Fluorescence spectroscopy and imaging of dynamics and microstructure of acrylic polymer emulsions
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Summary

Waterborne organic coatings are an attractive alternative to solventborne coatings. Due to environmental and health concerns, the demands of waterborne coatings are continuously increasing. Achieving a high tech film with superior mechanical properties is still one of the major challenges faced by the paint industry. Film formation of waterborne coating material is less straightforward than with solventborne paints. It is a rather complex multistage process, challenging from an academic perspective, and of immediate practical interest for the industry. This research work aims at improving the understanding of film formation by means of fluorescence methodologies.

Chapter 1 illustrates the use of fluorescence spectroscopy for the investigation of a diverse set of questions in polymer science. Because of the extreme sensitivity of fluorescence, and its high spatial and temporal resolution, it can reveal information on a wide variety of length and time scales. The investigation at the molecular level is one of the major advantages of fluorescence methods, which is not possible with other techniques.

Chapter 2 describes the investigation of coalescing agents ("co-solvents") in waterborne latex emulsions using a co-polymerized environment-sensitive fluorogenic fluorophore nicknamed Maleimidofluorotrope (MFT). A molecular model compound of this fluorophore was prepared by adding n-butylamine to the maleimide double bond. The adduct thus obtained showed an enormous shift of its emission maximum of ca. 250 nm to longer wavelength going from nonpolar to polar solvents. Low and high T_g hydrophobic and hydrophilic latices were prepared via seeded emulsion polymerization. A set of latex batches was prepared which include dye co-polymerized (labeled) latices and neat (nonlabeled) latices. Five coalescing agents of industrial use were studied in these latex materials. The co-polymerized MFT quantitatively detected the amount of coalescing agents present in the latex materials. Its emission maximum was red shifted by up to 20 nm by the presence of co-solvent (0 – 9%) in the latices. This was primarily the effect of softening of the material, which allowed structural relaxation on the nanosecond timescale of the fluorescence. These findings form the basis for the investigation of the repartitioning of coalescing agents in latices in the next chapters.

Chapters 3 and 4 deal with the repartitioning behavior of coalescents in latices having different T_g s and chemical compositions. The MFT-copolymerized latices described in
Chapter 2 were employed in this study. It was observed that repartitioning of co-solvents differing in their polarity and water solubility was very fast in the low $T_g$ latices ($< 1$ min) and slower ($< 1$ hour) in high $T_g$ latices. Repartitioning was a bit faster in high $T_g$ hydrophilic latices than in high $T_g$ hydrophobic ones. These experiments were further elaborated in latex blends of different compositions and $T_g$s, which are discussed in Chapter 4. Texanol was the co-solvent selected to perform these studies. Blending of different compositions and $T_g$s revealed that the distribution of Texanol over the different polymers was essentially independent of the composition and $T_g$ of the latex materials. Texanol is poorly soluble in water, but apparently equally compatible with hydrophobic and hydrophilic latices.

Chapter 5 describes the development of a methodology to investigate latex film formation using confocal microscopy. A chemically inert and photostable fluorophore, Perylene Red, was used to label the latex. This dye was added to the latex after emulsion polymerization and has no covalent link with the copolymer. Due to the highly hydrophobic nature of this fluorophore it was assumed that the dye would reside exclusively in the polymer phase. Experiments were performed in one, two and three-dimensional modes to investigate various phenomena occurring during latex film formation. The 1D z-scanning experiment served simply to monitor the thickness of the drying film demonstrating the loss of most of the water within ~ 20 min. Confocal imaging provides a quick and visual analysis of the real time information on the surface as well as in the bulk of the film. The x-y (2D) images obtained at various z-positions revealed information about the size and shape of individual latex particles in the films. Different amounts of co-solvent were added to the latex. The apparent particle size was found to be increased slightly as a function of co-solvent concentration, but at 8% w/w of co-solvent, the noncovalently attached dye was quickly spread out throughout the latex. For lower co-solvent concentrations, the interparticle boundaries apparently prevented such a rapid diffusion. Only after prolonged drying and annealing the Perylene Red dye diffused out of the originally labeled latex particles. Importantly, the confocal imaging technique enabled us to clearly “see” individual latex particles in fresh and aged latex films.

Chapter 6 deals with the application of the methodology developed in Chapter 5. The aim of this part of our study was to investigate the interdiffusion of polymer chains during the last stage of film formation. To achieve this goal a covalently linked fluorophore was required. The synthesis of perylene monoimide and diimide based fluorophores was carried out that could be co-polymerized in low and high $T_g$ hydrophobic and high $T_g$ hydrophilic latices. Latex film formation with these co-polymerized dye latices was studied using 2D and 3D imaging modes. The effect of co-solvent and of annealing of the films above the minimum film formation temperature (MFFT) of the latex was investigated. No
changes in the film morphology were observed when high $T_g$ hydrophobic latex film was annealed at 50 °C for 45 h.

The interdiffusion of polymer chains was observed, however, in the high $T_g$ hydrophobic latex films when heated well above their $T_g$, i.e., at 90 °C. The disruption of particles was observed by the migration of the covalently linked fluorophore over the x-y area of the films. The annealing of high $T_g$ hydrophobic latex films for 30 h at 90 °C showed that further extensive interdiffusion of polymer chains had occurred. The depth resolved imaging provided some interesting information. It was observed that film formation had not evolved to the same extent at various z-positions. The surface and bulk layers of the film showed faster coalescence, and in the bottom layers close to the glass substrate spherical particles were still observed after 30 h of annealing at 90 °C.

Chapter 7 describes preliminary studies aimed at the monitoring of latex film drying by means of fluorescence spectroscopy. It was expected that photophysical properties of co-polymerized dye in latex could reveal information about the progress of film formation. Unfortunately, and unexpectedly, we observed a drastic decrease in the emission intensity of fluorescent labels in drying latex films. The emission maximum of the solvatochromic emitters, however, exhibited the expected hypsochromic shift when the medium became rigid in the dry film.

Many experiments were performed to resolve this issue. We tried film drying under nitrogen, different ways of excitation and collection of the fluorescence, change of fluorescent label from MFT to highly stable and inert Perylene Red, functionalization of the substrate to change its wetting properties, film formation from additives free latex, and removal of water soluble components of the latex by dialysis. None of these fully resolved the issue. Because the dialysis gave the best results, we assume that water soluble fluorescence quenchers were mostly responsible for the decrease of emission.