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Influence of anti-caking agent kaolin on film formation of ethylene–vinylacetate and carboxylated styrene–butadiene latex polymers

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ABSTRACT

Colloidal stabilizers (e.g. PVOH) and anti-caking aids (e.g. kaolin) are commonly added during the spray drying of liquid latex dispersions to produce re-dispersible polymer powders for the drymix mortar industry. Here, the influence of kaolin and polyvinylalcohol on polymer film formation of an ethylene–vinylacetate (EVA) and a carboxylated styrene–butadiene (SB) latex dispersion in water and cement pore solution was investigated. Time-dependent ESEM analysis was conducted to analyze the progress of particle coalescence. The results show that both EVA and SB powders form a homogeneous film much faster than their liquid precursors. Surprisingly, this effect was found to result from the presence of kaolin. Consequently, this additive fulfills a dual purpose in re-dispersible powders, it serves as anti-caking agent and also accelerates film formation while polyvinylalcohol retards particle coalescence. The SB latex achieves a coherent polymer film faster than the EVA dispersion, due to its smaller particle size (~200 nm).

1. Introduction

Latex polymers are among the most important admixtures used in cement based building materials. Most latex polymers applied in the construction industry are based on ethylene/vinylacetate, styrene/butadiene or acrylate chemistry. Latex polymers are synthesized as liquid aqueous dispersion via emulsion polymerization. For drymix mortars which are widely used in tile adhesives, tile grouts or external thermal insulation composite systems (ETICS), re-dispersible polymer powders are fabricated by spray drying from a liquid mother latex. During spray drying, protective colloids (e.g. polyalcohols) and anti-caking agents (e.g. clay, silica, calcium carbonate, kaolin, diatomaceous earth etc.) are fed in together with the mother liquor. The addition of latex polymers can improve the properties of fresh and hardened cement. Latex-treated mortars exhibit better cohesion and adhesion and higher flexural strength. The reason behind those improvements is the formation of polymer films within the cementitious matrix as a consequence of latex particle coalescence [1–3].

The impact of anti-caking agents such as kaolin on film formation of re-dispersible polymer powders has not been reported so far. Only few literatures address the interaction between latex particles and mineral substrates such as silica, mica or ceramic tiles [4,5] while a large number of articles focus on the material properties of polymer-modified concrete or mortar [6–11] and composites made from latex polymers and inorganic fillers such as clays [12–15]. Some articles are dealing with film formation in the presence of electrolytes. There, it was shown that in highly ionic systems such as cement pore solution film formation can occur much later, compared to fresh water systems [16–21]. Several reasons have been identified for this effect, the main two being surface coverage of latex particles with adsorbed Ca^{2+} ions from cement, and formation of a salt skin. Both phenomena hinder particle coalescence. These examples suggest that the additives used in the spray drying of latex powders may also strongly impact film formation.

The process of polymer film formation can be divided into four main stages which are illustrated in Scheme 1. Starting from an aqueous latex dispersion (stage I), a dense particle packing (stage II) is the result of dehydration due to evaporation or water consumption during cement hydration. In stage II, particles now are in contact with each other and the interstitial spaces of the dense particle packing are filled with water. After water removal from the interstitial spaces, the latex particles start to deform in order to minimize their interfacial tension. This step only occurs if the temperature is above the so called minimum film forming temperature (MFFT). Now the polymer chains become mobile and particle coalescence into coherent polymer films can occur. The driving force behind the interdiffusion of the polymer chains is minimization of interfacial tension between the latex particles. The result is a molecularly continuous, coherent and homogeneous polymer film [22–24].

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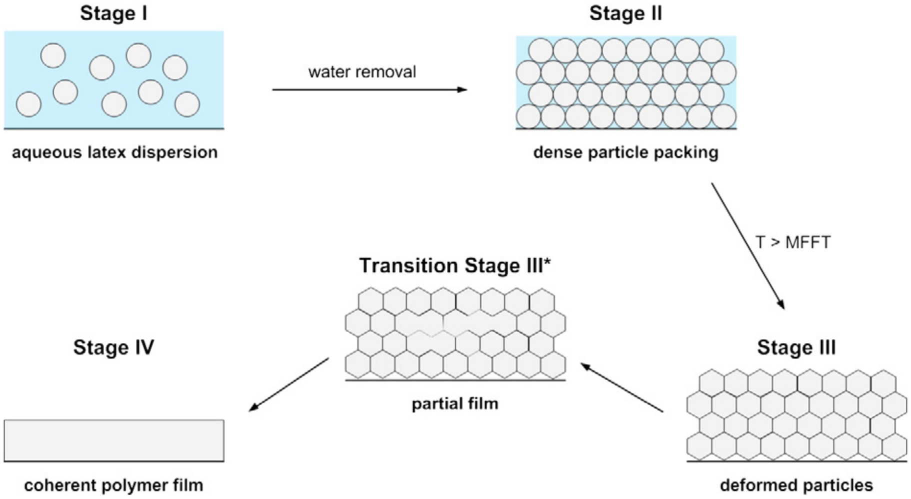

Scheme 1. Schematic illustration of the four main stages occurring during polymer film formation from an aqueous latex dispersion.

Environmental scanning electron microscopy (ESEM) offers the possibility to track the polymer film formation because it allows imaging of wet and insulating samples in their native state such as liquid latex dispersions. In contrast, conventional SEM is not suitable because it requires a high vacuum which will immediately dehydrate the sample and cause premature particle coalescence, compared to actual application conditions. This unique capability of ESEM is owing to the usage of a multiple aperture graduated vacuum system which generates a relatively low vacuum of 1–10 mbar. The atmosphere in the specimen chamber is decreased from ambient conditions to a water vapor pressure of e.g. 7.5 mbar. In combination with cooling of the sample to 3 °C, a saturated water atmosphere can be maintained above the specimen which is thus prevented from dehydration and maintains its original wet state. To achieve this saturated water vapor atmosphere, performance of a specific pump-down sequence is required. The pump-down procedure consists of several evacuation and water vapor addition steps to approach the final water atmosphere in the specimen chamber while ensuring that water is retained in the sample [25–29].

The goal of this study was to investigate whether polymer particle coalescence is hindered or accelerated by the presence of the anti-caking agent kaolin and the protective colloid PVOH. As latex polymers, ethylene–vinylacetate (EVA) and a carboxylated styrene–butadiene (c-SB) latex polymer were used. The kinetics of film formation of the liquid latexes was compared with that of the re-dispersible polymer powders containing kaolin and PVOH. To elucidate the impact of each individual spraying aid, kaolin or PVOH, model powders of c-SB polymer were prepared which contained only either kaolin or PVOH. As fluid systems, deionized (DI) water and synthetic cement pore solution (SCPS) were utilized. The first step in the film forming process, the evaporation of water from the aqueous latex dispersion, was quantified gravimetrically via the weight loss of the dispersions over time. The kinetics of stages II–IV were investigated by time-dependent ESEM monitoring whereby particle coalescence and polymer film formation were recorded. Additionally, the elemental composition of the polymer films formed in the presence of kaolin was determined by means of energy dispersive X-ray (EDX) analysis.

2. Materials and methods

2.1. Materials

EVA liquid latex (solid content 52 wt.%), EVA re-dispersible powder, SB liquid latex (solid content 45 wt.%) and SB re-dispersible powder were provided by Dow Olefinverbund GmbH, Schkopau/Germany. The re-dispersible powders were produced by spray drying of the EVA or SB mother liquors under addition of kaolin as anti-caking agent and polyvinylalcohol as protective colloid. The ratios between polymer, anti-caking agent and colloidal stabilizer were kept constant for all samples. To analyze the effect of individual kaolin or polyvinylalcohol on the film formation of the SB latex, SB model powders were spray dried containing only either kaolin or PVOH. Again, the ratio of SB latex polymer to kaolin or PVOH was kept constant. The composition and properties of the liquid latex dispersions and powders are presented in Table 2.

Kaolin (KAMIN HG 90) was obtained from KaMinLLC, Macon/United States. Polyvinylalcohol (Mowiol 4-88) was purchased from Kuraray Europe, Frankfurt/Germany. $CaSO_4 \cdot 2H_2O$, KOH, Na_2SO_4, and K_2SO_4, were purchased from Merck, Darmstadt/Germany. Poly-diallyl dimethyl ammonium chloride (ZETAG 7568) was obtained from Ciba Specialty Chemicals Ltd, Bradford/UK.

All chemicals were utilized without further purification. Ultrapure water (resistivity > 18 MΩ cm) was used for all experiments.

Synthetic cement pore solution (SCPS) was composed based on the characteristic ion concentrations present in the pore solution of an ordinary Portland cement (CEM I) at a w/c ratio of ~0.5 [30]. The pore solution was prepared by dissolving 1.72 g $CaSO_4 \cdot 2H_2O$, 6.96 g Na_2SO_4, 4.75 g K_2SO_4 and 7.12 g KOH in 1 L of deionized water. First, the $CaSO_4 \cdot 2H_2O$ were dissolved in 700 mL of water under vigorous stirring. Next, 6.96 g of Na_2SO_4 were solubilized in 150 mL of this $CaSO_4$ solution. Upon complete dissolution of the sodium sulfate, the solution was combined with the remaining $CaSO_4 \cdot 2H_2O$ solution. Next, 4.75 g of K_2SO_4 were added and solved. Afterwards, 7.12 g KOH dissolved in 150 mL of water were introduced into this mixture. Finally, water was added to a volume of 1 L. This method produces a clear, stable solution free of precipitate which incorporates the ion concentrations displayed in Table 1. The pH of the SCPS was 12.6.

Table 1
Concentration of ions present in the model cement pore solution used in the study.

Ion	Concentration [g/L]
K^+	7.1
Na^+	2.2
Ca^{2+}	0.4
SO_4^{2-}	8.2
OH^-	0.7