



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



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ARTICLE INFO

Article history:

Received 25 November 2014
 Received in revised form 16 June 2015
 Accepted 27 June 2015
 Available online 19 July 2015

Keywords:

Latex film formation
 FRET
 Mechanical properties
 Electrosteric stabilizers
 Controlled sized acidic hairy layer

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 NH₄OH 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 NH₄OH.

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1. 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

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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 synthesized 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 analyzed 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.

2. Materials and methods

2.1. 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 5 N 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. Fig. 1 shows the structure of the used RAFT agent as well as of the expected block copolymers.

Table 1 shows the number average molecular weight (M_n) and molar mass dispersity (\mathcal{D}) of the final block copolymers obtained, analyzed 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.

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.

2.2. 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 ($2 \mu S/cm$). Final properties of the dialyzed latex were the following ones; average particle diameter: 273 nm, THF insoluble fraction: 20%, weight average molar mass: 6×10^5 g/mol and \mathcal{D} : 3.3.

Water solutions of the block copolymers were prepared under basic conditions (pH \sim 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.

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