate with the vinyl group of the resin. In the case of reaction with alkyds, it has been postulated that, due to steric features, methacrylate groups were more prone to abstract allylic hydrogens from the resin yielding a quite stable (and inactive) alkyd radical by conjugation with the adjacent double bond [5]. According to this hypothesis, these stable radicals would cause the limiting conversion. On the other hand, it has been postulated that addition to a resin double bond was favored for acrylates. As this alkyd radical is more reactive than the one produced by hydrogen abstraction, this mechanism was not considered as the main cause of limiting conversion in acrylate-based latexes [5]. Furthermore, it has been proposed that segregation results in alkyd-rich regions where the radicals cannot enter, either because of the hard shell, as in the methyl methacrylate (MMA)/alkyd system or because the high viscosity of the particle-phase, as in butyl acrylate (BA)/alkyd system [5]. Hence the monomer solubilized in those alkyd-rich domains cannot be polymerized. Tsavalas et al. [5] suggested that both mechanism, retardative chain transfer and segregation could be applied. But their simulation studies showed that the retardative chain transfer was not capable of producing the limiting conversion for the MMA/alkyd system, and that phase segregation was the most likely cause of the limiting conversion [7]. However, it was reported that complete conversion was achieved during polymerization of acrylic monomer-alkyd dispersions in the presence of preformed acrylic latex [8]. This seems to challenge the segregation model because it shows that monomer may diffuse not only out of the segregated resin but also through the aqueous phase to the alkyd-free particles.

The use of redox initiators during the synthesis of the hybrid alkyd–acrylic latex can improve monomer conversion, but still the concentration of residual monomer is unacceptable [9]. The

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residual monomer contained by the latex at the end of the polymerization is usually removed by devolatilization and/or post-polymerization [10–12]. Devolatilization is a unit operation in which the latex is stripped under vacuum conditions using either steam or inert gas, until acceptable low concentrations of residual monomer are reached. For this particular case, devolatilization is not adequate because the amount of residual monomer is high and because, due to the low water solubility of the (meth)acrylic monomers used and their low vapour pressure, the efficiency of devolatilization is limited and the complete elimination of the residual monomer could hardly be achieved [12].

Post-polymerization consists of adding, after the end of the main polymerization process, fresh radical generating initiators to polymerize the residual monomer. Water-soluble redox systems yielding hydrophobic radicals were found to be advantageous in either acrylic or vinylic latexes, because they yield a higher flux of radicals, in particular under mild conditions, having easy access to the place where the monomer is located (i.e., polymer particles) [13]. However, in polymer–polymer hybrid latexes post-polymerization can be a challenging matter, because the presence of the resin can severely reduce the efficiency of the radical [5,6]. On the other hand, Ilundain et al. [14] showed that post-polymerization using an initiator system producing highly reactive *tert*-butoxyl radical was able to modify the polymer structure of either vinylic or acrylic latexes. In VAc-rich copolymers, the *tert*-butyl radicals led to a decrease of the molecular weight, while in BA-rich copolymers, an increase of the gel content was observed. If a similar mechanism is operative for acrylic/alkyd systems, this is both a threat because the properties achieved during the synthesis of the latex may be modified during post-polymerization and an opportunity to extend the range of properties achievable. In order to turn the threat into an opportunity it is necessary to understand the mechanisms involved in the changes in polymer structure and particle morphology during post-polymerization of acrylic/alkyd hybrid latexes.

In this work, the performance of post-polymerization for removing the residual monomer in high solids alkyd/acrylic hybrid latexes was studied aiming at producing hybrid latexes with residual monomer lower than <100 ppm, to fulfill the requirements of commercial latexes. Also, the evolution of molecular architecture and particle morphology during post-polymerization was investigated. Two hybrid latexes with different acrylic monomers were considered: BA-based monomer system (BA/MMA/AA: 49.5/49.5/1 wt%) and BMA-based monomer system (BMA/MMA/AA: 49.5/49.5/1 wt%). Because of the reactivity ratios, in the first case, the residual monomer is mainly butyl acrylate while in the second case both methacrylates can be present. The different nature of the residual monomer could affect the grafting mechanism and in consequence the final architecture of the polymer.

2. Experimental

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA) and butyl acrylate (BA), supplied by Quimidroga, and acrylic acid (AA) and butyl methacrylate (BMA) supplied by Aldrich were used without purification. The alkyd resin (SETAL 293, acid value 11 mg KOH/g) was supplied by Nuplex Resins. Potassium persulfate (KPS, Panreac), 2,2-azobis(2-methylbutyronitrile) (V59, Wako Chemicals); *tert*-butyl hydroperoxide (TBHP, Panreac), ammonium persulfate (APS, Panreac), H_2O_2 (Aldrich); ascorbic acid (AsAc, Panreac), and sodium metabisulfite (SMB, Fluka) were used as initiators. GPC grade tetrahydrofuran (THF, Scharlau) and diethyl ether (Sigma Aldrich) were used as received. Distilled water was used throughout the work.

2.2. Synthesis of the latexes

Table 1 summarizes the latexes used in this work. All latexes had a 50% of solids content and 50 wt% (based on organic phase) of alkyd resin. In the upper part of Table 1, the latexes employing the BA-based monomer system (BA/MMA/AA 49.5/49.5/1 wt%) are presented, while the bottom part shows the latexes produced with the BMA-based monomer system (BMA/MMA/AA 49.5/49.5/1 wt%). The latexes were synthesized in batch by miniemulsion polymerization at 70 °C. Polymerizations were carried out in a 1 L glass reactor equipped with a reflux condenser, stirrer, sampling device, nitrogen inlet, and two feed inlet tubes. The thermal initiator KPS was injected as a shot at the beginning of the process. When V59 was used, it was dissolved in the organic phase before miniemulsification. The reaction was allowed to react for 4 h. When the redox initiator system was used, APS and SMB were fed separately during 4 h, and then the system was allowed to react in batch for 1 more hour. The particle diameter (d_p) and the monomer conversion (x) achieved after the polymerization are also indicated in Table 1. Notice that latexes 2A and 2B, as well as 4A and 4B have been produced under the same conditions but in different batches. Details about the kinetics of most of those latexes can be found elsewhere [9].

2.3. Post-polymerization

Two different redox initiators were used in the post-polymerization: TBHP/AsAc, and H_2O_2/AsAc. Post-polymerizations were carried out in the same reactor used for synthesis of the latex, at 70 °C. The aqueous solutions of the oxidant and the reductant were separately fed into the reactor. Two different feeding times were used (30 min and 90 min), and they are specified in the description of the corresponding experiment. After the feeding of the initiator system was completed, the reactor temperature was held at 70 °C for 30 min.

2.4. Characterization

Residual monomers were measured by headspace gas chromatography using the full evaporation technique. The analysis was performed with a Hewlett–Packard HP 7694E Headspace Sampler interfaced to a Hewlett–Packard HP 6890 GC system with electronic pneumatic control and a flame-ionization detector. Pentanol was used as the internal standard.

Polymer architecture was characterized in terms of the fraction of gel content, sol molecular weight, the fraction of acrylic polymer that contained grafted alkyd (acrylic degree of grafting, ADG), the fraction of the alkyd resin that is grafted to the acrylic (resin degree of grafting, RDG), and the fraction of reacted double bonds (RDB).

The sol fraction of the latex was separated from the gel fraction using soxhlet extraction with THF. The filter containing the samples was dried under vacuum (<10 kPa) and then the sol fraction was extracted using THF under reflux during 24 h. The non-soluble part

Table 1
Summary of employed latexes.

Latex	Monomers	Initiator	d_p (nm)	x (%)
1	BA/MMA/AA	V59	134	66
2A	BA/MMA/AA	KPS	117	78
2B	BA/MMA/AA	KPS	126	83
3	BA/MMA/AA	APS/SMB	123	95
4A	BMA/MMA/AA	V59	140	73
4B	BMA/MMA/AA	V59	129	68
5	BMA/MMA/AA	KPS	125	98

Table 2
Effect of redox initiator type used in the post-polymerization on the residual monomer and polymer architecture.

Latex 2A	Residual Monomer (ppm)	Initiator (% wbm)[a]	Gel (%)	ADG (%)	RDG (%)	RDB (%)	M_w (g/mol)
Before post-polymerization ($x = 78\%$)	55,000		0	97	22	12	331,000
After post-polymerization (TBHP/AsAc)	<50	4.5	0	Not measureable[b]	47	20	$>3 \times 10^6$
After post-polymerization (H_2O_2/AsAc)	1500	1.7	0	98	27	14	906,000

[a] Oxidant weight% based on the total acrylic monomer in the formulation. Oxidant/AsAc = 2/1 (molar ratio).

[b] Due to high M_w, large fraction of grafted polymer did not dissolve in DEE.

was considered to be the gel fraction. The sol fraction was directly injected into the SEC equipment to determine RDG and sol MWD. The SEC measurements were carried out with a LC-20AD Shimadzu pump fitted with a set of 3 fractionation columns (Waters Styragel HQ2, HQ4, HQ6) and two on-line detectors: differential refractometer (DR) and UV (Waters).

The method to determine the mass fraction of alkyd resin grafted to the acrylic polymer (RDG) [15] is based on the fact that the acrylic polymer is not detected by the UV sensor at a wavelength of 263 nm; and thus the area of the baseline corrected UV-chromatogram of an acrylic/alkyd hybrid material is proportional to the resin concentration in the sol fraction of the sample. Then, the fraction of grafted (and ungrafted) alkyd resin is obtained by comparing the UV baseline corrected chromatograms of the total hybrid sample and that of the original alkyd.

The molecular weight distribution (MWD) and the corresponding average values ($\overline{M}_n$ and $\overline{M}_w$) of the sol part were determined using the baseline corrected DR-chromatogram and a 3rd order-direct calibration obtained with 20 narrow polystyrene standards in the range 10^3–10^6 g/mol. Therefore, the values of the MW presented in this article are referred to linear-equivalent apparent molecular weights. The MWDs of the total hybrid samples were very broad because they include the relatively high molecular weight acrylic polymer (both neat acrylic and alkyd grafted) and the low molecular weight ungrafted alkyd resin. The molecular weights of the acrylic polymer (ungrafted and grafted), which was calculated as the difference between the MWD of the total hybrid sample and that corresponding to the ungrafted alkyd resin obtained from the UV signal, [15] is the value reported in this article.

The mass fraction of acrylic polymer grafted to the alkyd resin (*ADG*) was determined by soxhlet extraction with a selective solvent (diethyl ether, DEE). Filters containing the latex sample were dried in a vacuum oven at room temperature and weighted before and after the extraction. The soxhlet extractions were carried out during 24 h. Although it has been reported that DEE dissolves the free alkyd resin and the hybrid alkyd–acrylic component, but not the neat acrylic polymer [1] it has been recently found that the ADG determined by this method is overestimated because the solvent dissolved about 25% of the neat acrylic polymer [15]. For high ADG values, the error is small, but substantial errors could be made at low ADG values.

The fraction of reacted double bonds of the resin was determined by iodine titration based on the Wijs method [16].

The morphology of the latex particles was studied by means of transmission electron microscopy, TEM, using a TECNAI G^2 20 TWIN (200 kV, LaB6). Latexes were diluted up to 5 mL in deionized water, and stained with 0.5 mL of a 4 wt% solution (in water) of osmium tetroxide (OsO_4). Samples were allowed to react during 7 days with the stain. Positive staining with osmium tetroxide was used to increase contrast between both phases. OsO_4 reacts with double bonds of the resin, showing a dark image of the resin. Then, 0.1 mL of a 0.5% aqueous solution of phosphotungstenic acid (PTA) stain was added to each sample. The objective of this negative staining was to harden and to increase electronic density in the surroundings of the particles, and therefore the contrast. Then, a drop of each of the diluted latexes was placed on copper grids covered with Formvar® (polyvinyl formal) and dried at room temperature in a UV lamp.

3. Results and discussion

3.1. Post-polymerization of BA-based hybrid latexes

3.1.1. Effect of initiator type

BA-based latex polymerized with KPS (Latex 2A), with a residual monomer content of approximately 5.5×10^4 ppm was post-polymerized with two different redox systems: TBHP/AsAc and H_2O_2/AsAc. In both cases, the feeding time was 90 min and a molar ratio of 100/25/12.5 (residual monomer/oxidant/reductant) was used. This ratio has been reported to be the minimum required for the complete elimination of VAc residual monomer [17].

Table 2 shows that TBHP/AsAc was very efficient and that the final value of the residual monomer (<50 ppm) exceeded the industrial requirements (<100 ppm). It is worth pointing out the relation between monomer conversion, which is referred to the acrylic monomer in the formulation (25 wt% of the total formulation) and the ppm values, which are referred to the total weight of the formulation. H_2O_2/AsAc was able to eliminate most the residual monomer but the amount remaining was still too high. Almost all the acrylic polymer contained grafted alkyd resin, whereas most of the alkyd resin remained ungrafted. This is simply a matter of the relative size of the acrylic (long) and the alkyd (short) chains [9]. Both initiators caused an increase in the resin degree of grafting, the fraction of reacted double bonds in the alkyd resin and the molecular weight. The effect was stronger for TBHP/AsAc than for H_2O_2/AsAc. These results show that the limiting conversion may be overcome by adding enough radicals to the system, which supports

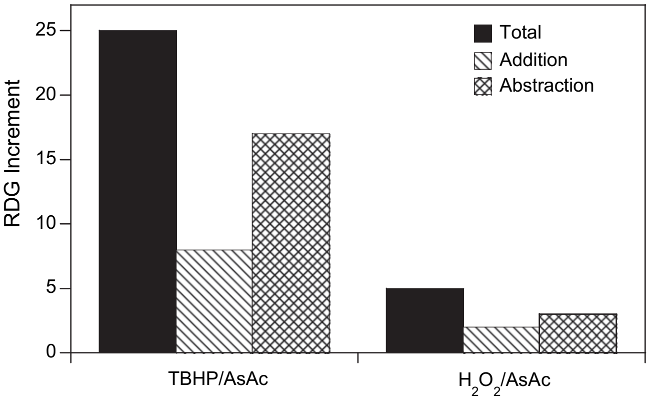

Fig. 1. Contribution of the hydrogen abstraction and addition to the alkyd double bonds to the increment of the resin degree of grafting for TBHP/AsAc and H_2O_2/AsAc.

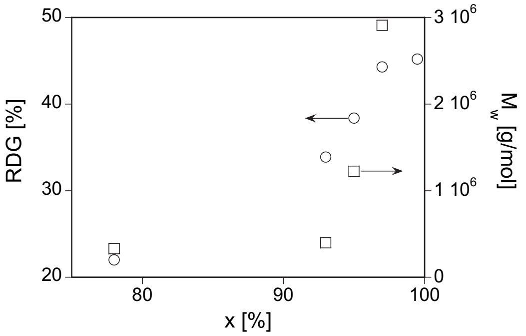

Fig. 2. Evolution of RDG and M_w during the post-polymerization with TBHP/AsAc of Latex 2A.

the hypothesis that the limiting conversion was mainly due to the alkyd resin acting as a radical sink.

Grafting may occur by abstraction of the allylic hydrogens of the alkyd resin and by radical addition to the alkyd double bond [18]. Because the alkyd double bonds are consumed only by direct addition, the ratio between the increment of RDB and RDG allows to estimate the fraction of grafted alkyd formed by direct addition during the post-treatment. Fig. 1 shows that when TBHP/AsAc was employed, the fraction of alkyd grafted by hydrogen abstraction doubled the alkyd grafted via direct addition. For H_2O_2/AsAc, hydrogen abstraction was also the main cause of grafting but the contribution of the direct addition was substantial (about 40%).

The differences between the two initiators were due to the kind of radical generated. TBHP/AsAc gives *tert*-butoxyl radicals, which are hydrophobic and hence can enter directly into the polymer particles. H_2O_2/AsAc gives hydroxyl radical, which are hydrophilic. Although these radicals may enter directly into the polymer particles [19] the rate of direct entry is very slow, and the main entrance of the hydroxyl radicals into the particles is through reaction with monomer in the aqueous phase to become hydrophobic enough. During post-polymerization, this reaction is hindered by two facts. First, because the overall monomer concentration in the system is low. Second, because the equilibrium partition of the monomers between polymer particles and aqueous phase, shifts towards the polymer particles as the overall monomer concentration decreases [20]. Because the hydroxyl radicals spend a comparatively long period of time in the aqueous phase, it is likely that they suffer bimolecular termination, namely, the fraction of the generated radicals that enters into the polymer particles is lower than for the TBHP/AsAc system. This results in a lower efficiency for monomer removal.

Table 2 shows that the nature of the radicals also affected polymer architecture. TBHP/AsAc yields oxygen-centered hydrophobic radicals that can enter directly into the polymer particles. Because oxygen-centered radicals are efficient hydrogen abstractors, [21] the *tert*-butoxyl radicals directly abstracted both allylic hydrogens from the alkyds and hydrogens from the tertiary carbons

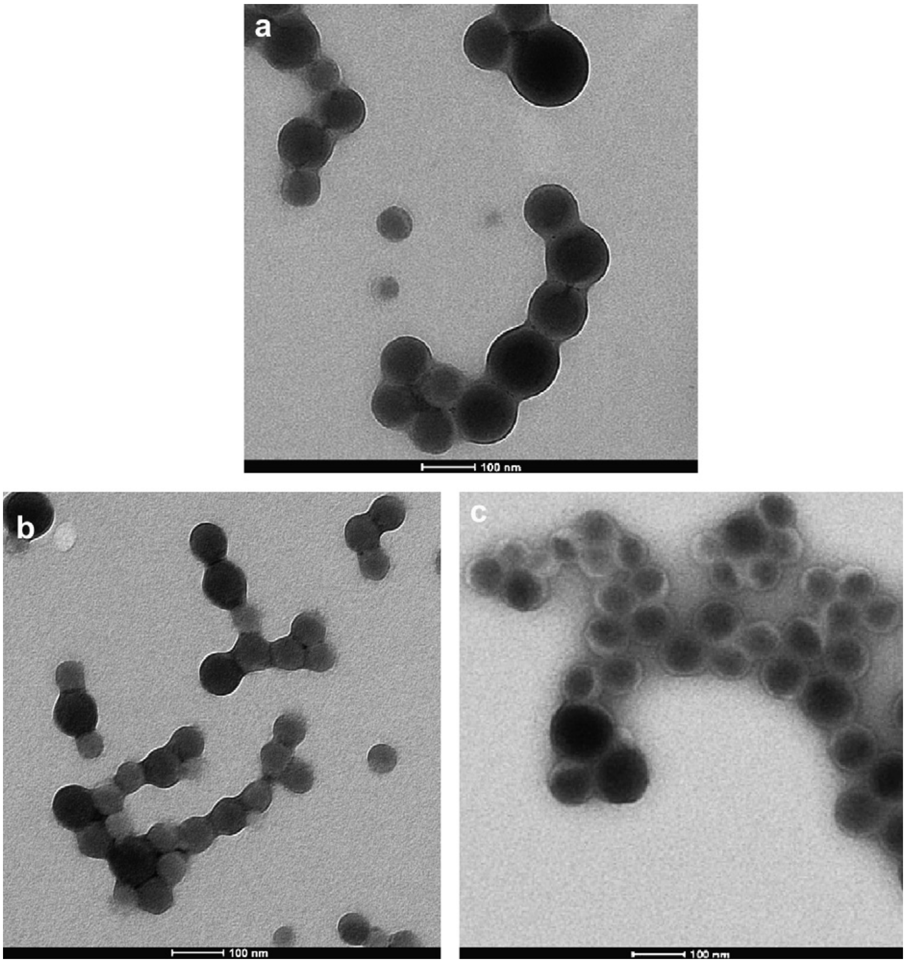

Fig. 3. TEM micrograph of Latex 2A (a) before post-polymerization and after post-polymerization with (b) TBHP/AsAc and (c) H_2O_2/AsAc.

Table 3
Effect of the initial concentration[a] of residual monomer on monomer removal and polymer architecture.

Latex	Residual Monomer (ppm)	Gel (%)	ADG (%)	RDG (%)	RDB (%)	M_w (g/mol)
1	85,000 ($x = 66\%$)	0	97	14	0	74,000
After post-polymerization	21,300 ($x = 91.6\%$)	0.7	92	28	9	197,000
2B	42,500 ($x = 83\%$)	0	81	17	3	264,000
After post-polymerization	680 ($x > 99.7\%$)	0	Not measurable[b]	39	8	1,225,000
3	12,500 ($x = 95$)	0	97	17	5	216,000
After post-polymerization	<50	0.5	98	33	5	859,000

[a] TBHP/AsAc was used as initiator: 2.5% wbm of TBHP and the molar ratio TBHP/AsAc = 2/1.
[b] due to high M_w, a large fraction of grafted polymer did not dissolve in DEE.

of the BA units of the acrylic chains. These mechanisms respectively enhanced the incorporation of the resin to the acrylic chains and the molecular weight of the acrylic polymer (through propagation followed termination by combination). Fig. 2 shows that most of the increase in both the resin degree of grafting and the molecular weight occurred above $x = 90\%$, but the increase was very modest during the final stages of the post-polymerization. This strongly suggests that a certain amount of monomer was needed for an efficient grafting and to increase the molecular weight through long chain branching formation followed by termination. H_2O_2/AsAc also produces oxygen-centered radicals, but as they are rather hydrophilic, before entering into the particles they have to react with the free monomer in the aqueous phase, becoming carbon-centered radicals, which are less efficient than the oxygen-centered ones for hydrogen abstraction.

Summarizing, TBHP/AsAc yields a higher overall concentration of radicals in the particle and a higher concentration of oxygen-centered radicals. The higher overall concentration of radicals was responsible for the lower final residual monomer, and, partially, for the increase in both the resin degree of grafting and the molecular weights. The higher concentration of oxygen-centered radicals was the reason for the high abstraction/addition ratio (Fig. 1), and, partially, for the increase of both the resin degree of grafting and the molecular weights.

Fig. 3 shows the particle morphology of Latex 2A before and after post-polymerization with the redox systems. It can be observed that at the end of the regular process, core–shell particles were obtained. In these particles, the alkyd resin (darker part) was in the core and the acrylic rich polymer (lighter part) formed the shell. The latex post-polymerized with H_2O_2/AsAc did not show any appreciable change, whereas the one post-polymerized with TBHP/AsAc presented a more homogeneous particle morphology. The change in particle morphology occurred because, on one part, the grafted polymer (that includes practically all the acrylic polymer) contained more alkyd resin (*RDG* = 47%), increasing its compatibilization with the free alkyd resin, and on the other part, the amount of the free alkyd resin decreased.

3.1.2. *Effect of the initial concentration of residual monomer*

Fig. 2 shows that the variation during post-polymerization of both RDG and molecular weight occurred in a narrow range of monomer conversion. This suggests that the changes in both polymer architecture and particle morphology may depend on the conversion achieved in the synthesis of the latex, namely on residual monomer contained by the latex before the post-polymerization (hereafter called initial concentration of residual monomer). Therefore, the effect of the initial concentration of residual monomer on polymer architecture and particle morphology was analyzed. Three BA-based latexes were post-polymerized with TBHP/AsAc. In all the cases, the same amount of TBHP was used (2.5 wt% based on the total acrylic monomer in the formulation) and the feeding time was 30 min. It is worth pointing out that this strategy is different to that presented in the previous section where the amount of initiator was proportional to the initial concentration of residual monomer. Table 3 summarizes the characteristics of the latexes before and after post-polymerization. It can be seen that when the amount of initiator was limited, the final residual monomer content depended on the conversion achieved in the synthesis of the latex. With the amount of TBHP/AsAc used, only for Latex 3 a concentration of residual monomer less than 100 ppm was achieved. This shows that the minimum amount of initiator required to reduce the concentration of residual monomer below a target value depended on the initial concentration of residual monomer.

Table 3 shows that, under the conditions used in the post-polymerization, the modification of the polymer architecture during polymerization was strongly affected by the initial concentration of residual monomer. In the post-polymerization of Latex 1, the conversion was significantly increased but the final value was only 91.6%. In spite of this appreciable reduction of residual monomer during post-polymerization, a modest increase of both the resin degree of grafting and molecular weight was observed, whereas the increase in the reacted double bonds was significant. In the post-polymerization of Latex 2, monomer conversion increased from 83% to over 99.7%, and substantial increments of both resin degree of grafting and molecular weight were observed. In addition, the increase of the fraction of reacted double bonds was less than for Latex 1. The post-polymerization of Latex 3, which spanned from $x = 95\%$ to $x > 99.995\%$ caused increases in both *RDG* and molecular weight which where stronger than for Latex 1, but more modest than for Latex 2. In addition, no alkyd double bonds were consumed. These results are in agreement with Fig. 2, where it can be seen that most of the variation of RDG and molecular weight occurred between 90 and 95% conversion.

Fig. 4 presents the estimated contribution of the hydrogen abstraction and the addition to the double bonds of the alkyd to the

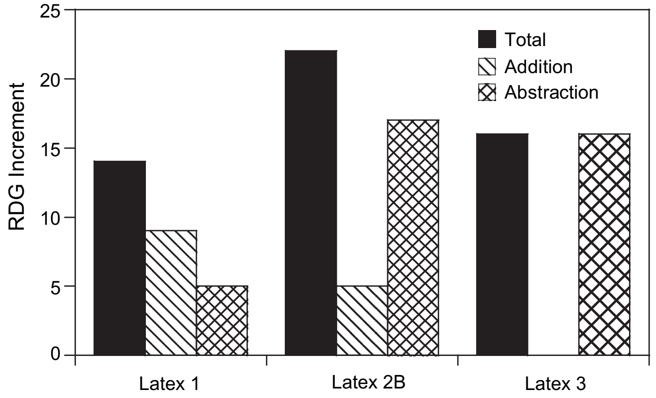

Fig. 4. Contribution of the hydrogen abstraction and addition to the alkyd double bonds to the increment of the resin degree of grafting in the post-polymerization of BA-based post-treated latexes.

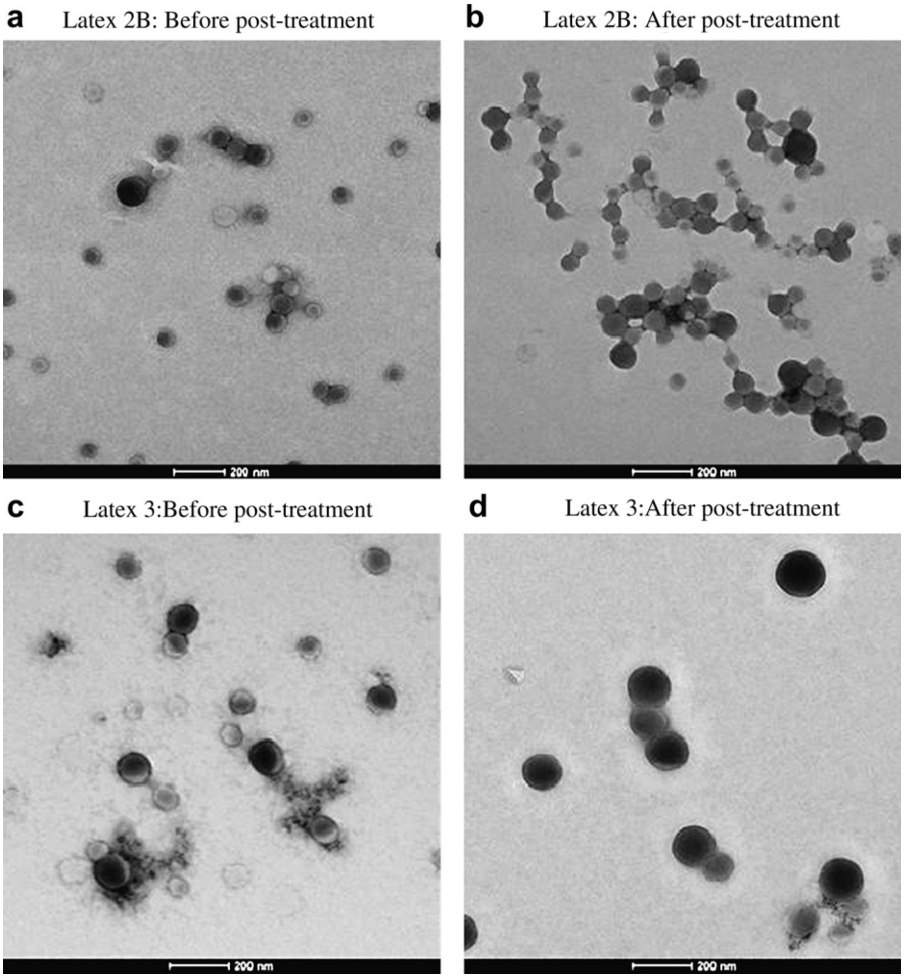

Fig. 5. TEM micrograph of BA-based Latex 2B (a–b) and Latex 3 (c–d).

increment in RDG for Latexes 1, 2 and 3. It can be seen that the contribution of the addition to the increment of RDG decreased from Latex 1 to Latex 3 (where it was nil).

The results in Table 3 and Figs. 2 and 4 suggest the following mechanism for the post-polymerization of BA-based latexes with TBHP/AsAc. The hydrophobic oxygen-centered *tert*-butoxyl radicals, produced in the aqueous phase, directly enter into the polymer particle. There, they can react with the double bonds of either the monomer or the alkyd resin and to abstract hydrogens from the alkyd resin and the BA units of the acrylic chains. The fact that the fraction of residual double bonds of the alkyd did not vary during the post-polymerization of Latex 3 suggests that the addition to the double bonds of the alkyd is not a preferred reaction for the *tert*-butoxyl radicals. Therefore, the relative importance of the addition with respect to hydrogen abstraction depends on the concentration of monomer. For high monomer concentrations, a substantial fraction of the *tert*-butoxyl radicals reacts with monomer giving carbon-centered radicals. These carbon-centered radicals are less efficient abstracting hydrogens than the oxygen-centered ones. This leads to a decrease of the relative contribution of the hydrogen abstraction at high monomer concentrations as observed in Fig. 4. It has been postulated that in the reactions of carbon-centered radicals with the alkyd resins, BA terminated radicals preferably react through addition to double bonds whereas the MMA terminated ones preferably abstract hydrogens [18]. However, the results in Fig. 4 do not fully support

Table 4
Post-polymerization of BMA-based latex with TBHP–AsAc.

Latex	Residual Monomer (ppm)	Initiator (% wbm)[a]	Gel (%)	ADG (%)	RDG (%)	RDB (%)	M_w (g/mol)
4A	67,500 ($x = 73$ %)		0	91	12	2	66,000
Post-polymerization	19,800 ($x = 92$%)	2.5	0	94	18	2	72,000
4B	80,000 ($x = 68$ %)		0	80	10	2	81,000
Post-polymerization	185	5.6	0	94	41	5	394,000
5	10,000 ($x = 96$ %)		0	98	15	5	148,000
Post-polymerization	500	2.5	0	100	18	5	103,000

[a] TBHP weight % based on the amount of residual acrylic monomer before the post-polymerization. TBHP/AsAc = 2/1 (molar ratio).

this, because as the polymerizations were carried out in batch (with respect to the monomers) and in this copolymerization, MMA is more reactive than BA ($r_{MMA} = 2.64$; $r_{BA} = 0.31$) [22], the BA/MMA ratio increased from Latex 1 to Latex 3, but no increase of the reacted double bonds of the alkyd was observed in the post-polymerization of Latex 3. However, this effect can be concealed by the high concentration of *tert*-butoxyl radicals.

Both, the *tert*-butoxyl radicals and the carbon-centered radicals can abstract hydrogens from the BA units of the acrylic chains. The rate of this process depends on the efficiency of the radicals for hydrogen abstraction and the concentration of polymerized BA units in the system. Because both the concentration of polymerized BA units and the concentration of *tert*-butoxyl radicals increased as monomer conversion increases, the rate of formation of tertiary radicals in the acrylic chains also increases with conversion. Propagation of these tertiary radicals leads to long branching formation, namely to the increase of the molecular weights. This increase is enhanced by bimolecular termination. It is worth pointing out that increase of molecular weight depends on both the number of long branches formed and their length. The number of branches increases with conversion but their kinetic length decreases. The fact that the molecular weight increased during post-polymerization indicates that the effect of the high number of branches overcome the decrease in length.

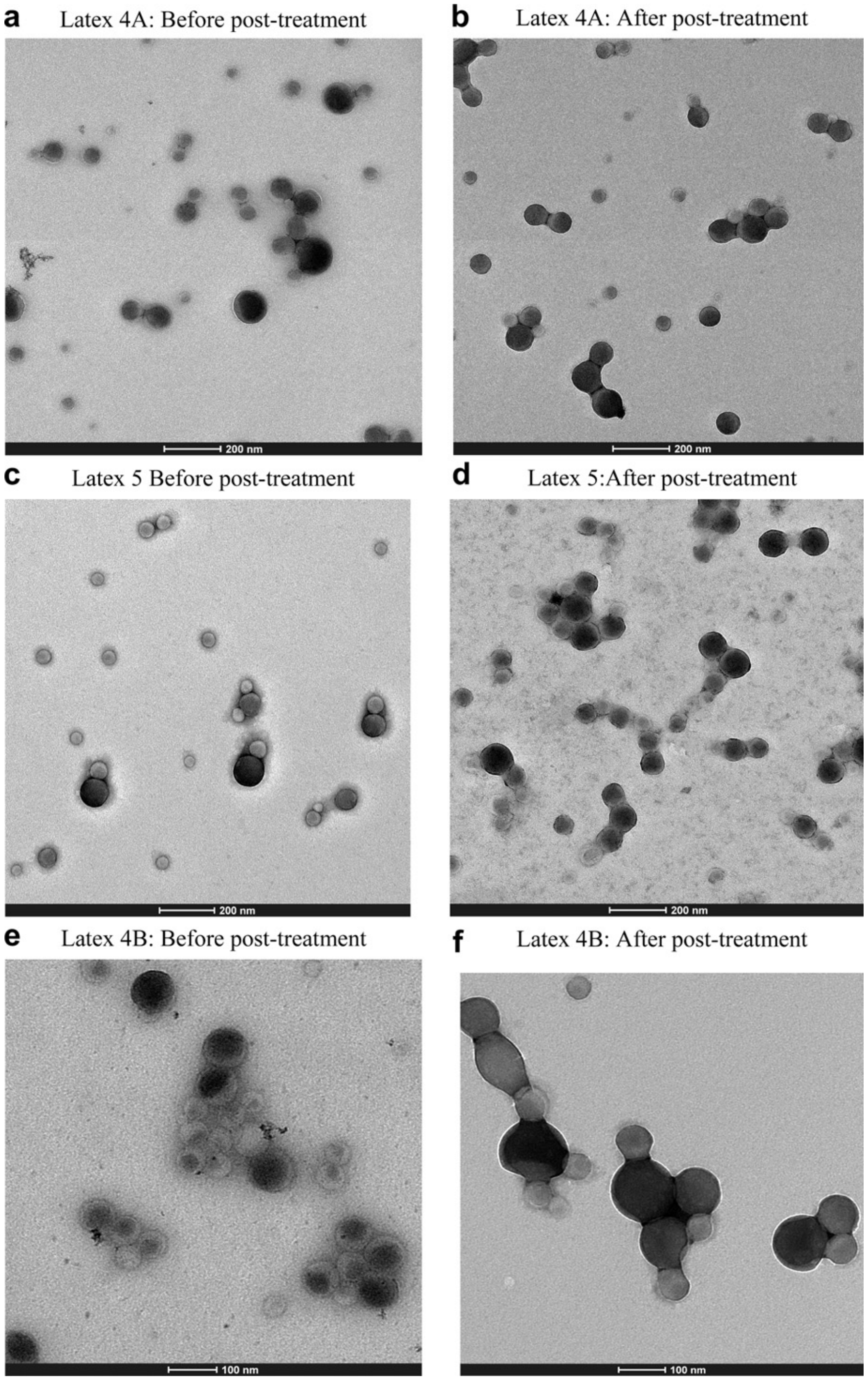

Fig. 6. TEM micrograph of BMA-based Latex 4A (a–b), Latex 5 (c–d), and Latex 4B (e–f).

Fig. 5 shows the effect of the post-polymerization with TBHP/AsAc on the particle morphology evolution of Latexes 2B and 3. The particle morphology turned more homogenous after post-polymerization, due to the higher incorporation of alkyd to the acrylic chains, which increased the compatibility of the grafted resin (mainly formed by acrylic chains) and reduced the amount of free alkyd resin.

3.2. Post-polymerization of BMA-based hybrid latexes

In the previous sections it has been shown that the presence of BA in the formulation had an important effect on the mechanisms occurring during post-polymerization with TBHP, and hence on the final polymer architecture and particle morphology. In order to further study the BA contribution, the effect of the post-polymerization with TBHP/AsAc of methacrylate latexes (i.e., using BMA instead of BA) on the residual monomer, polymer architecture and particle morphology was investigated. Table 4 summarizes the reactions carried out. Latexes 4A and 4B were post-polymerized with different concentrations of TBHP/AsAc (2.5 wt% and 5.6 wt%, respectively, of TBHP referred to the initial concentration of residual monomer). In both cases, TBHP/AsAc molar ratio was 2/1. Latex 5 contained a lower initial concentration of residual monomer and was post-polymerized under similar conditions of Latex 4A (2.5 wt% of TBHP referred to the initial concentration of residual monomer).

Table 4 shows that, as for BA-latexes, a minimum concentration of TBHP/AsAc is needed to reduce the residual monomer concentration below the target value and that this minimum concentration depends on the initial concentration of residual monomer. Latexes 4A and 5 were post-polymerized under the same conditions as those in Table 3, but the polymer architecture was not significantly modified and no alkyd double bonds were consumed. However, a strong modification of resin degree of grafting and molecular weight, with a low consumption of alkyd double bonds, was obtained when Latex 4B was post-polymerized with a high amount of initiator, under conditions comparable to Latex 2A in Table 2.

These results can be explained as follows. After entering into the polymer particle, the *tert*-butoxyl radicals can react with the double bonds of either the methacrylic monomers or the alkyd resin, and can abstract hydrogens from the alkyd resin. Hydrogen abstraction from the methacrylate units in the polymer backbone is limited because they do not have labile hydrogens. The fact that RDB was very low at the end of the synthesis of the latex, and that it practically did not vary during post-polymerization support the hypothesis that the methacrylate radicals are relatively unreactive with the double bonds of the alkyd. The efficiency of the methacrylate radicals for abstracting hydrogens from the alkyd resin cannot be estimated from the data available. Nevertheless, it is a positive contribution to the hydrogen abstraction by *tert*-butoxyl radicals, and hence the total extent of hydrogen abstraction should be higher than for BA-based latexes. Under these circumstances, the modest increase of RDG occurring during post-polymerization suggests that the radicals created in the alkyd chains are less reactive towards methacrylates than towards acrylates. At high concentrations of TBHP/AsAc, the number of radicals created in the alkyd chains was very high and this somehow overcame the low reactivity with the methacrylates leading to a substantial increase of the resin degree of grafting. Grafting may also occur through bimolecular termination of radicals, but this route might be hindered by the relatively high Tg of the methacrylic copolymer ($\approx 50\ ^\circ\mathrm{C}$), which would slow down the diffusion of chains.

Fig. 6 compares the particle morphology of those latexes before and after post-polymerization. No significant differences were observed for Latexes 4A and 5, mainly because the resin degree of grafting was only slightly affected during post-polymerization. Polymer particles became more homogeneous after post-polymerization of Latex 4B, due to the significant increase in the resin degree of grafting, which increased the compatibility of the grafted resin and reduced the amount of free alkyd.

4. Conclusions

In this work, the challenge of removing the high concentration of residual monomer commonly found in the synthesis of alkyd/acrylic waterborne hybrids is addressed. Because of the low water solubility and low vapor pressure of these monomers, devolatilization is not efficient and post-polymerization was used. It was found that TBHP/AsAc, which generates hydrophobic radicals in the aqueous phase, was more efficient than initiators yielding hydrophilic radicals in the aqueous phase. The minimum amount of initiator required to reduce the concentration of residual monomer below a target value depended on the initial concentration of residual monomer, which supports the hypothesis that limiting conversion is mainly due to the alkyd resin acting as a radical sink.

Polymer microstructure, which in turn affected particle morphology, was modified during post-polymerization. The extent of the modification depended on the initiator, monomer system and initial concentration of residual monomer used. Hydrophobic oxygen-centered radicals created in the aqueous phase that can enter directly into the polymer particles caused the strongest modification, by substantially increasing the resin degree of grafting through hydrogen abstraction from the alkyd resin. The extent of the modifications strongly depended on the monomer system. Acrylic monomers, which are fast reacting and contain easily abstractable hydrogens, led to stronger variations in both resin degree of grafting and molecular weights than methacrylic monomers.

Most of the variation of the RDG and molecular weight occurred between 90 and 95% conversion, which opens the possibility of modulating this variation by controlling the initial concentration of residual monomer, i.e., the conversion achieved in the synthesis of the hybrid latex.

Particle morphology was determined by the resin degree of grafting. RDG higher than about 35% yielded quite homogeneous particles, because it increased the compatibilization of the grafted polymer (that included practically all the acrylic polymer) and the alkyd resin, and reduced the amount of free alkyd resin.

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References

[1] Wang ST, Schork FJ, Poehlein GW, Gooch JW. J Appl Polym Sci 1996;60:2069–76.
[2] Nabuurs T, Baijards RA, German AL. Prog Org Coat 1996;27:163–72.
[3] van Hammersveld EMS, van Es J, Cuperus FP. Colloids Surf A 1999;153:285–96.
[4] Gooch JW, Dong H, Schork FJ. J Appl Polym Sci 2000;76:105–14.
[5] Tsavalas JG, Luo Y, Hudda L, Schork FJ. Polym React Eng 2003;11:277–304.
[6] Rodríguez R, Barandiaran MJ, Asua JM. Polymer 2008;49:691–6.
[7] Hudda L, Tsavalas JG, Schork FJ. Polymer 2005;46:993–1001.
[8] Overbeek GC, Scheerder J, Steenwinkel P, Tennebroek R. (Avecia Lmt.), WO 02/28977 A2; April 11, 2002.
[9] Goikoetxea M, Minari R, Beristain I, Paulis M, Barandiaran MJ, Asua JM. J Polym Sci Part A Polym Chem 2009;47:4871–85.
[10] Araujo PHH, Sayer C, PoÇo JGR, Giudici R. Polym Eng Sci 2002;42:1442–68.

[11] Barandiaran MJ, Asua JM. Removal of monomers and VOCs from polymers. In: Meyer T, Keurentjes J, editors. Handbook of polymer reaction engineering. Weinheim, Germany: Wiley-VCH GmbH & Co.; 2005. ISBN 3-527-31014-2.

[12] Salazar R, Ilundain P, Alvarez D, Da Cunha L, Barandiaran MJ, Asua JM. Ind Eng Chem Res 2005;44:4042–50.

[13] Ilundain P, Alvarez D, Da Cunha L, Salazar R, Barandiaran MJ, Asua JM. J Polym Sci Part A Polym Chem 2002;40:4245–9.

[14] Ilundain P, Alvarez D, Da Cunha L, Salazar R, Barandiaran MJ, Asua JM. J Polym Sci Part A Polym Chem 2003;41:3744–9.

[15] Minari RJ, Goikoetxea M, Beristain I, Paulis M, Barandiaran MJ, Asua JM. J Appl Polym Sci 2009;114:3143–51.

[16] Official Methods of Analysis of AOAC International. AOAC official method 28.023, iodine absorption number Wijs method. Arlington: AOAC International; 1984.

[17] Ilundain P, da Cunha L, Salazar R, Alvarez D, Barandiaran MJ, Asua JM. J Appl Polym Sci 2002;83:923–8.

[18] Tsavalas JG, Luo Y, Schork FJ. J Appl Polym Sci 2003;87:1825–36.

[19] Goicoechea M, Barandiaran MJ, Asua JM. Macromolecules 2006;39:5165–6.

[20] Hiller S, Arlt W, Mokrushina LV. Macromolecules 2003;36:6607–12.

[21] Moad G, Solomon DH, editors. The chemistry of free radical polymerization. Elsevier Science Ltd; 1995. p. 26–7.

[22] Bandrup J, Immergut Edmund H, Grulke Eric A, Abe Akihiro, Bloch Daniel R. Polymer handbook. 4th ed. New York: Wiley; 2005.