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Polymer 46 (2005) 9555–9561
polymer
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Independent control of sol molar mass and gel content in acrylate polymer/latexes

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Received 27 April 2005; received in revised form 19 August 2005; accepted 22 August 2005
Available online 13 September 2005

Abstract

Poly *n*-butylacrylate latexes are commonly used as the base ingredient in the formulation of pressure sensitive adhesives, PSA. In the typical starved semi-batch process carried out to produce this latex and due to the non-linear nature of the kinetics, chain transfer to polymer plus bimolecular termination by combination, polymer networks are produced. The molar mass distribution of these polymer latexes is characterized by a soluble and an insoluble fraction, so-called gel. Both fractions strongly affect the adhesion properties, but unfortunately the independent control of these properties is a difficult task, that has not been solved yet. In this work, the concentrations of chain transfer agent and cross-linker were used in an attempt to exercise control over the molar mass of the soluble part and the amount of gel polymer. It was found that by simultaneously manipulating both variables it was possible to modify the gel content of the polymer without completely sacrificing the sol molar mass. The adhesion properties, tack and resistance to shear, measured on films cast from the latex demonstrated that a good PSA can be obtained by properly balancing the amount of CTA and cross-linker in the formulation.

Keywords: Sol molar mass; Gel fraction; Acrylate latexes

1. Introduction

Acrylic polymers/latexes find an extensive use in adhesives, coatings and impact modifiers among other products [1–3]. These are highly branched polymers that are often characterized by their solubility in a given solvent (e.g. THF). The non-soluble fraction is called gel and it is formed by a highly branched and/or reticulate polymer. The application properties of the acrylic polymer depend on the T_g of the polymer, the relative amounts of the sol and gel polymer as well as on the molar mass distribution of the sol fraction and the cross-linking density of the gel fraction. The T_g is easily controlled by varying the relative amounts of the soft (e.g. *n*-butyl acrylate) and hard (e.g. methyl methacrylate) comonomer. The independent control of the sol MMD and the gel fraction has proved to be challenging. Thus, in the semicontinuous emulsion polymerization of *n*-butyl acrylate the amount of gel formed was almost independent of the initiator concentration and the monomer feed rate, whereas the molar mass of the sol fraction decreased as the initiator concentration increased and the monomer feed rate decreased [4–6].

On the other hand, the gel fraction decreased with the concentration of chain transfer agent (CTA) whereas the sol molar mass remained essentially unaffected [7].

Addition of cross-linking agents led to a substantial increase of the gel content (from 55–60% without cross-linker to 90–95% with 2.3 mol% of cross-linkers such as diacrylates, allyl methacrylates or diallyl maleate). However, the molar mass decreased severely [8–11].

Copolymerization of butyl acrylate with styrene [12] and methyl methacrylate [13] led to a decrease of the gel fraction for increasing concentrations of these comonomers (10 wt% of St or MMA reduced gel content to almost nil). On the other hand, the sol molar mass increased with the comonomer concentration. In addition, the gel content of these polymers may be varied by post treatments [14]. However, copolymerization involves a change in T_g that may be undesirable. In this work, we explored the possibility of decoupling gel content and sol molar mass

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0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.08.061

during the polymerization of *n*-BA by simultaneously introducing in the formulation CTA (that decreases de gel content and the sol molar mass) and a cross-linking agent (that increases gel content and decreases molar mass). The goal was to control these microstructural properties without affecting the T_g of the polymer latex. The polymers produced were characterized in terms of their adhesion properties (tack and shear resistances).

2. Experimental section

2.1. Materials

n-Butyl acrylate (*n*-BA, Quimidroga, Spain), potassium persulfate as initiator ($K_2S_2O_8$, Fluka, Spain), sodium lauryl sulfate (SLS, Merck, Spain) and Dowfax 2-A1 (sodium dodecyl diphenyloxide disulfonate, Dow, Spain) as surfactant, acrylic acid (AA, Quimidroga) as stabilizer, sodium hydrogen carbonate as buffer ($NaHCO_3$, Panreac, Spain), *n*-dodecyl mercaptan as CTA (Fluka) and allyl methacrylate as cross-linker(Aldrich) were all used as received. SLS was used to prepare the seed and Dowfax 2-A1 was used for the seeded semicontinuous experiments. All polymerizations were carried out using deionized water.

2.2. Polymerizations

All reactions were seeded. The poly(*n*-BA) seed was prepared batchwise following the formulation shown in Table 1 in a 2 L reactor at 65 °C, and kept overnight at 90 °C in order to decompose the unreacted initiator. Table 1 also shows the properties of the seed.

The semicontinuous emulsion polymerizations were carried out at 75 °C in 1 L glass reactor fitted with a reflux condenser, a sampling device, a nitrogen inlet, two feed inlet tubes and a stainless steel stirrer composed by an anchor plus a set of three pitch-blade impellers rotating at 200 rpm. Table 2 shows the formulation used. The experimental procedure was as follows: the seed and a fraction of surfactant, initiator and water were initially charged into the reactor. The rest was fed in two streams having both the same feeding time. One was a monomer pre-emulsion (that was formed by continuously stirring, by means of a magnetic bar, a surfactant solution plus the comonomers and CTA, when employed) and the other an initiator solution. Both streams were added at a constant flow rate for 180 min. Table 3 presents a summary of the experiments carried out in this study in terms of the concentration of chain transfer agent and cross-linker used in the polymerizations.

Table 1
Seed formulation and properties

n-Butyl acrylate (g)	250
Water (g)	1000
SLS (g)	5
$NaHCO_3$ (g)	1.25
$K_2S_2O_8$ (g)	1.25
Particle size (nm)	99
Solids content (%)	19.7
Gel content (%)	9

Table 2
Formulation used in the seeded semicontinuous emulsion polymerizations of *n*-BA

	Initial charge	Stream 1	Stream 2
Seed (g)	102	–	–
H_2O (g)	30	20	255
Dowfax (g)	1.66	–	3.34
n-BA (g)	–	–	225.4
Acrylic acid (g)	–	–	4.6
$K_2S_2O_8$[a] (%)	0.15	0.15	–
CTA[a] (%)	–	–	0–0.6
AMA[a] (%)	–	–	0–0.23

[a] Based on the *n*-BA monomer weight.

2.3. Polymer characterization

2.3.1. Conversion measurements

Samples withdrawn from the reactor during the polymerization were short-stopped with hydroquinone and analyzed gravimetrically to determine the instantaneous (based on the amount of monomer fed), and the overall conversion (based on the total amount of monomer in the formulation), X_i and X_0, respectively.

2.3.2. Particle size

Particle size was measured by dynamic light scattering (DLS, Coulter N4 plus). For the DLS analysis, samples were diluted to such low concentrations ($<1.10^{-3}$ g/L) that one can safely assume that no monomer was present in the polymer particles, namely that unswollen particle sizes are measured. The analysis performed in the DLS equipment was carried out at 25 °C, with a run time of 120 s and using the unimodal analysis option. Each sample was analysed three times and only samples containing baseline error below 1% were considered to calculate the average particle size. The results obtained by this technique were used to calculate the total number of particles of the latex at time *t*.

2.3.3. Fraction of gel

The emulsion polymerization of *n*-butyl acrylate yields a polymer containing a significant gel fraction [4–6]. The gel content was measured by two different methods that are reported below.

The first method to determine the gel fraction consisted in a continuous extraction with tetrahydrofuran (THF) under reflux during 8 h [5,9,11]. The extraction was achieved in a 2 L-glass reactor. A filter (weight W_1), where a few droplets of latex were deposited, was dried overnight at room temperature. This filter plus the dried polymer was weighed

Table 3
Structural (sol weight-average M_w and gel content) and adhesive properties (tack and resistance to shear) for the n-BA latexes produced using different concentrations of CTA and AMA

Run	1	2	3	4[a]	5	6	7
CTA (wt%)	0	0.15	0.6	0	0.15	0.2	0.15
AMA (wt%)	0	0	0	0.23	0.23	0.23	0.13
Gel fraction (%)	60	3	0	88	82	71	77
M_w (g/mol)	249,000	168,000	58,000	125,000	100,000	65,000	68,000
Swelling (w/w)	22.8 ± 1.6[b]	–	–	11.5 ± 0.8	–	–	–
Tack (cm)	5.1 ± 0.7	1.7 ± 0.2	0	5.5 ± 0.9	3 ± 1	0.91 ± 0.45	1.95 ± 0.6
Shear	20 h 30 min ± 1 h	6 min ± 1 min	0	7 min ± 2 min	1 h ± 7 min	47 min ± 7 min	2 h 30 min ± 15 min

[a] This latex was taken from Ref. [10] and characterized in this work for the adhesive properties.

[b] Data measured to a latex synthesized under the same conditions (Ref. [10]).

(W_2) before performing the continuous extraction with THF under reflux. After 8 h of extraction the filter, which contained the non-soluble polymer (gel), was dried at room temperature during 1 night and weighed again (W_3). Two filters were used for each sample.

The amount of gel was calculated as:

$$\text{Gel content} = \frac{W_3 - W_1}{W_2 - W_1}$$

The second method consisted in a standard THF extraction in a Soxhlet apparatus. The latex was first coagulated in a solution of $CaCl_2$ and the coagulum dried for 2 days at 50 °C in a ventilated oven. The cartridge (weight W_1) was then loaded with about 1 g of coagulated latex (W_2) and the extraction was carried out under reflux during 24 h. The cartridge was dried again in a ventilated oven at 80 °C and weighed (W_3) to calculate the gel fraction as in the previous method. The THF was evaporated and the extracted sol polymer was recovered to measure the sol weight-average molar mass by size exclusion chromatography (SEC) as it will be explain in the next section.

2.3.4. Molar masses

The sol weight-average molar mass of the polymer collected by the THF extraction was determined by SEC. The sol fraction was added drop-wise to THF until a polymer concentration of approximately 0.4 g/L was reached. The sample was filtered (0.45 μ, Albet NY-045-13-BL) before injection in the SEC instrument (Waters) that consisted of a pump, three columns (Styragel of porosity 10^2, 10^4 and 10^6 Å) and a refractive index detector.

Chromatograms were obtained at 35 °C using a THF flow rate of 1 mL/min. Polystyrene standards were used for the calibration. The molar mass was computed by applying the universal calibration concept using the following Mark–Houwink–Sakurada relationship for Pn–BA: $K = 12.2 \times 10^{-5}$ dL/g and $a = 0.700$ [15]. It is important noting that the M–H–S constants did not correspond to highly branched poly n-BA, but to relatively low branched poly n-BA polymer. Therefore, the molar mass values reported in Table 3 cannot be taken as the actual values, but they are useful for comparison purposes. The raw data (detector signal vs elution time) was used to compare the molar mass distributions of the different latexes.

2.3.5. Swelling

The swelling value of a polymer is inversely proportional to the cross-linking density, namely, the more cross-linked the polymer the less its swelling capability. In this work, the swelling values of some of the copolymers produced were measured. Swelling experiments were carried out in methyl ethyl ketone, for 24 h at ambient temperature. The swelling of the copolymer samples was calculated as the ratio between the weight of swollen gel polymer and the dry weight of the gel polymer.

2.3.6. Adhesive tests

An important application of acrylic latexes is their use as pressure sensitive adhesives (PSAs), mainly employed for labels, tapes, decorative films and protective materials. Each specific application requires appropriate end-uses properties, characterized by a combination of specific values of tackiness, resistance to shear and resistance to peel. It has been proven that several latex properties, such as copolymer composition, molar mass distribution, gel content, and cross-linking density strongly affect the values of the adhesive properties [16–22].

Adhesive properties (tack and resistance to shear) were measured for the latexes produced under several operational conditions. The purpose of these measurements was to determine the effect of the microstructure of the polymer, namely, fraction of gel and sol M_w, on the PSA properties.

The backing for the adhesives prepared in this work was an electrostatically discharge-treated polypropylene film 29 mm wide. The latexes with solids content of about 40 wt% were applied on the polypropylene film by means of a metallic applicator ensuring the formation of a continuous 60 μm coat and then introduced for 20 min in an oven at 60 °C. The adhesive tape was then cooled at room temperature and after this period, the tack tests were carried out at room temperature whereas the shear tests were carried out in an oven at 50 °C.

The rolling ball tack test was used to measure the tack of the polymer films [23]. For each latex, five measurements were carried out and the average and the variation coefficient were calculated. Note that the larger the distance the less tacky the adhesive.

Shear resistance is the ability of pressure sensitive tapes to remain adhered under load applied parallel to the surface tape. The method used here consists of holding a mass of 1000 g on a standard area tape (25×25 mm^2) applied to a panel 2° from the vertical (SAFT tester 12 machine, Sneep Industries S.V, The Netherlands) [24]. The purpose of the final inclination from vertical is to ensure that the tape will experience no peeling action, only shear. The time elapsed between the application of the load and the complete separation of the tape from the panel is the measurement of the resistance to shear test. For each latex, four measurements were carried out and the average and the variation coefficient were calculated.

Note that all the adhesive tests were performed 2 days after casting the films from the polymer latexes.

3. Results and discussion

3.1. Polymerization reactions

Seven experiments have been carried out with the recipe of Table 2 and the concentrations of CTA and AMA described in Table 3. In Run 1, a homopolymerization of *n*-BA without any chain transfer agent and cross-linker was carried out as a reference. Run 2 and 3 contained a 0.15 and 0.6 wt% of CTA, but no cross-linker, and Run 4 contained 0.23 wt% cross-linker, but no CTA. The rest of runs had both CTA and cross-linker in different concentrations.

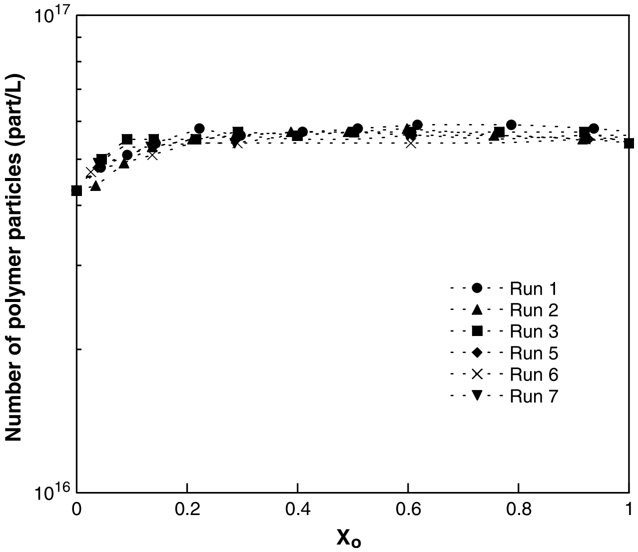

Fig. 2. Evolution of the total number of particles for the experiments carried out with varying amounts of CTA and AMA.

Figs. 1–3 display the instantaneous conversion, the total number of polymer particles and gel content evolution for the seven experiments. Table 3 presents the final gel content, sol weight-average molar mass, and swelling values (for Runs 1 and 4) of the final latexes.

Fig. 1 shows that the addition of either CTA or AMA had no significant effect on the kinetics. All the experiments evolved under rather starved conditions and the slight increase of the conversion during the feeding period can be attributed to an increase of the average number of radicals per particle caused by the particle growth. The polymerization rate was controlled by the feeding rate of the monomer.

Fig. 2 shows that the evolution of the total number of polymer particles presented the same trend for all the experiments. After an initial slight increase on the number of polymer particles, it remained constant during the rest of

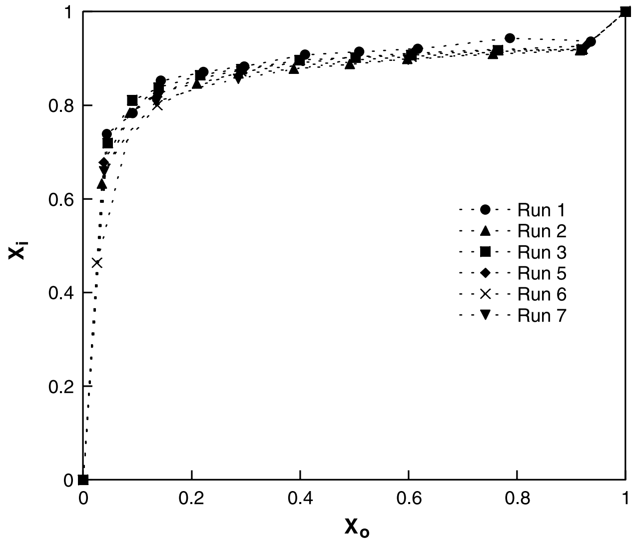

Fig. 1. Evolution of instantaneous conversion for the seeded semibatch emulsion polymerizations of *n*-BA.

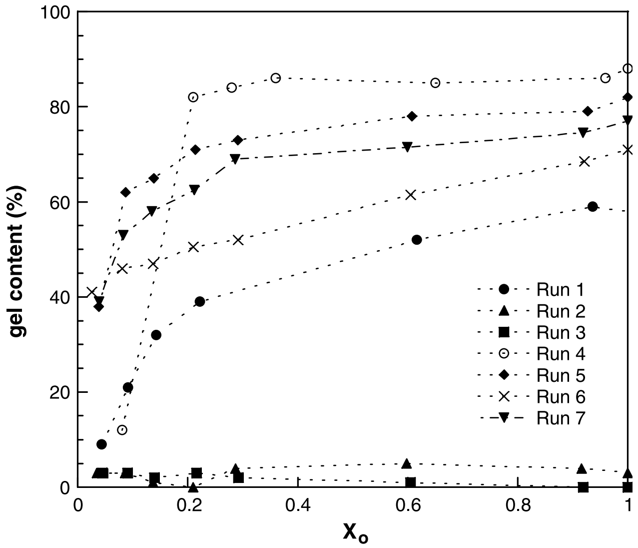

Fig. 3. Evolution of the fraction of gel for the experiments carried out with varying amounts of CTA.

the polymerization. These results are in agreement with the data gathered by Plessis et al. [4–7] and Bouvier et al. [8–11] for the homopolymerization of *n*-BA with CTA and AMA, respectively.

Fig. 3 displays the gel content obtained in these experiments. It is worth noting that both methods provided similar values of gel content. In the experiment without CTA and AMA, Run 1, the amount of gel increased from the amount of gel of the seed up to 60%. In the homopolymerization of *n*-BA gel is formed by the occurrence of intermolecular chain transfer to polymer plus termination by combination. In Runs 2 and 3 (0.15 and 0.6 wt% of CTA) the final amount of gel was almost negligible (3 and 0%, Table 3). The reduction of the gel content was basically due to the decrease of the kinetic chain length caused by the predominant chain transfer to CTA, which made the transfer of sol molecules to gel almost insignificant [7]. Table 3 shows that the sol weight-average molar mass decreased as the amount of CTA was increased. In Run 4 (0.23 wt% AMA), the amount of gel increased to 88% because the propagation to pendent double bonds become the predominant cross-linking mechanism, leading to highly cross-linked polymer networks within the polymer particles. The swelling values, inversely related to the cross-linking density of the polymer, indicated that the gel fraction produced with 0.23 wt% of AMA was significantly more cross-linked than the homopolymer of BA, namely, that the network structure was tighter for the polymer formed with AMA.

Runs 4–6 were carried out with the same amount of cross-linker but with an increasing concentration of CTA (from 0 to 0.2 wt%). Interestingly, in these experiments the amount of gel decreased from 88 to 71%, and the sol average molar mass from 125,000 to 65,000 g/mol. The decrease being more important when the CTA was increased from 0.15 to 0.20%. Runs 5 and 7 had the same amount of CTA (0.15 wt%) and different amounts of AMA. In this case decreasing the amount of the cross-linker led to a decrease in the gel content from 82 to 77%. At the same time the sol molar mass was also slightly reduced.

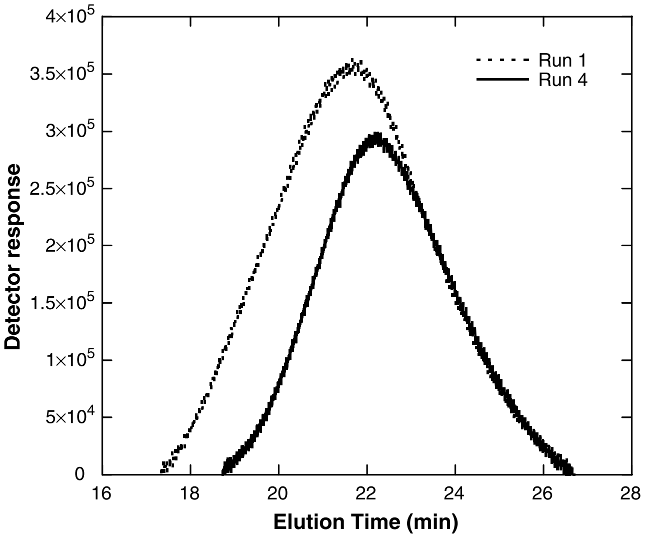

Fig. 4. SEC chromatograms of the sol polymer fraction of latexes 1 and 4.

These results can be rationalized in the following way. The ratio monomer to CTA controls the kinetic chain length of the primary chains, and the monomer to polymer ratio the propagation to pendent double bonds or cross-linking reactions. Therefore, when for a given concentration of cross-linker, the amount of CTA was increased (Runs 4–6) the gel content was reduced because termination by combination occurred between shorter polymer chains that reduced the contribution of this mechanism to gel formation. Hence, more cross-linking reactions were needed to produce gel polymer, which as a consequence was reduced. The sol molar masses were also reduced because the kinetic chain length was shorter and the gel polymer preferentially incorporated longer chains. Nevertheless, the effect of the CTA was modest as compared with formulations were the cross-linker was not present (Runs 1 and 2). The same rationale explains the experiments with the same CTA and an increasing amount of AMA (Runs 7 and 5).

These results indicate that the simultaneous usage of CTA and cross-linking agents expanded the range of polymer microstructures achievable by emulsion polymerization. In particular, poly *n*-butylacrylate with gel contents in the range of 60–90% and molar masses of the sol polymer in the range 50,000–250,000 g/mol were obtained. In the next section the adhesion properties of these latexes will be studied and the effect of gel content and sol molar masses on the performance of the adhesives based on these latexes determined.

3.2. Adhesive properties of the latex

The tackiness and the resistance to shear of the *n*-BA latexes prepared with different concentrations of CTA and AMA were measured as described in the Section 2. The results of the adhesive properties as well as the molar masses, gel content, and swelling (Runs 1 and 4) of each latex are shown in Table 3.

Comparison of Runs 2 and 3 shows that, in absence of gel polymer, the lower the sol molar mass, the better the tackiness (note that the adhesive is tackier when the distance is lower). However, the results obtained with latexes 1 and 4 show that the molar mass of the sol fraction was not the sole variable affecting tackiness. Latex 4 had a lower sol average molar mass, but significantly higher gel content (88 over 60%) than latex 1, but both latexes presented a similar tack.

Interestingly, the SEC chromatograms of the sol fraction of latexes 1 and 4 (Fig. 4) present a similar fraction of polymer eluting at high elution times for both samples; namely that low molar mass polymer chains are similar in both latexes.

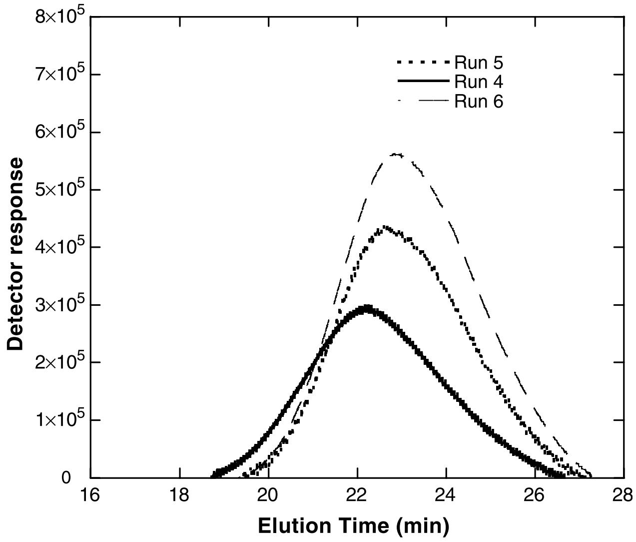

Fig. 5. SEC chromatograms of the sol polymer fraction of latexes 4–6.

Fig. 5 presents the SEC chromatograms of latexes 4–6. In this case the fraction of low molar mass polymer (fraction of polymer eluting at higher elution times) is higher for the latexes with higher tack.

Resistance to shear was also affected by the sol molar mass and the gel content. The best resistance to shear was found for latex 1, a pure homopolymer of *n*-BA, synthesized in absence of CTA and AMA. This latex had a gel content of 60% that was loosely cross-linked as indicated by the low swelling value. An small addition of CTA in the formulation, latex 2, reduced the molar mass and completely eliminated the formation of gel polymer and hence dramatically reduced the resistance to shear (from more than 20 h to a few minutes). An increase in gel content, as in latex 4 yielded the same effect, the resistance to shear dropped sharply. The reduction of the shear resistance can be attributed to the higher amount of gel polymer and to the tighter structure of the polymer network (as revealed by the higher cross-linking density of this polymer) formed when AMA was used as cross-linker; namely, the chain length between cross-link points was much shorter when AMA was used. The rigidity (higher cross-linking density) of the network likely reduced the interpenetration of particles during film formation and hence produced a weaker adhesive [25].

In latexes produced with both CTA and AMA, the resistance to shear as well as the tack can be modified. In the latexes with the same amount of AMA (0.23 wt%), but increasing amount of CTA (latex 4–6), the resistance to shear increased with CTA content (latex 5), but a further increase (latex 6) slightly reduced its value. However, tackiness significantly improved from latex 4 (no CTA) to latex 6 (CTA 0.2 wt%).

A good compromise was found for latex 7 where the CTA concentration was as in latex 5, but the amount of AMA employed was reduced. In this case both resistances to shear and tack increased leading to a well balanced adhesive.

Notwithstanding, it is worth pointing out that no attempt to optimize the concentrations of CTA and AMA to produce a better adhesive performance was done in this work.

4. Concluding remarks

The effect of the simultaneous addition of chain transfer agent and cross-linker in the seeded semibatch emulsion polymerization of *n*-BA was investigated. The effect of these variables on kinetics and microstructural properties (sol molar mass distribution and gel content) of the latexes was addressed. It was found that the amount of gel produced in the experiments with CTA and AMA could be controlled between the maximum level achieved in the presence of only AMA (88%) and the amount of gel achieved in the pure homopolymerization of *n*-BA (60%). The sol molar mass was always lower than the molar mass achieved in absence of CTA and AMA, although could also be modified. The adhesive properties were strongly affected by the gel content and the MMD of the sol fraction. Tack depended on the fraction of low molar mass chains. In general, increasing gel content (adding cross-linker in the formulation) above a certain critical value damaged the adhesive properties. However, relatively high gel content with moderately low sol molar mass (achieved by adding also CTA in the formulation) allowed enhancing the adhesive properties. Thus, a good balance of resistance to shear and tack was found for a latex produced with 0.15 wt% of CTA and 0.13 wt% of AMA.

Acknowledgements

J. Chauvet gratefully acknowledges the scholarship from ENSCM de Montpellier. The financial support from the University of the Basque Country (Grant UPV 0021.215-13594/2001) is also appreciated.

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