Film Formation from Industrial Waterborne Latices

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Abstract

Experimental evidence is given for the mechanism and completeness of film formation from industrial waterborne latices using the technique of Inverse-Micro-Raman-Spectroscopy (IMRS). Until first particle contact, the mass transfer from aqueous latex dispersions is gasside controlled. Then, drying is accelerated, presumably due to additional mass flow and particle deformation. Redissolution experiments show, that films from hard latices have a porous structure, due to insufficient particles deformation. The addition of a film forming aid lowers the polymers glass transition temperature (T_g) and then particle deformation leads to a smooth and protective surface, where water cannot intrude.

1. Introduction

In the paint industry, a great effort is put into the development of waterbased paint systems, that show a drying behaviour, which is equal to that of established solvent-based formulations. This requires a fundamental understanding of the film formation mechanism from colloidal dispersions. Good film formation is achieved, if a dispersion of polymer particles in water transforms into a crack and void free polymer film which shows similar or even better physical properties than a film obtained from a solvent-borne solution of the same polymer. This also includes the fact, that an aqueous dispersion, after drying, forms a protective polymer film, which cannot be redissolved again by water. Incomplete film formation is normally the result of insufficient particle deformation and polymer interdiffusion. Then, the dispersion properties have to be changed in the way as to soften the polymer. As will be shown later, the film properties of latices can be tuned by changing their glass transition temperature (T_g), adding an organic film formation aid.

2. Latex film formation

Regarding the film formation process and the forces which are responsible for film formation, there exist a number of models and theories. Brown [1] claims that particle coalescence can only start, as soon as the forces which favour film formation like capillary forces and van-der-Waals forces are greater than the repulsive forces which are electrostatic repulsion and resistance against deformation. In contrast, Dillon [2] states that drying and particle coalescence occur separately and that dry sintering of the latex particles is due to the interfacial tension of particles and air. Sheetz [3] describes film formation as a process where an osmotic pressure difference, caused by a dry skin layer on top of the wet polymer film, is responsible for particle deformation and coalescence. None of the theories seems to be universally valid to describe the complex process of latex film formation. So far, existing experimental data have not been satisfying to prove one or the other theory. A number of good review articles on this topic can be found in the literature [4, 5, 6].

Commonly, the process of film formation is described by a mechanism which includes three consecutive stages. (1.) the concentration of the latex dispersion, (2.) the particle deformation and their irreversible contact and (3.) the interdiffusion of the polymer chains across the particle boundaries and the formation of a mechanically stable film. Due to the fact, that the latex particles are often surrounded by a layer of surfactants a forth stage is often included in the model which describes the rupture of this layer to allow complete polymer interdiffusion and film formation. In figure 1 the different stages towards film formation are illustrated: phase (1.) is characterised by a constant loss of water with time. The concentration of latex particles continually increases and - depending on the drying conditions, the nature and strength of particle stabilisation and the ionic strength of the serum - particles come into close contact and pack in a more or less ordered way. The closest packing of monodisperse spheres would have an effective volume fraction of 0.74. The effective particle volume depends on the thickness of the enveloping hydrophilic layer. Phase (2.) of the model starts where the undeformed particles first come into contact. At this point, significant particle deformation could only take place if drying was at temperatures well above the polymers minimum film forming temperature (T_{mft}) and close to or above its glass transition temperature (T_g). Only then the particles could behave like a viscous fluid which is synonymous to a slow water evaporation compared to the stress relaxation time of the polymer. For a space filling structure spherical particles would have to deform into rhombic dodecahedrons.

If drying was very close to the minimum film forming temperature, particle deformation would be only partially and incomplete. At this stage, the particle boundaries would still be present and often there might be a layer of surfactants still surrounding the particles. Although the final film is transparent and optically clear, it might still be a porous structure of minor film quality. According to many authors there exists a phase (2.b), where a rupture of the surfactant layer, separating the deformed latex particles, is prerequisite to further polymer interdiffusion and the development of mechanical strength [7]. In phase (3.) the film properties are fully obtained long after the water has left the film. Here, the polymer chain mobility is said to depend on the difference between drying temperature and the polymers glass transition temperature (T_g). The time needed for sufficient polymer interdiffusion decreases for soft latices.
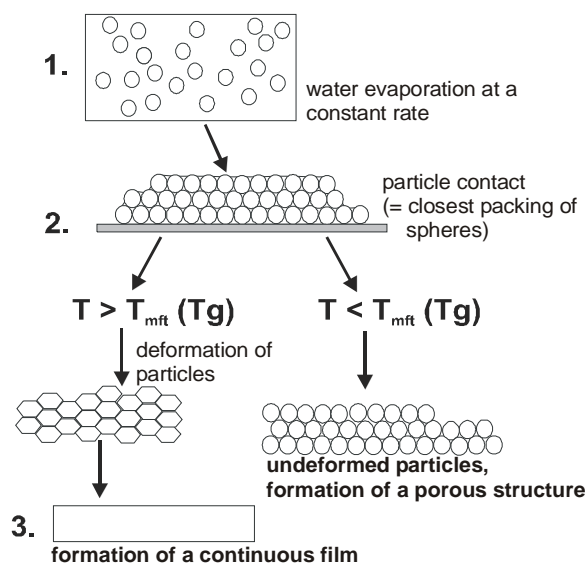

Figure 1: the different stages of latex film formation

3. The measurement technique

The experimental investigation of film drying by gravimetric measurements, where the drying curve of the polymer film is measured by means of a balance, is state of the art. Only a few other experimental methods are available to investigate latex film formation and film drying, such as, e.g., small-angle neutron scattering (SANS) and X-ray scattering [8, 9].

A new measurement technique, called Inverse-Micro-Raman-Spectroscopy (IMRS) has been developed in Karlsruhe in 2003 to determine the local solvent content within polymer films with an optical resolution of 1-2 µm [10]: As shown in figure 2, a monochromatic laser beam is focused into the sample by a system of mirrors and optical lenses. Within the polymer film a small part of the light is scattered -elastically or inelastically- due to the interaction of the monochromatic laser beam with the molecules of the sample. Coming back the same path only the inelastically scattered light -which is the Raman light- can pass the interference pattern of a notch filter. High spatial resolution is achieved from the confocal pinhole which is optically coupled with the objective's focus. It allows only backscattered light from the plane of focus to pass to be detected by the CCD camera.
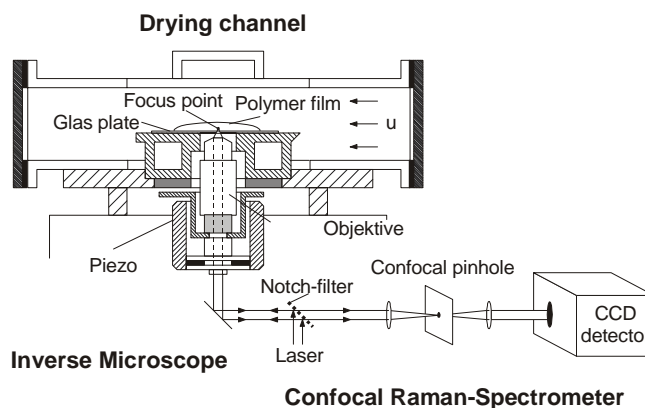

Figure 2: Inverse-Micro-Raman-Spectroscopy (IMRS)

With IMRS one can follow the solvent content within thin films online and with a high optical resolution. This is also valid for nano-disperisons, where the particle diameter is by far smaller than the detection volume of the laser focus. Using a special calibration procedure, data can be evaluated quantitatively. Concentration profiles within the film and the shrinking of the film during drying help to identify the film formation mechanism and conclusions can be drawn concerning the final structure and the properties of a coating.

4. Characterisation of the used latex and experimental conditions

For the experiments a dispersion of an acrylic-styrene copolymer of the hard type was used. In comparison to a real paint, this formulation does not contain pigments. The dispersion of solid content ~50 % has a particle size of ~100 nm, verified by photon correlation spectroscopy and a minimum film forming temperature of T > 15 °C. The film formation aid has a structure similar to the elements of the polymer chain. It can easily diffuse into the polymer particles, which makes it very efficient in lowering the polymers glass transition temperature (T_g).

The drying conditions were ambient, as often observed for application of paint. In detail, this was at a temperature of T= 23 °C, a relative humidity of rH= 30 % and an overflow air velocity of u= 0,05 m/s which corresponds to natural air convection.

5. Experimental Results

In figure 3 a film of initial film thickness d= 90 µm and an initial solvent content of X= 1,08 g water / g polymer dries at a constant rate. The solvent content within the film was obtained by IMRS depth scans. Here, the laser focus was moved from the bottom of the film (left side) to the film surface (right side) in steps of 2-3 µm. It takes about one minute to scan through the total film as can be seen from the inbox of figure 3. Obviously, unlike film drying of solvent-based films [11], drying of aqueous latex dispersions at ambient conditions is always gas side controlled. Until the very end of drying no concentration gradients form, which would indicate some kind of filmside diffusion resistance. After a solvent content of X= 0,7 g/g is reached, evaporation from the aqueous dispersion increases. This is possibly the result of first particle contact and connected with additional mass flow in horizontal direction. A comparison with the calculated mass flow shows, that the evaporation rate is initially the same as was predicted for total gas side controlled mass transfer.
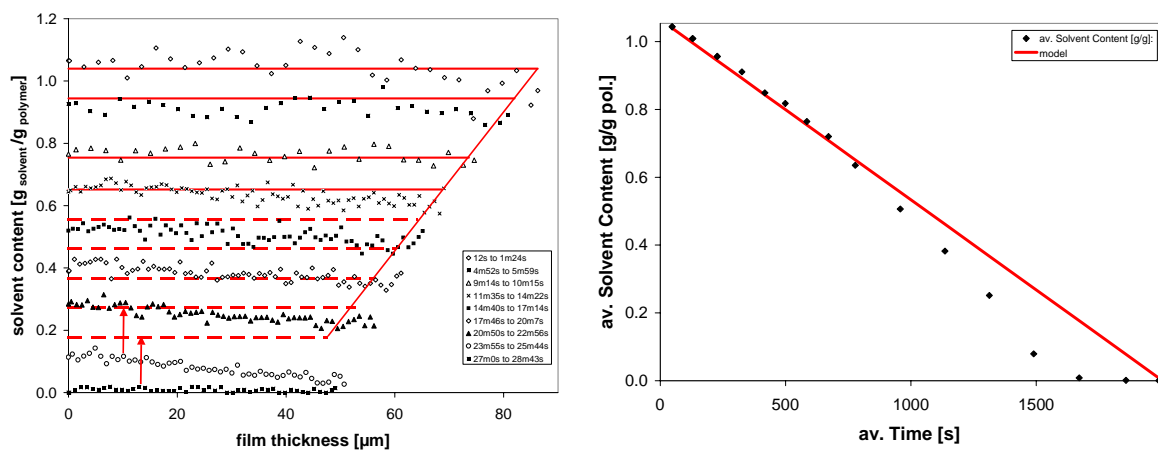

Figure 3: solvent concentration within a drying latex film and drying curve

Redissolution experiments were performed to verify the model of latex film formation described earlier, which states, that complete film formation is only possible for films above their minimum film forming temperature (T_{mft}). The experimental set-up for this kind of experiment is sketched in figure 4.
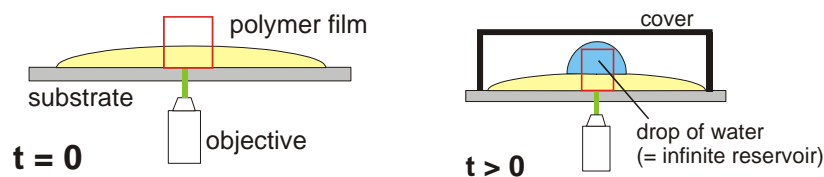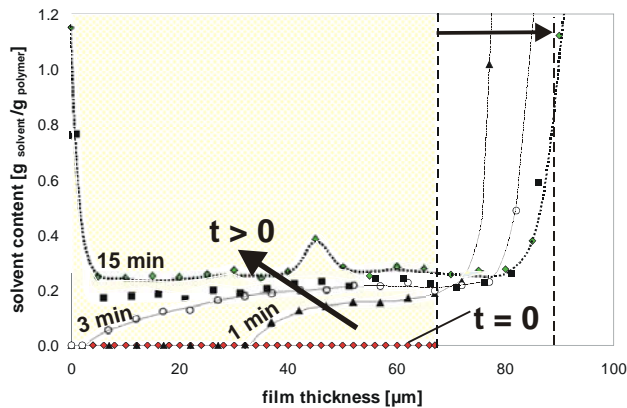

Figure 4: experimental procedure for redissolution experiments

Here, a drop of water, providing a water reservoir, was applied on top of the dry polymer film. Scans through the film show the water uptake within the film and concentration profiles respectively (figure 5).

For the redissolution experiments, the hard latex dispersion had been dried at ambient drying conditions, close to the minimum film forming temperature. From the model, it is expected, that a porous, non-complete film structure forms, which is not water-resistant. Figure 5a) shows the water content within the polymer film over the film thickness. The substrate, a glass plate, is on the left and the free surface of the polymer film on the right. The dry film has an initial thickness of 70 µm and is illustrated by the shaded background. A drop of water is applied. Right after application water invades into the film, visible by the concentration profiles. At the same time the film starts to swell. Non-complete film formation could also be proven by atomic force microscopy (AFM) (figure 5a), right), where undeformed single particles are clearly visible.

The addition of a hydrophobic film forming aid to the same polymer lowers its minimum film forming temperature (T_{mft}), which enables more complete particle deformation and the formation of a non-porous film according to theory. Comparing the water content within the film with that of the formulation with no plastiziser, there is considerably less water intrusion and no swelling of the film. The AFM picture shows a closed, non porous surface and deformed particles.

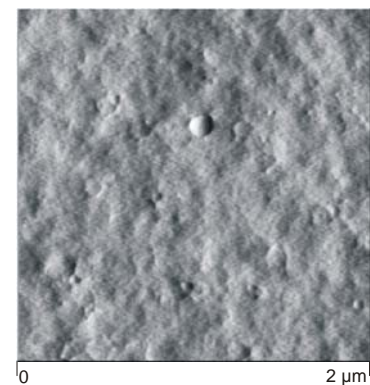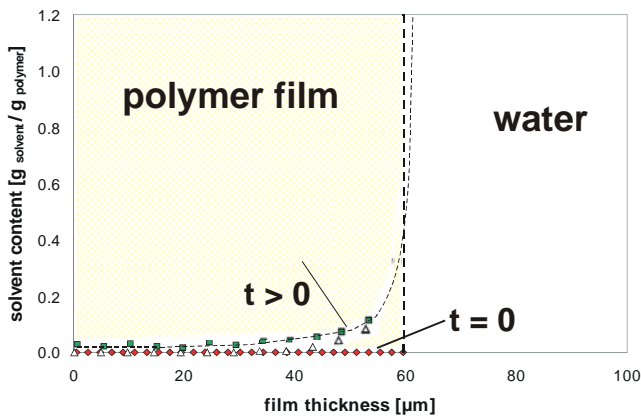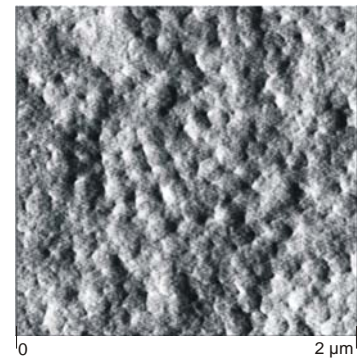concentration profiles within the polymer film (IMRS)   surface profile (AFM)

Figure 5: redissolution experiments for   a) the initial acrylic-styrene dispersion (high Tg)

b) the dispersion plus added coalescing aid (low Tg)

6. Conclusion

The initial drying rate of a film of aqueous acrylic-styrene polymer dispersion is gas side mass transfer controlled. The predicted mass flow (gas side controlled) and experimental values for the latex dispersion coincide very well until a solvent content of X ~0,7 g water / g polymer is reached. This is when the polymer particles come into contact to form a more or less ordered structure. The capillaries that form will create an additional horizontal mass flow, which makes, that the solvent content at the measurement position in the middle of the film decreases faster than for pure evaporation.

For a hard polymer, deformation forces are not strong enough to fill all the void spaces in the porous film structure, which is visible from atomic force microscopy (AFM) data. Redissolution experiments show that water can invade this structure and penetrate the film. Within minutes water accumulates at the glass substrate – polymer film interface. In the worst case, the film looses contact with the substrate. Within the film all pores are filled with water; interparticular contact is to some degree reversible, which results in local accumulation of water within the film. Addition of a film forming aid lowers the polymers glass transition temperature (T_g). Now, the AFM picture shows a closed surface without any pores. The redissolution experiment shows almost no water intrusion into the polymer film. Even after 20 minutes the solvent content within the film is very low.

7. Acknowledgement

8. References

1. G. L. Brown, Formation of films from polymer dispersions, *Journal of Polymer Science*, **22**, 423-434 (1956)
2. R. E. Dillon, L. A. Matheson, E.B. Bradford, Sintering of synthetic latex particles, *Journal of Colloid Science*, **6**, 108-117 (1951)
3. D. P. Sheetz, Formation of films by drying of latex, *Journal of Applied Polymer Science*, **9**, 3759-3773 (1965)
4. J. L. Keddie, Film formation of Latex (Review), *Material Science Engineering Reports*, **21**, 101-170 (1997)
5. M. A. Winnik, Latex film formation, *Current Opinion & Colloid and Interface Science*, **2**, 192-199 (1997)
6. P. A. Steward, J. Hearn, M.C. Wilkinson, An overview of polymer latex film formation and properties, *Advances in Colloid and Interface Science*, **86**, 195-267 (2000)
7. A. Toussaint, M. De Wilde, A comprehensive model of sintering and coalescence of unpigmented latexes, *Progress in Organic Coatings*, **30**, 113-126 (1997)
8. Y. Chevalier, Small-angle neutron scattering for studying latex film structure, *Trends in Polymer Science*, **4**, 197-203 (1996)
9. M. Ballauf, SAXS and SANS Studies of Polymer Colloids, *Current Opinion in Colloid & Interface Science*, **6**, 132 (2001)
10. W. Schabel, P. Scharfer, M. Müller, I. Ludwig, M. Kind, Messung und Simulation von Konzentrationsprofilen bei der Trocknung binärer Polymerlösungen; *Chemie Ingenieur Technik*, **75** (9), 1336-1344 (2003)
11. Schabel W., Ludwig I., Kind M.: Measurements of Concentration Profiles in Polymeric Solvent Coatings by Means of an Inverse-Confocal-Micro-Raman-Spectrometer – Initial results, *Drying Technology*, **22**, 285-294 (2003)