Isolation of the effect of the hairy layer length on the mechanical properties of waterborne coatings.

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ABSTRACT

The effect of the acidic hairy layer length on the interdiffusion of polymer between particles and as a consequence on the mechanical properties of the films produced from waterborne coatings has been studied. In order to isolate this effect, latexes with the same particle diameter and molecular weight but stabilized with poly(acrylic acid)-*block*-poly(butyl acrylate) (PAA-*b*-PBA) block copolymers of controlled and different lengths were prepared. Tensile strength measurements showed at the macroscopic level that the presence of AA chains in the particle surface reduced the mechanical properties of the films dried at room temperature, being its effect worse the longer the AA chain length. Higher annealing temperatures erased the negative effect of the acidic hairy layer on mechanical properties. The neutralization with NaOH instead of with NH_4OH also led to worse mechanical properties. These macroscopic results were supported by Fluorescence Resonance Energy Transfer (FRET) experiments that showed that at the microscopic level, the extent of interdiffusion occurred slower when the AA chains in the particles surface increased, the annealing temperature was lower and when NaOH was used as neutralizing agent instead of NH_4OH.

Keywords: Latex film formation, FRET, mechanical properties, electrosteric stabilizers, controlled sized acidic hairy layer.

INTRODUCTION

Surfactants are the necessary evil in emulsion polymers. They are necessary to impart colloidal stability to the polymer particles but, on the other hand, they may present serious drawbacks in the final film applications. During the film formation, most commonly used anionic surfactants may migrate to the film interfaces or form aggregates in the interior of the films reducing properties such as gloss or adhesion and increasing water sensitivity [1-7]. A strategy to avoid this negative influence is to use macromolecular surfactants with reduced mobility. Among different macromolecular surfactants, amphiphilic polyelectrolyte block copolymers are particularly interesting. The hydrophobic blocks of the block copolymers can anchor onto the particle surface while the hydrophilic blocks extend into the water-phase and create a well-defined hydrophilic shell named hairy layer. Amphiphilic polyelectrolyte block copolymers offer significant advantages for their use as surfactants, as they have proved to be powerful stabilizers in emulsion polymerization [8-11] and they confer electrosteric stabilization to the latex which is a combination of the usual steric and electrostatic stabilizations [12]. Even if amphiphilic polyelectrolyte block copolymers have been used as emulsifiers in emulsion polymerization reactions in several works [8-11], not much about the film properties of those latexes was reported.

The hydrophilic blocks of these amphiphilic block copolymers are usually composed by acidic comonomers, such as acrylic acid (AA) or methacrylic acid (MAA). Apart from conferring colloidal stability to the dispersed polymers, these monomers may improve application properties of the latex films such as freeze-thaw and pigment mixing stability, as well as promote the adhesion of the film to the substrate, which are of primary importance in polymer coatings.

On the other side, the use of acidic comonomers has been reported to produce polymer diffusion retardation [13-17] in the last step of the film formation, which is an essential step to obtain high performance coatings. It has been found that if the amount of carboxylic groups on the particle surface is large enough, it may form a hydrophilic membrane during film formation that could act as a barrier and could prevent or retard polymer interdiffusion between particles. As a consequence, the mechanical properties of the films might be affected since a good cohesion of a latex film is not achieved until the polymers from neighbouring particles have interdiffused across the particle boundaries [18-20]. This continuous membrane can be disrupted by annealing the films at higher temperatures and therefore by increasing the mobility of the polymer chains [13, 17].

According to previous works on these cellular films [13, 14], interdiffusion of polymer chains between neighbour particles was suppressed or retarded until the membranes were broken up by annealing the films at temperatures higher than the T_g of shell polymer, i.e. the PAA chains on the surface of the polymer particles. Further works of Winnik et al. [15, 16] revealed that neutralization of the carboxylic acid groups in the particles surface retarded even more the interparticle polymer diffusion and divalent salts retarded interdiffusion more than monovalent ones. It must be pointed out that, even if all these works studied the effect of the presence of acidic monomers in the particles surface, all of them used the acidic monomers as a comonomer in the initial reaction recipe. Thus, none of these works have controlled the exact length nor the composition of the hairy layer on the particles surface.

In our previous work [21] we used poly(acrylic acid) homopolymers and block copolymers of different lengths as emulsifier during emulsion polymerization reactions with the objective to investigate the effect of the length of electrosteric stabilizers on latex stabilization and film properties. It was observed that longer PAA chains led to worse

mechanical properties, likely as a consequence of the slower interdiffusion between polymer particles in the last step of film formation. However, in those experiments the latexes had not only different hairy layers but also different particle diameters and polymer molecular weights, which in turn could also affect the final film properties.

Therefore, in order to isolate both effects, the one of the polymer microstructure and the one of the length of the acidic hairy layer, in the present work, latexes were prepared by adsorbing the block copolymers of different lengths on a surfactant-free latex. To this end, first, poly(acrylic acid)-*block*-poly(butyl acrylate) (PAA-*b*-PBA) block copolymers of different and controlled lengths were synthesised to later be used as surfactant of a conventional film forming latex, with the objective to obtain latexes with hairy layers of different and controlled lengths. The use of an asymmetric RAFT molecule that leads to the formation of asymmetric block copolymers, which would adopt an extended configuration, was chosen in this work in contrast to the symmetric RAFT molecule used in our previous work [21]. Interdiffusion between particles was analysed performing two different experiments; on the one hand, tensile strength of the films was measured as indicator of the cohesive strength of the films. On the other hand, the extent of interdiffusion was measured at microscopic level by Fluorescence Resonance Energy Transfer (FRET) experiments. Even if the post-addition of different surfactants on clean latexes has been carried out before [5], it should be remarked that, up to our knowledge, this is the first time that tensile strength and FRET experiments are performed with latexes of the same molecular weight and particle diameter but with AA hairy layers of different and controlled lengths.

MATERIALS AND METHODS

Materials

2-([[(butylsulfanyl) carbonothioyl] sulfanyl) propanoic acid (BCPA) was used as RAFT agent and it was synthesized following the work carried out by Ferguson and co-workers [22]. Trimethylsilyldiazomethane 2 M in hexane solution (TMS-diazomethane, Sigma-Aldrich) was used for the methylation of the carboxylic acid groups of the block copolymers before Size Exclusion Chromatography (SEC) measurements. Deuterium oxide (D_2O, Sigma-Aldrich) was used as solvent for Nuclear Magnetic Resonance (NMR) sample preparation. Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Fluka) were all used as supplied. 4,4´-azobis(4-cyanopentanoic acid) (V-501, Fluka) and sodium dodecyl sulfate (SDS, Aldrich) were used as initiator and emulsifier respectively. (9-Phenanthryl)methyl methacrylate (Phe-MMA, Toronto Research Chemicals) and [1-(4-nitrophenyl)-2-pyrrolidinmethyl] acrylate (NNP-A, Aldrich) [23] were used as donor/acceptor pair for FRET experiments. GPC grade tetrahydrofuran (THF, Scharlab), sodium hydroxide (NaOH, Panreac) and ammonium hydroxide 5N solution (NH_4OH, Fluka) were used as received. Deionized water was used in all the reactions.

The PAA-*b*-PBA block copolymers of different and controlled lengths used in this work were synthesized by solution polymerization in ethanol using BCPA as RAFT agent and V501 as initiator. Figure 1 shows the structure of the used RAFT agent as well as of the expected block copolymers.
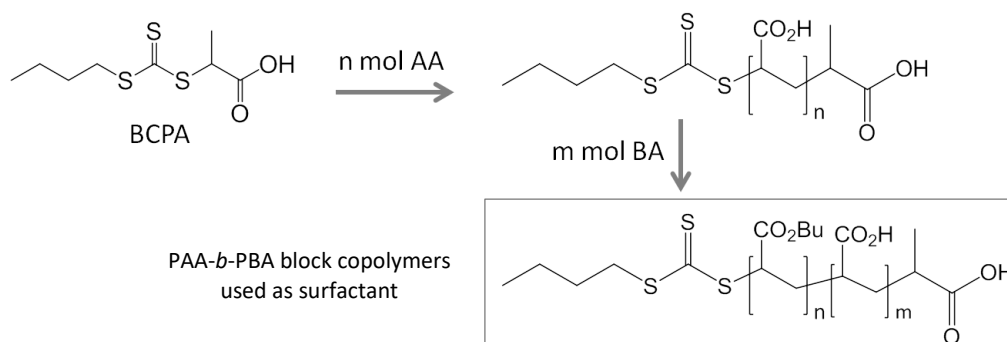
Figure 1 Scheme of the formation of PAA-*b*-PBA block copolymer using BCPA as RAFT agent.

Table 1 shows the number average molecular weight (Mn) and molar mass dispersity (Đ) of the final block copolymers obtained, analysed by Size Exclusion Chromatography equipped with a Refractive Index detector (SEC/RI) (after methylation of carboxylic acid groups [24]) and using polystyrene standards. Absolute molecular weight measured by SEC coupled with Multiangle Light Scattering detector (SEC/MALS) and number of monomer units measured by NMR (the experimental procedure is shown in the Supporting Information). The name of each copolymer has been selected as the abbreviation of the monomer used with the number of designed monomer units in it.

Table 1 Characterization of the block copolymers synthesized by RAFT polymerization: Number average molecular weight and molar mass dispersity by SEC/RI, monomer units by NMR and absolute molecular weight by SEC/MALS.

	SEC/RI		NMR			SEC/MALS	
	Mn (g/mol)	Đ	AA units	BA units	Calculated Mn (g/mol)	Mn (g/mol)	Đ
AA10-BA20	3010	1.1	9	17	3062	3200	1.1
AA20-BA40	5010	1.2	17	27	4918	5100	1.1
AA30-BA50	6580	1.3	26	33	6334	6800	1.1

As it can be seen in Table 1, the coincidence between the number of AA units designed to be in the homopolymer and those really present is quite good. However, the amount of BA units in the copolymer is less than the ones initially desired. Nevertheless, all the techniques show a good coincidence in the final molecular weight of the copolymers and very low molar mass dispersities of the block copolymers. Furthermore,

it can be pointed out that these block copolymers were water soluble, which could not be said for copolymers with the same AA length and longer BA chain length. Finally, it should be pointed out that even if both, the PAA and PBA chain lengths changed among the different block copolymers in order to maintain a similar hydrophobic/hydrophilic balance, in this work just the effect of the PAA chain length has been considered. While the PAA chains of the block copolymers are expected to be located outside the polymer particle forming the hairy layer, the hydrophobic PBA tails are assumed to be completely buried and mixed with the polymer inside particles, not having any significant influence on the film formation.

Preparation of latexes with hairy layers of controlled and different lengths

The MMA/BA (50/50 wt %) latex was produced using SDS as emulsifier (the experimental procedure is shown in the Supporting Information). The obtained latex was dialyzed against distilled water in order to remove all the emulsifier (SDS) and to obtain a surfactant-free latex. Spectra/Por (M_wCO: 12,000-14,000) was used as membrane. Dialysis was allowed to run until the conductivity of the dialysate was close to that of the DDI water (2 µS/cm). Final properties of the dialyzed latex were the following ones; average particle diameter: 273nm, THF insoluble fraction: 20 %, weight average molar mass: $6 \ 10^5$ g/mol and Đ: 3.3.

Water solutions of the block copolymers were prepared under basic conditions (pH~10) using two different neutralizing agents, NaOH or NH_4OH. Then, the emulsifier solutions were added to the clean latex. In this case 8 wt % of block copolymers was added. This corresponds to around 2 wt % of AA with respect to the total amount of polymer, which is the amount of AA usually used in conventional formulations [3, 5, 25]. Additions were carried out at room temperature and dropwise. Finally, the mixtures were

stirred overnight. Some previous tests performed at higher temperatures did not show different emulsifier absorption efficiencies.

Mechanical properties: tensile test

In order to carry out the tensile texts, the latexes were dried in Teflon moulds during one week under controlled conditions (23 ± 2 ºC and 50 ± 5 % of humidity). Some of the films were later annealed at 60 ºC for two days more. Tensile test measurements were carried out in a universal testing machine (TA.HD plus Texture Analyzer) at 23 ± 2 ºC and 50 ± 5 % relative humidity, applying a crosshead speed of 25 mm/min to an approximately 0.5 mm thick latex film. At least five specimens per sample were tested and the average values are reported. Reproducibility between samples was good.

Preparation of dye labelled latexes

Donor and acceptor dye labelled latexes with similar characteristics to the latex presented above were synthesized. The same polymerization strategy and recipe as the one used for the synthesis of the above latex were used, except for the fact that, in this case, during the semibatch step 1 mol % of dye monomers was added to the preemulsion. The semibatch emulsion polymerization reactions were performed using a Multiplant M100 (Chemspeed Technologies) reactor of 100 mL and using the same initial unlabelled seed as the one used for the previous latex.

As a second step, the dye labelled latexes were dialyzed against distilled water in order to remove all the anionic emulsifier (SDS) and 8 wt % of the different block copolymers were adsorbed onto different fractions of the cleaned latexes using the same procedure as the one followed previously.

FRET data acquisition and analysis

Mixtures of 1:1 weight ratio of donor and acceptor labelled particles stabilized by the same block copolymer surfactant were prepared and few drops of the mixture were spread on a small quartz plate (25 x 25 cm) to form a film. The films were allowed to dry at 23 ± 2 °C and 50 ± 5 % relative humidity. The time at which the films appeared dry and transparent was considered as time zero (within 35 minutes in the samples of this work). After this period, two different drying protocols were followed; room temperature drying or higher temperature drying (60 °C and 100 °C).

Fluorescence decay profiles were determined by Time Correlated Single Photon Counting (TCSPC) measurements carried out using the Fluoromax-4 apparatus (Horiba Jobin–Yvon) equipped with a single photon counting controller (FluoroHub, Horiba Jobin–Yvon) and a pulsed diode light source NanoLED emitting at 300 nm. Emission from the sample was detected at 360 nm. Each measurement was continued until 10000 counts were acquired in the maximum channel.

The polymer interdiffusion process was monitored following the evolution of the fluorescence decay profile. As polymer diffused across particles boundaries, donor and acceptor dyes get into proximity leading to an increment in the extent of energy transfer and therefore to a faster decrease in the fluorescence decay profile [26-29]. In our experiments, each fluorescence decay profile was standardized to unit intensity and t=0 and fitted to the following equation: [30-34]

$$I_D(t) = A_1 exp\left[-\frac{t}{\tau_D^0} - 2\delta\left(\frac{t}{\tau_D^0}\right)^{0.5}\right] + A_2 exp\left(-\frac{t}{\tau_D^0}\right) \tag{1}$$

The first term of the equation corresponds to the region where donor and acceptor molecules are mixed, whereas the second corresponds to the unmixed region where energy transfer does not occur. Fixed values for τ_D^0 (τ_D^0 is the donor fluorescence lifetime in the absence of acceptor which was experimentally measured for Phe-MMA labelled

latex film as 43.5 ns) and δ (constant parameter proportional to the concentration of acceptor and the Föster distance which in our work was taken as 0.45) [23, 35] were used. Parameters A_1 and A_2 were obtained from the fitting of each decay profile. Parameterized expressions were later used to integrate $I_D(t)$ analytically and to calculate the quantum efficiency of energy transfer.

The area under each standardized fluorescence decay profile is equal to the total fluorescence intensity from the sample, which is proportional to the quantum efficiency of fluorescence. The quantum efficiency of energy transfer (Φ_{ET}) can be calculated from the changes in the area under the decay profiles. Thus, Φ_{ET} can be related to the fraction of molecular mixing in a system of labelled particles and it is defined as shown in equation 2 [31, 33, 36-38].

$$\phi_{ET}(t) = 1 - \frac{\int_0^\infty I_D(t)dt}{\int_0^\infty I_D^0(t)dt} \tag{2}$$

where $I_D(t)$ and $I°_D(t)$ represent the donor fluorescence decay functions in the presence and absence of acceptors. Considering that $\int_0^\infty I_D^0(t)dt = \tau_D^0$, equation 2 can be rewritten as:

$$\phi_{ET}(t) = 1 - \frac{\int_0^\infty I_D(t)dt}{\tau_D^0} \tag{3}$$

In our analysis of donor fluorescence decay data, we assumed that all deviations from a strictly exponential donor decay profile are due to energy transfer.

Another useful parameter is the extent of mixing, $f_m(t)$, expressed in terms of the increase in energy transfer, normalized by the maximum change associated with complete mixing [31, 33, 36-38].

$$f_m(t) = \frac{\phi_{ET}(t) - \phi_{ET}(0)}{\phi_{ET}(\infty) - \phi_{ET}(0)} \tag{4}$$

Where $[\phi_{ET}(t) - \phi_{ET}(0)]$ represents the change in the efficiency of energy transfer between the initially prepared film and a film annealed for time t.

RESULTS AND DISCUSSION

Effect of the hairy layer length

Figure 2 shows the stress-strain curves of latexes stabilized by block copolymers of different lengths neutralized by using NaOH. When the films were dried at room temperature during one week, it was found that the higher the length of the AA hairy layer (i.e. the higher the AA chain length of the block copolymer used as stabilizer) the lower the elongation at break of the final film. Thus, it can be inferred that the shortest hairy layer on the particles surface created a weaker barrier between particles during the film formation, making interdiffusion between particles easier and therefore leading to tougher films.

(a)

(b)
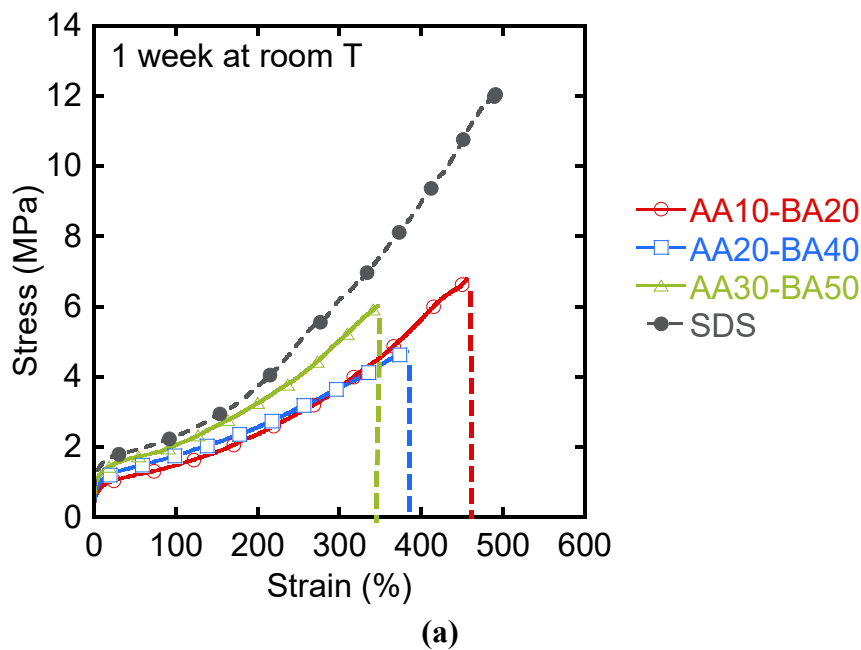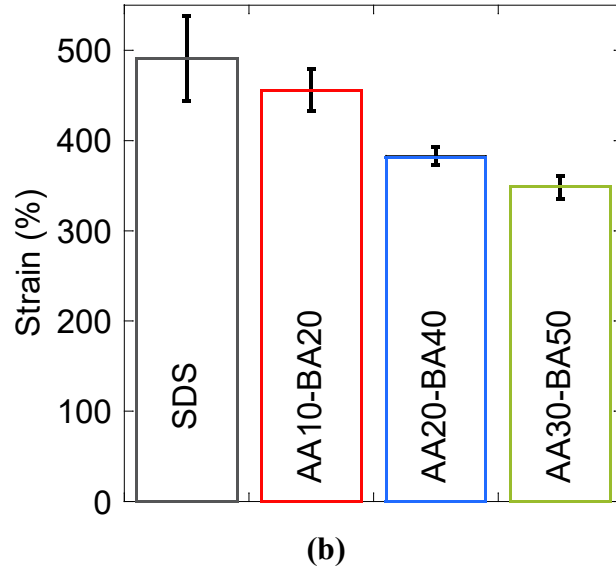
Figure 2 Stress-strain curves for the films containing block copolymers and SDS. **(a)** Films dried during one week at room temperature and **(b)** their strain at break.
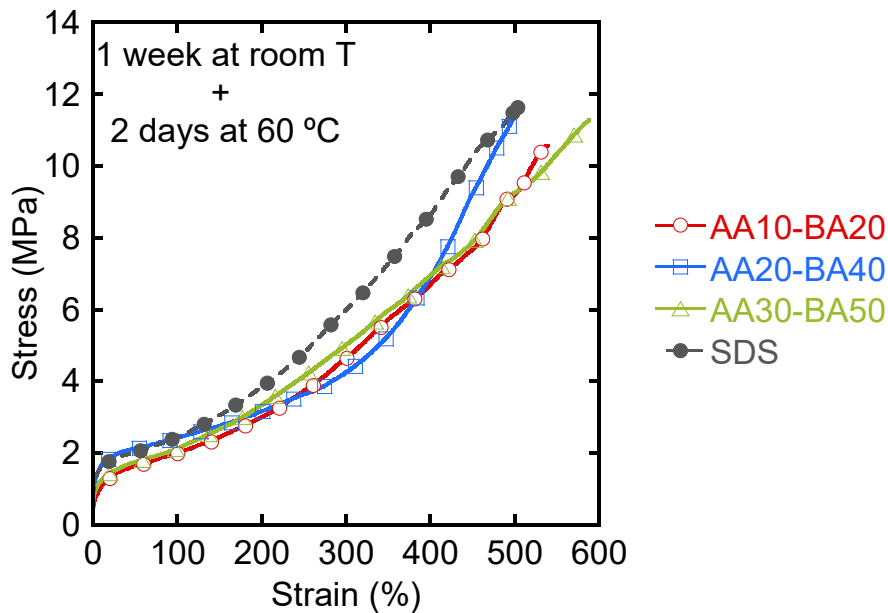

Figure 3 Stress-strain curves for the films containing block copolymers and SDS. Films dried during one week at room temperature and later annealed at 60 ºC for two days more

When the films were annealed for two days at 60 ºC (Figure 3), the elongation at break and the breaking stress of the latexes stabilized by block copolymers increased remarkably, whereas the curve corresponding to the latex stabilized by SDS did not change too much. Moreover, all the curves became more similar among them. It can be inferred that at high temperatures the mobility of polymer chains increased, enhancing the interdiffusion of the core polymers and causing the disruption of the AA chains barrier

12

between particles. As a consequence, the mechanical properties of the films were improved. The lack of improvement when annealing at 60ºC in the case of the latex stabilized with SDS, is related to the lack of interdiffusion retardation of SDS, which produced already well interdiffused polymer films when drying at room temperature for one week.

FRET experiments were carried out in order to check the hypothesis drawn on the effect of the AA hairy layer on the interdiffusion between particles. FRET experiments (Figure 4) show that when films were dried at room temperature the quantum efficiency energy transfer (ϕ_{ET}) values were maintained constant over the time range studied (it must be taken into account that the experimental uncertainty of quantum efficiency is $\pm$ 0.02 [39]). What it is remarkable from these results is that the values of the energy transfer were lower for the latexes stabilized by block copolymers than for the latex stabilized by SDS. These results indicate that the interdiffusion degree was higher in the latex stabilized by SDS from the very beginning of film formation. Furthermore, even if the differences are very small, ϕ_{ET} values were lower as the length of the AA chain on the particle surface increased. Thus, the longer the hairy layer length, the stronger the created barrier between particles during the film formation and the lower the interdiffusion degree of polymer chains between neighbour particles. These results support the ones observed in tensile strength measurements where lower elongations were achieved as the length of the hairy layer increased and a tougher film was obtained when the polymer particles were stabilized by the shortest hairy layer.
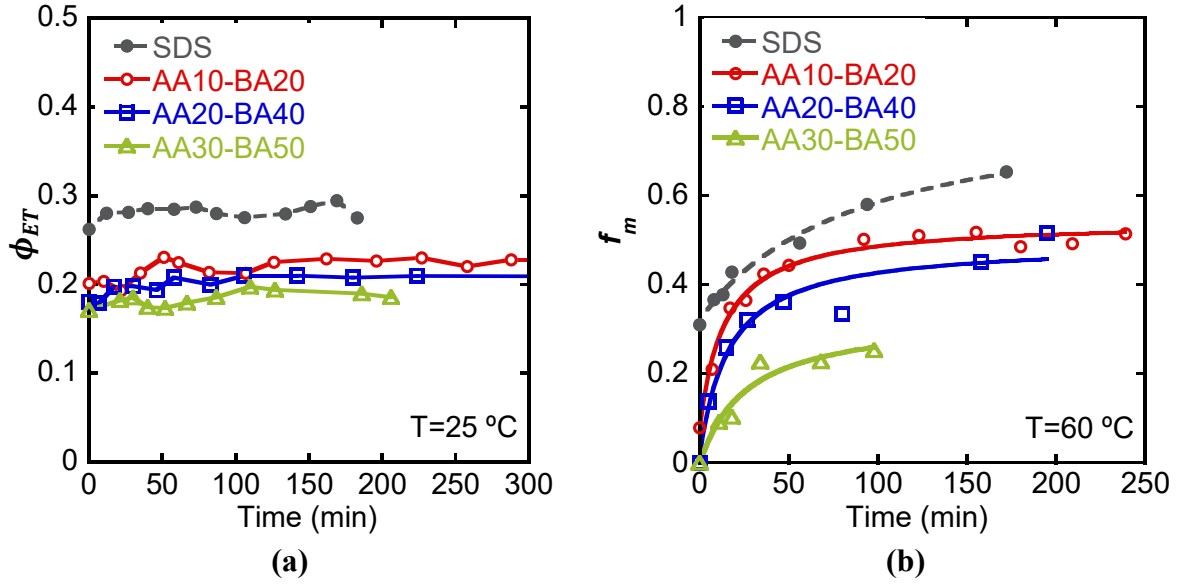
Figure 4 (a) Evolution of quantum efficiency energy transfer (ϕ_{ET}) for films dried at room temperature. **(b)** Evolution of fraction of mixing for films annealed at 60 ºC

In the case of films annealed at 60 ºC, the evolution of the fraction of mixing ($f_m(t)$) of each sample was also measured (Figure 4 (b)). As $f_m(t)$ is a measurement of the extent of mixing in the system, a value for $\phi_{ET}(\infty)$ was needed (see equation 4). $\phi_{ET}(\infty)$ should describe the maximum interdiffusion that can be achieved in the polymer system and should not be influenced by the effect of the block copolymers [31, 32, 34]. For this reason, the value chosen was the one obtained for the latex stabilized by SDS annealed at 90 ºC for two days; $\phi_{ET}(\infty)$=0.42. As it can be observed in Figure 4 (b), the longer the length of the hairy layer on the particle surface, $f_m(t)$ increased slower and reached lower values indicating that interdiffusion between particles was more retarded. It could be argued that these FRET measurements do not match the tensile strengths measured after annealing at 60ºC, which were similar for all the films. But it has to be mentioned that FRET measurements were carried out during 4 hours at 60ºC and tensile strength was measured after 48 hours at 60ºC. Therefore FRET shows interdiffusion rate, which is faster for the particles having shorter AA hairy lengths, while tensile strength had probably shown the equilibrium stage after 48h at 60ºC.

Effect of the neutralizing agent

Figure 5 compares the stress-strain curves of the films of the latexes stabilized by block copolymers neutralized either by NH_4OH or NaOH.
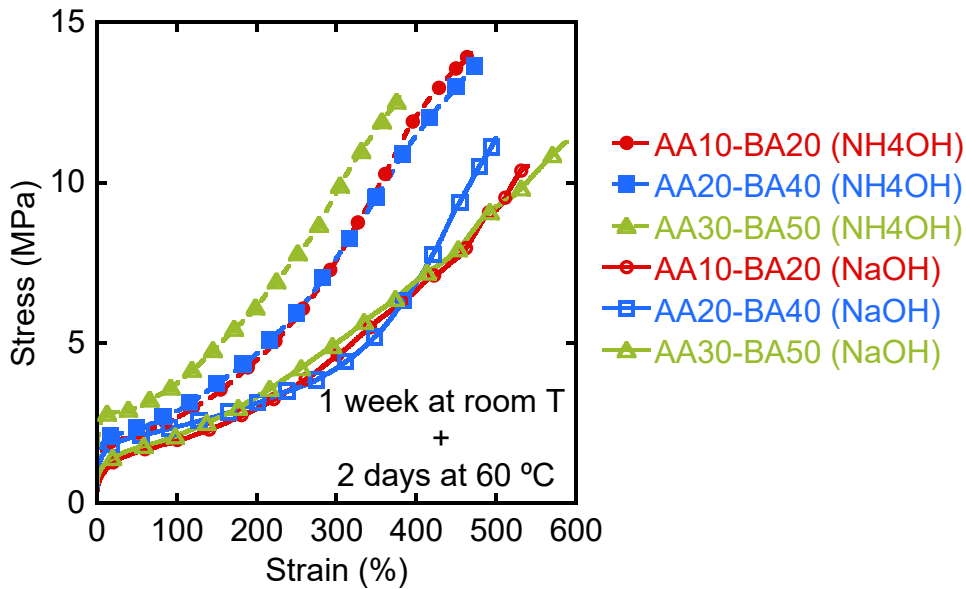

Figure 5 Stress-strain curves for the films in which NaOH or NH_4OH were used as neutralizing agent

It can be clearly observed that the used neutralizing agent had a substantial effect on the mechanical properties of the final films. Stronger films were obtained when NH_4OH was used as neutralizing agent, which is an indication of the enhanced polymer interdiffusion in these samples.

Figure 6 shows the evolution of $f_m(t)$ vs annealing time for films annealed at 60 ºC, when different neutralizing agents had been used for the solubilisation of the block copolymers. In all the cases, $f_m(t)$ increased faster and reached higher values when NH_4OH was used as neutralizing agent than when NaOH was used. These results demonstrate that interdiffusion between neighbour particles was more retarded when

NaOH was used as neutralizing agent instead of NH₄OH and explains why the mechanical properties of the films containing NaOH are worse.
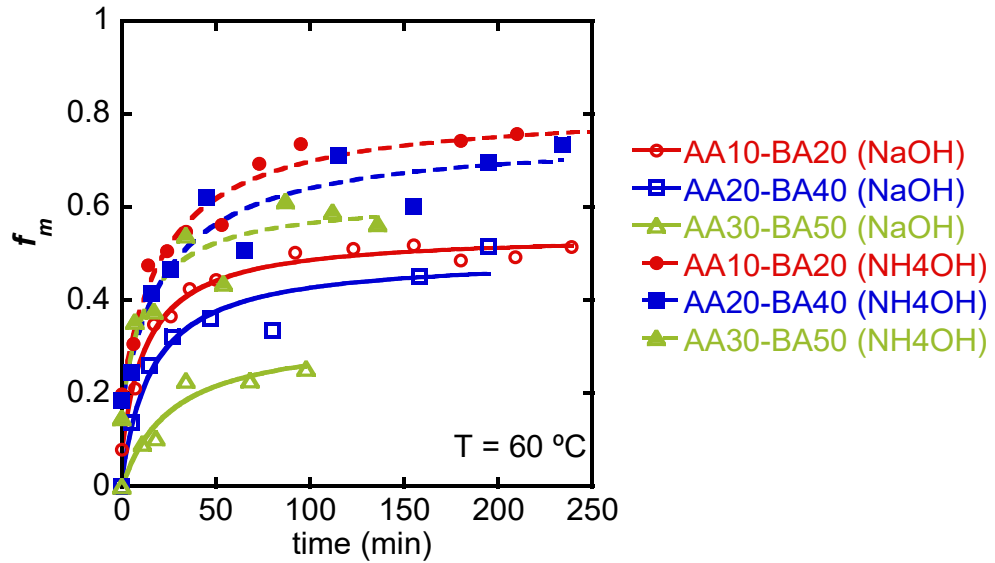
Figure 6 Evolution of f_m along the annealing time for films stabilized by block copolymers neutralized with NaOH or NH₄OH, annealed at 60 ºC

One of the main differences between using NH₄OH or NaOH as neutralizing agent is the volatility of NH₃. Since NH₄OH is a weak base there will be an equilibrium between ammonium cation (NH_4^+) and ammonia (NH_3) in aqueous solution. As NH₃ is a volatile compound, during the film drying process it will evaporate shifting the equilibrium toward the ammonia formation and decreasing the concentration of NH₄OH. The effect of NH₃ evaporation leads to a pH drop and to the protonation of the carboxylate groups of the hairy layer as the film dries [30]. As a consequence, in our system, when NH₄OH was used as neutralizing agent, most of the acid groups of the hairy layer were in their protonated form once the film was formed. On the contrary, when NaOH was used as neutralizing agent, there was not any change on the protonation of the carboxylic acid groups of the hairy layer during the film formation. Thus, once the film was formed the acid groups present in the surface of the polymer particles continued being deprotonated. Taking into account that the T_g for pure poly(acrylic acid) is 105 °C, whereas the one for

poly(sodium acrylate) is 230 °C [13], it can be concluded that the use of NaOH as neutralizing agent led to particles surrounded by a harder polymer shell making more difficult the interdiffusion of core polymer chains between neighbour particles, worsening the mechanical properties of the final films. Differences in the interdiffusion by the use of different neutralizing agent have already been observed by other authors [15, 16, 40], even if in those cases the acidic moieties had been introduced as comonomers in the formulation and not as a controlled chain block copolymer as in this study.

As an overall conclusion it should be mentioned that short hairy layer lengths and the use of NH₄OH as neutralizing agent, lead to the formation of films with enhanced interdiffusion of polymer chains between neighbouring particles and therefore to films with better mechanical properties.

CONCLUSIONS

The objective of this article was to study the effect of the hairy layer length on the interdiffusion of polymer between particles and as a consequence on the mechanical properties of the films. To this end, latexes of the same particle diameter and molecular weight but stabilized with PAA-*b*-PBA block copolymers of controlled and different lengths were prepared. Two different experiments were performed. On the one hand, interdiffusion was studied at a macroscopic level through tensile test measurements. On the other hand, FRET experiments were performed, which allowed to measure interdiffusion degree between particles at a molecular level. Furthermore, the effect of the used neutralizing agent, NaOH or NH₄OH, was also studied.

Tensile strength measurements showed that the presence of AA chains on the particle surface reduced the mechanical properties of the films dried at room temperature. Furthermore, as the AA chain length was increased, elongation at break of the films

decreased. Higher fracture energies were obtained with the shortest hairy layer length. These results were supported by FRET experiments that showed that extent of interdiffusion occurred slower as the AA chain lengths in the particles surface increased. Moreover, it was observed that interdiffusion of polymer chains between neighbour particles was more retarded when NaOH was used as neutralizing agent instead of NH$_4$OH, leading to films with worse mechanical properties.

ACKNOWLEDGMENTS

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