



# Electrochemical impedance spectroscopy study of waterborne coatings film formation



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## ABSTRACT

In order to establish electrochemical impedance spectroscopy (EIS) as a viable quantitative method for characterization of latex film formation, three waterborne acrylate and styrene–acrylate polymer dispersions were periodically analyzed during a course of 2 weeks. Impedance spectra were fitted on the base of equivalent circuit consisting of a capacitor in parallel with a Warburg element representing film capacitance and the extent of ion diffusion through the film. Calculated EIS parameter values showed a decrease in Warburg diffusion over time, which is a result of particle coalescence and in agreement with the established theory of latex film formation. Atomic force microscopy (AFM) of the samples showed a smoothing of the surface and blurring of interparticle boundaries which confirmed that EIS can be used to study film formation of latex.

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## 1. Introduction

In the last few decades there has been a growing trend toward development of high quality water-based replacements for traditional solvent-based coatings. These efforts are driven by concerns for the environment and relevant legislations, such as the European directive on the limitation of emissions of volatile organic compounds [1] and regulations enforced by the US Environmental Protection Agency. The production and use of water-based coatings, containing little or no organic solvents, is a popular solution for the reduction of volatile organic compound (VOC) emissions during paint and coating application. Superior safety due to generally low toxicity and low flammability is an attractive aspect of water-based coatings. Compared to other low VOC solutions such as high-solids coatings, powder coatings and radiation cure coatings, water-based coatings can be used in a wider range of applications and are especially popular in the consumer segment.

However, because of physical properties of water, they differ greatly from classical solvent-based coatings. Water-based coatings require a whole new approach and are by nature much more complex and more difficult to formulate than solvent-based coatings. Owing to the fact that nonpolar organic polymer binders are not soluble in highly polar water, water-based coatings are usually available in the form of aqueous dispersions. An aqueous dispersion synthesized via emulsion polymerization is commonly termed as latex [2]. In contrast to simple solvent-based coatings, where the binder is completely dissolved in a suitable solvent, latex is comprised of colloidal solid polymer particles dispersed in water. Polymer particles are stabilized with an outer layer of hydrophilic groups which prevent particle aggregation through electrostatic repulsion and steric effects. This structure, which is coupled with a high latent heat of evaporation and a high surface tension of water, is responsible for the complexity of the film formation of latex [3].

According to numerous publications summarized in several excellent reviews [2,4–7], there are extensive theories that try to explain the processes taking place during film formation of latex, but in general, film formation can be described with a three-stage process. In the first phase, a significant amount of water evaporates which increases particle concentration and results in ordering of the particles. In the second phase, a combination of interfacial forces and osmotic pressure deforms the particles from sphere-shaped to space-filling polyhedrons. In the last phase of film

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**Table 1**  
Sample and polymer properties.

Sample	Solids content	BG content	Polymer type	$T_g$ ( $^{\circ}\text{C}$ )	$M_w$	$M_n$	Dry film thickness ( $\mu\text{m}$ )
SA-80	29.5 wt.%	6.93 wt.%	Styrene–acrylic	80	67685	14891	73 $\pm$ 8
SA-32	30.4 wt.%	7.14 wt.%	Styrene–acrylic	32	168716	31806	83 $\pm$ 8
A-62	33.0 wt.%	7.85 wt.%	Acrylic	62	45581	20014	85 $\pm$ 10

formation, macromolecules interdiffuse across the particle boundaries and form a homogenous polymer film.

The success of particle deformation depends on whether the temperature is higher than the minimum film formation temperature (MFFT) and, similar, interdiffusion is only possible if annealing temperature is higher than the polymer's glass transition temperature ( $T_g$ ). In practice a sufficiently low MFFT is required for proper film formation and a suitably high  $T_g$  ensures desired mechanical properties of the cured film. MFFT and  $T_g$  are properties of the polymer binder but during coating formulation they are generally manipulated with the addition of plasticizers or coalescing agents – organic solvents which soften latex particles and thus facilitate particle deformation and macromolecule interdiffusion. The presence of organic solvents can prevent skin formation during drying and also accelerate drying through azeotrope formation which is especially beneficial under high relative humidity conditions [8]. Often, however, the solvents must eventually evaporate in order for the film to achieve the desired mechanical properties. Depending on the components and conditions the whole film maturation process can take anywhere from a few hours to several months.

Many characterization techniques for studying film formation have been used by researchers, including but not limited to, atomic force microscopy (AFM) [9–16], diffusing-wave spectroscopy [17], nuclear magnetic resonance [18], fluorescence resonance energy transfer [19] and environmental scanning electron microscopy [20]. A host of other techniques and references is listed in literature [7].

The aim of this paper is to establish electrochemical impedance spectroscopy (EIS) as a viable method for quantitative study of latex film formation. EIS is a well-established technique for studying anticorrosion performance of organic coatings [21–34]. Not only does it provide a direct and sensitive method for detecting corrosion reactions on coated metal substrates but it also provides information about properties of the protective coating such as dielectric properties, the extent of ion diffusion and porosity of the film [23,35]. In the last few decades the sophistication of the equipment for carrying out EIS has progressed to a point where reliable measurements of high impedance protective coatings are possible. This enables determination of film properties in the absence of measurable substrate corrosion which extends the usefulness of EIS beyond the traditional evaluation of protective anticorrosion coatings to a broader field of protective coatings research and development.

In this article we present EIS study of film formation of three different latexes compared with observations made by atomic force microscopy. EIS is in our opinion the only technique which can be used to directly observe the film formation process and also provide a quantitative measure of film quality. Our paper is the first to demonstrate such a comprehensive and practical EIS study of the latex film formation process.

## 2. Experimental

The film formation of three commercial quality waterborne polymer dispersions was studied. Two of them were styrene–acrylate copolymers (samples SA-80 and SA-32) and the third was an acrylate polymer (sample A-62). Glass transition

temperatures of the polymers were determined by differential scanning calorimetry using DSC1 by Mettler Toledo. Weight and number averages of polymers' molecular weights ( $M_w$  and  $M_n$ ) were determined against a polystyrene standard by gel permeation chromatography using Alliance 2690 by Waters Corporation. Properties of the polymers are summarized in Table 1. Since the glass transition temperatures of the samples were too high, proper film formation was not possible under normal ambient conditions. An addition of butyl glycol ether (BG) lowered the MFFT of the samples which permitted observation of film formation at room temperature.

Samples for EIS were applied on zinc coated steel panels to a dry film thickness of approximately 80  $\mu\text{m}$ . Thicknesses of the dry coatings were measured with a Duoscope FMP20 by Helmut Fischer GmbH, using a magnetic induction probe in accordance with ISO 2178 [36]. Dry film thickness measurements of EIS samples are presented in Table 1. The samples were annealed in air at controlled ambient conditions. Air temperature and relative humidity were kept at (23  $\pm$  2) $^{\circ}\text{C}$  and (50  $\pm$  5)%, respectively. During a 2 week annealing period every coated panel was analyzed several times. Impedance measurements were carried out after 1, 2, 3, 11 and 14 days of annealing.

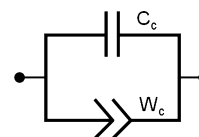
A three electrode setup based around the Tait Cell Kit by Princeton Applied Research was used to carry out EIS. Hastelloy C-276 metal alloy was used for counter and pseudo-reference electrodes and sample coated panels served as the working electrode with an area of 34  $\text{cm}^2$ . A 0.1 M aqueous NaCl solution was used as the connecting electrolyte.

Impedance data were collected using a Parstat 2273 potentiostat/frequency response analyzer by Princeton Applied Research. Measurements were performed at open circuit potential over a frequency range of 65.5 kHz–100 mHz with a 30 mV sinusoidal perturbation. The impedance spectra were analyzed with ZView software by Scribner Associates Inc.

Samples for AFM were applied on metal wafers and annealed under the same conditions as the EIS samples. Surface scans of the samples were made with non-contact atomic force microscopy after 1 and 10 days of annealing. The surface probe microscope used was a Park Systems XE-100. A silicon cantilever with a resonant frequency of 300 kHz and a force constant of 42 N/m was used, with 15 nm chosen as the amplitude setpoint. Topography images were analyzed using XEI software by Park Systems.

## 3. Results and discussion

Impedance data were analyzed using a circuit model presented in Fig. 1, where  $C_c$  represents capacitance of the coating and  $W_c$  is the Warburg element which describes the extent of diffusion of ions through the coating [35]. Since an organic coating is in



**Fig. 1.** Equivalent circuit used for analysis of EIS data, where  $C_c$  and  $W_c$  represent coating capacity and Warburg diffusion through the coating.

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