



Efficient strategy for hard nano-sphere usage: Boosting the performance of waterborne coatings



J.S. Nunes^a, S.J. Bohórquez^{b,*}, M. Meeuwisse^b, D. Mestach^b, J.M. Asua^a

^a POLYMAT and Grupo de Ingeniería Química, Departamento de Química Aplicada, University of the Basque Country UPV/EHU, Centro Joxe Mari Korta, Avda. de Tolosa, 72, 20018, Donostia-San Sebastián, Spain

^b Nuplex Resins BV, Synthesebaan 1, 4612 RB Bergen op Zoom, The Netherlands

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ABSTRACT

This work describes a study on the efficient use of waterborne hard-polymeric nanoparticles to improve properties of waterborne coatings such as: early hardness, blocking and resistance to fat. The waterborne nano-hard-spheres were synthesized by a special emulsion polymerization process enabling the use of low-surfactant concentration and high solid levels, and then blended with different commercial decorative binders. The colloidal stability of these bimodal systems was carefully analyzed, through rheology and dynamic light scattering analysis. Afterwards, different clear coatings were formulated, prepared, and applied onto different substrates to evaluate their properties. Results showed that the implementation of this waterborne technology enhanced the performance of the systems evaluated for decorative and industrial purposes.

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1. Introduction

In recent years, considerable efforts have been made by the polymer industry to develop environmentally benign processes avoiding the emission of volatile organic compounds (VOC), which are believed to be the primary cause of photochemical smog and ozone pollution. In the coatings field, waterborne dispersed polymers used as binders, appear as an environmentally friendly alternative to solvent-based coatings [1,2].

Among binders, waterborne acrylic dispersions have an important share in paint and coating industries. They are usually prepared through the emulsion polymerization of acrylic and methacrylic acids esters. The important characteristics of the acrylic coatings are their inertness towards degradation under the influence of UV light, hydrolysis, acids, bases, oxidizing agents and other corrosive chemicals [3].

In the industrial and decorative coatings market continuous changes are occurring since several old-fashioned solvent-borne coating products are being substituted by new waterborne ones. Waterborne 1K ambient-drying self-crosslinking coatings are steadily approaching to fulfill several requirements usually provided by traditional solvent-borne 2K polyurethanes (stain and scratch resistance, drying profiles, etc.). However, some properties such as hardness development in early drying stages, anti-blocking

or anti-stacking and resistance to fat require further improvement. The binders employed in waterborne decorative coatings should simultaneously comply with contradictory requirements. In one hand, they should have a low minimum film formation temperature (MFFT = 10–15 °C), to ensure a good film formation under application conditions, i.e., at room temperature. On the other hand, good hardness and anti-blocking resistance are required, which leads to polymers with a T_g above the room temperature. Traditionally, coalescing agents are used to plasticize the binder during film formation, decreasing its T_g and allowing the formation of a good film at room temperature. Once the film is formed, the cosolvent evaporates in time and the film recovers its hardness and anti-blocking characteristics. However, in addition to the environmental problem of releasing volatile organic compounds to atmosphere, in several industrial paint production lines, a fast build-up of the hardness and subsequent anti-blocking resistance is needed, and this requirement is not usually met by coalescing agents even when forced drying is used. Moreover, compatibility between coalescing agents and waterborne binders it is not always perfect in terms of final film aesthetic appearance. An alternative route to solve this issue is to introduce a harder phase into the system that might be in the form of polymer particles. The use of hard/soft particles latex blends in the coatings and adhesives industry has been the aim of study of several groups in industry and academia during the last years [4–12].

One of the first works on the use of soft and hard latex blends was attributed to The General Tire & Rubber Company (nowadays General Tire) in which blends of waterborne carboxylated

* Corresponding author.

E-mail address: Silfredo.Bohorquez@nuplex.com (S.J. Bohórquez).

polymers having a difference in T_g of around 60 °C were used to coat rubber parts and improve their anti-sticking properties while assembling [4]. The Rohm and Haas Company (nowadays Dow Chemical) patented a process in which single stage acrylic latexes (higher T_g) were blended with multistage latexes (soft core and hard shell) with the aim of designing a coalescent-free paint [5]. The work showed interesting results in terms of formulation for different applications, however, it resulted in a list of experiments to determine the best combination of single stage/multistage latexes (for the performance required) rather than employing the harder phase latexes as additives to enhance properties of a given latex.

Winnik and Feng [6] prepared blends comprising hard polymethyl methacrylate (PMMA) nanoparticles ($T_g = 105$ °C, $dp = 44$ – 400 nm) and soft poly(butyl methacrylate-co-butyl acrylate) latexes ($T_g = -33$ to 9.9 °C, $dp = 43$ – 49 nm). The possibility of reducing VOCs levels (compared to formulations containing coalescent that evaporates during film formation), and the production of transparent films that presented improved mechanical properties were the main advantages reported. Eckersley and Helmer [7] also made important contributions to the study of soft ($T_g \sim 0$ °C, $dp = 115$, 306 and 475 nm)/hard ($T_g \sim 60$ °C, $dp = 118$ and 441 nm) latex dispersions. Besides the improved mechanical properties observed, they demonstrated that the particle size ratio ($dp_{\text{soft}}/dp_{\text{hard}}$) had a dramatic effect on the concentration of hard nanoparticles at the surface of the film. Results were satisfactorily explained according the concept of continuity of the dispersed phase.

Based in concepts as continuity of the dispersed phase and particle deformability, Tzitzinou et al. [8] studied the film formation of soft ($T_g = 20$ °C, $dp = 50$ or 297 nm)/hard ($T_g = 80$ °C, $dp = 50$ or 286 nm) latex blends using a fixed large/small ratio (300 and 50 nm), and varying their relative concentrations. It was found that to obtain a transparent film, namely a film mostly devoid of voids a critical volume concentration of small particles is required. Colombini et al. [12] reported on the effect of thermal annealing on the viscoelastic properties of bimodal small hard ($T_g = 114$ – 118 °C, $dp = 54$ and 237 nm)/large soft ($T_g = 2$ – 3 °C, $dp = 86$ and 336 nm) latex blends (MMA, styrene and BA copolymers) was investigated. As the thermal annealing involved temperatures higher than the glass transition temperature of the hard phase, the small hard particles progressively lost their initial shape and formed a more continuous phase in the latex blends that resulted in an enhancement of the mechanical properties of the films. In addition, the authors observed that when the latex particle size of the dispersed phase was decreased, the improvement of the mechanical properties was more significant.

Regarding the use of nano-hard-spheres as additive in waterborne coatings, it is remarkable the work performed by Jones et al. [13]. In this work, conventional latex/nanolatex blends comprised of BMA, BA and methacrylic acid (MAA) monomers (soft/soft particles blends) were prepared. Small nanoparticles of around 20 nm were synthesized by using the semicontinuous microemulsion polymerization technique, in which a 10% of surfactant with respect to monomer was used to produce a latex with 11% of solids content. Compositions comprising between about 3:97 and 90:10 (w/w) nanolatex particles to conventional latex particles ($dp = 130$ nm) were used. The authors found that when the average particle size of the conventional latex is about six times larger than the average particle size of the nanolatex, a composition consisting of a ratio of 1 conventional latex particle for 25 nanolatex particles results in expected strong and smooth films.

The preceding works focused on the benefits of blending hard and soft latexes and the film formation process occurring (as compared to a regular monomodal binder), however, there is little information on the design of hard-polymeric nanoparticles towards their formulation as additives in clear and pigmented systems that

Table 1

Characteristics of the nanolatexes used in the formulation of waterborne paints.

Nanolatex	Composition	dp (nm)	SC (%)	P/S
NL1	MMA (100%)	33	31.3	47.0
NL2	MMA (95%)/MAA (5%)	45	30.6	46.7
NL3	MMA (95%)/HEMA (5%)	36	30.7	46.8
NL4	MMA (100%)	67	39.8	45.0

SC: solids content, dp: particle diameter measured by dynamic light scattering, P/S: polymer/surfactant weight ratio.

may find an application in decorative coatings. Moreover, high surfactant concentration is often used to synthesize nanoparticles and this leads to problems related with surfactant migration during film formation. In the present work, high-solids content low-surfactant hard nanolatexes were used as additives to improve the performance of waterborne coatings. Firstly, a study concerning the impact of hard nanolatexes addition on the colloidal stability and rheology of the blends is presented. Afterwards, the effect of the presence of these nano-hard-spheres in the formulation on film formation, hardness, blocking and fat resistance of a waterborne coating is described as well.

2. Materials and methods

2.1. Materials

Methyl methacrylate (MMA, $\geq 98\%$, Norsocryl), 2-hydroxyethyl methacrylate (HEMA, $\geq 97\%$, ECEM), methacrylic acid (MAA, $\geq 98\%$, Sojitz Europe plc), sodium dodecyl sulfate (SDS, $\geq 98.5\%$, Sigma-Aldrich), ammonium persulfate (APS, $\geq 99\%$, Sigma-Aldrich), hydroquinone ($\geq 99\%$, Acros Organic), dimethylethyl amine ($\geq 99\%$, Acros Organic), butyl glycol, butyl diglycol (Helm Chemicals BV), BYK 024[®] and BYK[®] 346 (BYK Additives & Instruments) were used without previous purification. Ultrapure water (Millipore) was used in all experiments.

2.2. Synthesis of low-surfactant high-solids nano-hard-spheres

The nanolatexes used in this work were synthesized according to the procedure reported elsewhere [14,15]. Initially, SDS (3.32 g) and water (654.57 g) were added to a glass reactor equipped with a glass stirrer, a reflux condenser, a sampling device, a nitrogen gas inlet tube and a temperature probe. When the reaction temperature reached 80 °C, an APS aqueous solution (0.44 g of APS and 10 g of water) was added as a shot and the monomer mixture (297.54 g) was fed very slowly over a 367 min. During polymerization, nucleation and particle growth led to a progressive decrease in the surface coverage of the particles by the emulsifier that eventually can result in particle coalescence, i.e., in larger particle sizes. Therefore, when the solids content of latex was 18 wt% (around 180 min of reaction time), a surfactant solution was continuously fed in order to increase the surface coverage of the particles. At the end of feeding period, the system was maintained at the reaction temperature for 60 min in order to minimize the amount of residual monomer. The final solids content of the nanolatexes was 30 wt%. For comparison, the synthesis of a nanolatex with 40 wt% of solids content was also carried out (NL4). The characteristics of the nanolatexes employed in this work are presented in Table 1.

2.3. Preparation and characterization of blends, and coatings formulation

To study the effect of nanolatexes addition on the performance of waterborne coatings, two commercial low- T_g dispersions often used in high performance clear wood finishes were used. STQ1

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