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Effect of acrylic binder type and calcium carbonate filler amount on the properties of paint-like blends

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ABSTRACT

The aim of this work has been to study the factors affecting the interaction between calcium carbonate ($CaCO_3$) filler and acrylic binders in waterborne coatings. Therefore, the minimum amount of additives has been used in order to isolate the interaction between the filler and the binder, while the production of an applicable coating was assured. In this paper we report the preparation of $CaCO_3$/poly(methyl methacrylate-co-butyl acrylate) P(MMA/BA) latex blends using only sodium polyacrylate as dispersing agent as additive. Paint-like blends were prepared with latexes of different nature in terms of particle size (120 nm–600 nm) and functional monomer (acrylic acid) and at different pigment volume concentration (PVC) values of 30, 40, 45 and 50. The effect of these variables has been investigated on the film properties (water uptake, gloss, mechanical properties and scrub resistance). Higher gloss values, more elastic mechanical properties and higher scrub resistances were observed for blends prepared with the latex of 120 nm particle size. The use of acrylic acid functional monomer led to slightly better properties. Therefore, this study overall demonstrated that better interaction is obtained when using the latexes with small particle size and with the acrylic acid functional monomer, leading to blends with $CaCO_3$ weight loadings of 70% without the complete loosing of the cohesive properties.

1. Introduction

In the recent years an increasing interest is observed in the development of waterborne paints, due to the more stringent regulations on the emission of volatile organic compounds (VOC) in industrial coatings [1–4]. Waterborne paints that surround us every day are mainly a mixture of a polymeric binder (latex) with pigments, combined with different additives. The binder is the film forming component and it has great impact on properties such as gloss, flexibility and toughness [5]. Acrylic latex polymers and copolymers are extensively used as polymeric binders in paints due to their flexible film formation temperature, good elasticity and stability under UV in the resulting films [6–8]. Besides, the pigment is the discontinuous phase giving additional or improved properties to the coatings, in the case of functional pigments such as TiO_2, or just space holding effect, in the case of fillers [9,10]. Nowadays, calcium carbonate ($CaCO_3$) is one of the most widely used fillers in paint and coating industries [11,12]. $CaCO_3$ comprises more than 4% of the earth's crust and is found throughout the world. After quarrying, milling is required to process natural calcium carbonates of the highest quality, known generically as Ground Calcium Carbonate (GCC). Due to its abundance, GCC is used to lower the final price of waterborne paints without significant losses of the films properties up to a certain amount of filler addition [13].

From this point of view, the pigment volume concentration (PVC) is one key-parameter in the formulated paints, which refers to the percentage of pigment with respect to the total solids volume (pigment + polymer) in a paint formulation. As it has been mentioned, there is a Critical Pigment Volume Concentration (CPVC) at which there is just enough binder to wet pigment particles. It was in the early 1940's when Asbeck and Van Loo [14] defined this transition in a pigment-binder system at which the properties of a paint film change dramatically to worse. The determination of the CPVC is important because coherent films can only be obtained below the CPVC. Many methods exist to determine CPVC experimentally based on change of coatinǵs properties, such as optical properties [15], mechanical properties [16], gas permeability [17] and water permeability [18].

However, it has to be pointed out that the CPVC of a pigment-binder system depends on many aspects. Evidently, the first parameter affecting the CPVC is the use of solventborne or waterborne binders [19]. Due to the polymer particle morphology in waterborne binders, the CPVC for latexes will be lower than the one for solventborne counterparts. On the other hand, the polymer particle size and the polymer particles surface functionality will also affect the CVPC. In fact Klein et al. already found that smaller particle sizes and the presence of acidic

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functionalities on the polymer particles surface favoured higher CPVC values [20–23].

Therefore the study of the interaction between the binder and the pigment is essential to improve the properties of the coatings. Several papers have already published the study of the interaction between various types of binder and pigments by different methods [15,24–26]. However it has to be mentioned that most of the papers studying the interaction between pigments and different latex types have been performed after including all types of additives to the paint formulation (dispersants, rheology modifiers, tackifiers, defoarmers…), and it cannot be neglected the effect that these additives have on the effective film formation and resultant quality of the film [27,28]. All components are having some degree of interaction with each other and these complex interactions must be considered in the wet state, drying stage and dry state [29]. In order to isolate the study of the interaction between the acrylic latex and the pigment, the challenge of this work has been to prepare waterborne paint-like blends using as less as additives as possible and with applicable rheologies. These applicable rheologies have been pursued in order to mimic as much as possible the film formation conditions of real paints.

Therefore, high solids content waterborne paint-like blends based on polymer latex/filler blends have been prepared using only a dispersing agent as additive and the effects of several variables (latex type, their surface coverage, particle sizes and filler/latex ratio) on the film properties (scrub resistance, tensile properties, water uptake and gloss) have been investigated. Ground calcium carbonate ($CaCO_3$) and poly (methyl methacrylate-co-butyl acrylate) P(MMA/BA) have been used as extender and latex respectively and sodium polyacrylate (NaPA) has been added as dispersing agent, which is a common dispersant of the calcium carbonate [30,29,31]. The conditions to obtain satisfactory waterborne paint-like blends with $CaCO_3$ weight percentages as high as 70% have been established.

2. Experimental work

2.1. Materials

Ground calcium carbonate (GCC) was kindly supplied by Omya (Omyacarb®-CL), with 90% of the particles with a particle size below 2 μm. The theoretical critical pigment volume concentration (CPCV) for this filler determined from the oil absorption value is 46 [32,33]. A SEM micrograph of $CaCO_3$ is shown in Fig. 1. Sodium polyacrylate (NaPA, molecular weight (MW) = 5100 g/mol, Sigma-Aldrich) was used to disperse the $CaCO_3$ particles in water.

Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Fluka) monomers were used as supplied. Sodium persulfate (NaPS, Sigma-Aldrich) was used as thermal initiator. The anionic surfactant used was Dowfax 2A1 (Dow Chemical, 45%). To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used.

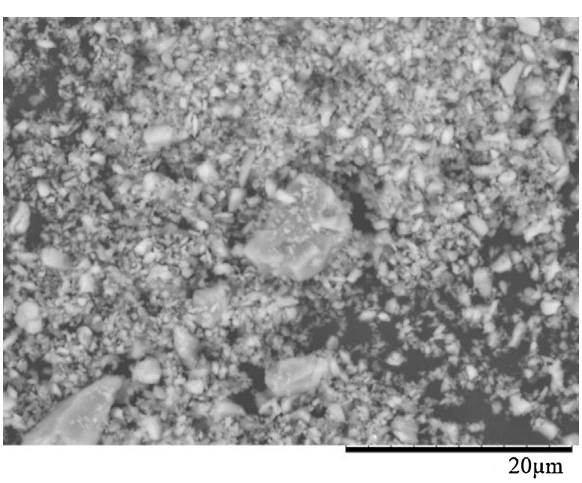

Fig. 1. SEM image of the $CaCO_3$ used in this study (Omyacarb®-CL).

Table 1
Formulation of the seed. Batch period: 120 min.

Ingredient	Charge(g)
MMA	63.17
BA	63.17
AA	1.28
Water	716.56
$Na_2S_2O_8$	1.28
Dowfax 2A1	5.67

2.2. Latex synthesis and basic characterization

High solids content Poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid) P(MMA/BA/AA) (49.5/49.5/1) latexes with particle sizes of 120 nm, 300 nm and 600 nm and a 300 nm latex without the acrylic acid functional monomer were synthesized by seeded semi-batch emulsion polymerization. First, a P(MMA/BA/AA) (49.5/49.5/1) seed with 15 wt% solids content and a particle size of 80 nm was prepared by batch emulsion polymerization (see Table 1). Afterwards, the seed was grown by the feeding of a preemulsion containing monomer, surfactant and water. The reaction temperature was kept constant at 75 °C and 0.5 wt based on monomer percent (wbm%) of NaPS initiator was injected as a shot before the preemulsion feeding. All syntheses were carried out with 1 wbm% of ammonia (see Table 2).

Particle size of the seed and final latexes was measured by Dynamic Light Scattering Spectroscopy, DLS (Malvern® Zetasier Nano). After the synthesis the final solids content for all latexes was obtained gravimetrically and it was around 60%. However the latex with the particle size of 120 nm was synthesized at a solids content of 25% and then it was concentrated using a rotavapor to attain a final solids content of 60%. All latexes showed a glass transition temperature around 17 °C, measured by differential scanning calorimetry (DSC, Q2000 TA Instruments) and no coagulation was observed.

2.3. Preparation of waterborne paint-like blends

Waterborne paint-like blends were prepared in two steps. In the first step the dispersion of the pigment and dispersing agent in water, the so-called mill base, was prepared. In the second step the mill base was blended with the latexes at pH 9 and the final blends were obtained.

In order to obtain the mill base, first distilled water and sodium polyacrylate (NaPA) dispersing agent were weighed in a 500 mL container and stirred using a Dispermat high speed disperser blade under low shear (350 rpm). $CaCO_3$ powder was then added slowly into the container and the shear rate was increased (up to 1300 rpm) during the addition. After $CaCO_3$ addition, the mill base was left at constant shear for 30 min. The optimum dosage of NaPA needed to disperse correctly the $CaCO_3$ particles, was obtained measuring the dispersion viscosity with a Brookfield viscometer as a function of the amount of NaPA in a high solids content $CaCO_3$ slurry.

Afterwards, the mill base was blended (500 rpm) with the different latexes at pH 9. To study the interaction between the acrylic latex and calcium carbonate particles, different blends were prepared with this strategy, changing the nature of the latex in terms of particle size and functional monomer and for different PVC values of 30, 40, 45 and 50. Waterborne blends were then stored at standard atmospheric conditions (23 °C and 50% relative humidity) 48 h, before performing the films and their characterization.