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## Progress in Organic Coatings

journal homepage: [www.elsevier.com/locate/porgcoat](http://www.elsevier.com/locate/porgcoat)

# Influence of cosolvent retention on film formation and surface mechanical properties of water based acrylic coatings by atomic force microscopy

Qi Chen\*, Jurgen Scheerder\*, Kristel de Vos, Ragna Tak

DSM Coating Resins, Sluisweg 12, 5145PE Waalwijk, The Netherlands

## ARTICLE INFO

## Article history:

Received 4 August 2016  
Received in revised form 14 October 2016  
Accepted 15 October 2016  
Available online xxx

## Keywords:

Film formation  
Cosolvent retention  
AFM  
Nano-indentation

## ABSTRACT

The influence of several common cosolvents on the level of film formation and surface mechanical properties of water-based acrylic coatings is investigated by atomic force microscopy (AFM) and AFM based nano-indentation technique. The amount of residual cosolvents in the coatings is determined and it is found that the aforementioned properties of coatings with the exact same polymer composition can be significantly different depending on the amount of residual cosolvents, which is related to the evaporation rate of the solvent as well as the interaction between the solvent, water and the polymer. Butyl glycol, for example, has good interaction with the acrylic polymer and water but due to its fast evaporation, does not improve film formation. Texanol, on the other hand, presents in the film at a large amount but it reduces the surface stiffness of the film and can have a detrimental effect on the surface mechanical properties of the coating.

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## 1. Introduction

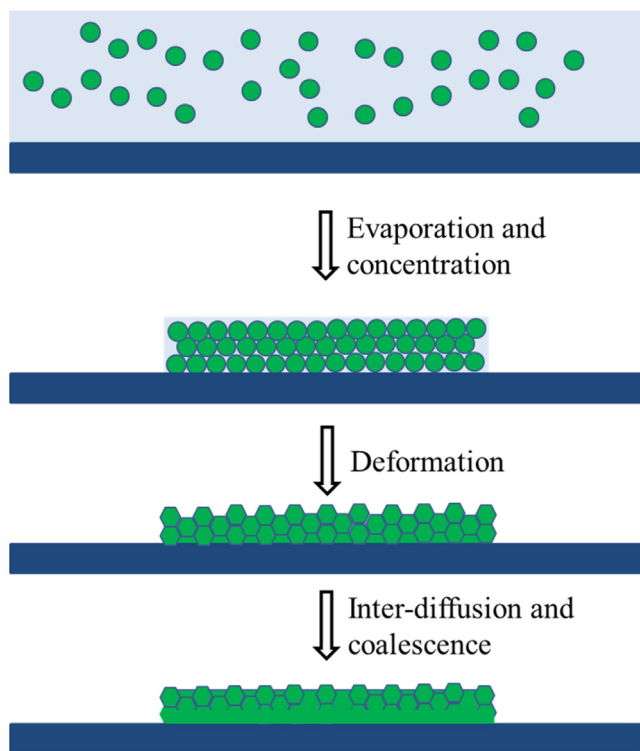
Film formation of polymer latices is one of the most crucial processes in water based coating applications. It is the process where a stable dispersion of colloidal polymer particles, *i.e.* the latex, transforms into a continuous film [1]. The process involves many steps that span from a dilute to concentrated dispersion, into a closed pack array of deformed particles, and eventually into a coherent polymer film [2]. A simplified schematics illustrating these steps in the film formation process is shown in Scheme 1. The degree of film formation, *i.e.* how much the latex particles will deform and inter-diffuse into each other, has a pronounced influence on the final properties of the coatings in their applications [3]. One of the recurring themes in the research of coating industry is how the film formation process and the properties of the coatings are inter-related. For example, in industrial wood coating applications, important coating properties such as the resistance of the film towards chemical stains, as well as the hardness development are both influenced by the degree of completion of the film formation process. Typically a balance in coating properties are needed such as high hardness yet a low demand of cosolvents.

In order to obtain good final properties of the coatings, film formation of the latex particles is key. The film formation is promoted by 1) careful design of the polymer composition; 2) introduction of multi-phase particle morphology [4], in particular to achieve the desired balance in properties; and 3) addition of film formation aids, which are usually volatile organic compounds (VOCs) that (hydro)plasticize the polymer dispersions [5]. These so-called cosolvents, or coalescents, are frequently used in water based coating applications to ensure good inter-diffusion of the polymer chains by lowering the glass transition temperature ( $T_g$ ). In general polymer with  $T_g$  well above room temperature is desirable for the final properties of the coating. However, film formation of such polymer without the addition of any cosolvents will result in cracking and disintegration of the polymer film. Due to environmental concerns the trend of coating industry is clearly towards minimizing and eventually elimination of the VOCs. Therefore, more careful and efficient use of these cosolvents is required and understanding of the cosolvent-polymer interaction as well as the influence of cosolvents on application properties of the coatings is beneficial.

The influence of cosolvent on latex film formation was extensively studied in the literature. By using fluorescence decay measurements, Juhué and Lang showed that the diffusion of polymer chains across latex particles depends strongly on the nature of the solvent, especially at the early stage of the film formation. And the rate of solvent evaporation appears to be a critical factor in the role of a filming aid [6]. Tsavalas and Sundberg investigated the  $T_g$

\* Corresponding authors.

E-mail addresses: [qi.chen@dsm.com](mailto:qi.chen@dsm.com) (Q. Chen), [jurgen.scheerder@dsm.com](mailto:jurgen.scheerder@dsm.com) (J. Scheerder).



**Scheme 1.** Illustration of the film formation process of polymer latices. As indicated in the last step, the degree of inter-diffusion and coalescence is not complete and would influence the final properties of the coating.

depression of emulsion polymers in the presence of water by means of differential scanning calorimetry and established model to predict the effect of hydroplasticization of (meth)acrylic polymers [7,8]. The effect of cosolvent on film formation was also reported by Winnik et al. The addition of solvents such as Texanol to a water borne poly(butyl methacrylate) latex was shown to increase the inter-particle polymer chain diffusion in a predictable manner [9].

Due to its high spatial resolution under ambient condition, Atomic Force Microscopy (AFM) is widely used by researchers to investigate the packing and deformation of latex particles in dry films [10]. The introduction of phase imaging in the 90s allowed not only surface topography but also materials properties of the surface being observed [11]. This was of great importance in the investigation of multiphase particles, where immiscible polymer domains with different  $T_g$ s can be differentiated [12]. However, phase imaging maps the phase lag of the cantilever oscillation, i.e. dissipation of energy into the sample, during topography scan. This signal is only qualitative and influenced strongly by experimental conditions. AFM based nano-indentation offers a quantitative approach to determine the mechanical properties of the surface [13–17]. In the past bulk mechanical properties of water based coatings were investigated by mechanical testing methods, such as Dynamic Mechanical Thermal Analysis (DMTA) [18]. However, nano-indentation methods, which focus on studying the surface mechanics of the samples, were not widely used in industrial coating research. We believe that surface mechanical properties are particularly important since many properties in the application area of coatings are surface related, e.g. mar and scratch resistance, dirt pick-up resistance, etc. Furthermore, it is known in the literature that polymers exhibit different chain dynamic behaviors when confined into the geometry of thin films [19] and  $T_g$  depressions due to the existence of a surface layer where chain dynamic is enhanced when compared to that in bulk were observed [20]. By using nano-indentation, mechanical properties that are more

**Table 1**  
Composition and theoretical  $T_g$ s of the model acrylic polymer (PA).

Composition	Methyl methacrylate/ <i>n</i> -butyl acrylate/ <i>n</i> -butyl methacrylate/acrylic acid
Dry $T_g$ ( $^{\circ}$ C)	54.3
Wet $T_g$ ( $^{\circ}$ C)	31.6
Difference between dry and wet $T_g$ ( $^{\circ}$ C)	22.7
pH	7.0
Solid content (% w/w)	40.0
Viscosity (25 $^{\circ}$ C, mPa s)	26
Average particle size (polydispersity index) (nm)	88.9 (0.03)

representative of coating performances can be studied, and details with depth resolution on the nanometer scale can be addressed.

In this article, surface morphology and mechanical properties of water based coatings prepared from latex particles composed of acrylic monomers are investigated by AFM and AFM based nano-indentation. It is found that the efficiency of the cosolvents on film formation is related to the amount of residual cosolvents present in the film, i.e. cosolvent retention, and the compatibility between the solvent and the polymer. Cosolvent retention is influenced by the evaporation rate of the solvent as well as the interaction between the cosolvent, water and the polymer. The surface stiffness of the coatings and its development as a function of drying time is determined by AFM based nano-indentation and is found to be strongly influenced by the type and residual amount of cosolvents.

## 2. Experimental section

### 2.1. Polymer synthesis

The model acrylic polymer (PA), which is a copolymer of methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA), *n*-butyl methacrylate (*n*-BMA) and acrylic acid (AA), was prepared according a semi-batch emulsion polymerization method. MMA (purity 99.8% min.), *n*-BA (99.5% min.), *n*-BMA (99.0% min.) and AA (99.0% min.) were purchased from Dow Chemicals. Ammonium persulphate (AP, >98%) was purchased from Sigma-Aldrich. *tert*-butyl hydroperoxide (70 wt% in water), isoascorbic acid (99.0% min.), and ammonia (24–26%) were purchased from Brenntag Nederland BV. Disponil FES993 (28–31% active material in water) was purchased from BASF. *N*-Dodecylmercaptane (*n*-LMKT, 98.0% min.) was purchased from Chevron Phillips. A four-neck reactor was equipped with a stirrer,  $N_2$  inlet, and two dropping funnels. The reactor was loaded with demineralized water (458.2 g) and Disponil FES993 (14.7 g, 28 wt% solution in water). In one dropping funnel an emulsified monomer feed was prepared from demineralized water (224.3 g), Disponil FES993 (14.7 g, 28 wt% solution in water), *n*-BA (91.6 g), MMA (319.3 g), *n*-BMA (137.3 g), AA (17.7 g) and *n*-LMKT (5.9 g). In another funnel a solution of AP (1.2 g) in demineralized water (75.7 g) was prepared. The reactor content was heated to 84  $^{\circ}$ C and 7.5 wt% of the monomer feed and a solution of AP (0.6 g in 6.0 g demineralized water and 7.4 g Disponil FES993) was added to the reactor. The temperature increased to 85–88  $^{\circ}$ C as result of the onset of the polymerization. Then, at 85  $^{\circ}$ C the remainder of the emulsified monomer feed and the initiator solution were added in 90 min. After completion of both feeds demineralised water was added (95.3 g) and the reactor content was kept at 85  $^{\circ}$ C for another 20 min. Next a post-reaction was done to consume the residual monomers by adding a solution of isoascorbic acid (1.0 g) in demineralised water (18.2 g) and *tert*-butylhydroperoxide (0.74 g of a 70 wt% slurry). Finally, the pH was adjusted at about 7 with a 10 wt% ammonia solution. Next the dispersion was allowed to cool, filtered

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