

Influence of the drying conditions on the distribution of PS and SiO₂ nanoparticles in waterborne PVA coatings

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Polymer particle composites have raised increasing interest of the material research community within the last decade. Incorporation of nanoparticles in a polymer matrix is a way to modify material properties such as tensile strength, biocompatibility or optical properties. The functionality of these composites depends on the material selection as well as on the component distribution. The latter is strongly affected by the dispersion stability as well as the process and boundary conditions during drying.

In this work the influence of drying conditions on the component distribution of polystyrene (PS) or silica (SiO₂) particles in a polyvinyl alcohol (PVA) matrix from highly diluted water-borne model dispersions was investigated experimentally and numerically. To predict the component distribution, a 1D model was developed, which includes evaporation, sedimentation of particles and diffusion of particles and polymer in the early drying stage. A quasi- binary approach was used to describe the diffusion in the ternary system. This approach combines data from the binary sub-systems, to predict particle and polymer diffusion. The simulations were validated experimentally. Composites were manufactured by coating a PVA solution with dispersed particles and subsequent drying. The drying conditions were varied systematically. The formation of particle gradients during drying in SiO₂-PVA films was evaluated by cryogenic scanning electron microscopy experiments. In the dried film, the component distribution of PS-PVA films was evaluated by means of 3D Confocal Raman Spectroscopy.

The simulations show that three different regimes exist: sedimentation, evaporation and diffusion regime. The relation of diffusion coefficient, film thickness, evaporation rate and particle sedimentation rate determines which regime is reached. In the

sedimentation regime, the sedimentation velocity is dominating the diffusion and evaporation velocity. Hence, particles accumulate at the bottom of the film. In the evaporation regime, the surfaces descends faster than particles sediment or diffuse, while polymer diffusion is relatively fast, resulting in polymer diffusing into the film. A particle layer forms at the top. In the diffusion regime, movement due to particle diffusion is faster than sedimentation or surface descending velocity and particles and polymer are distributed equally.

In Cryo-SEM experiments, films were dried for one fifth of the overall drying time and vitrified. The films were fractured to expose their cross-sections and imaged on a liquid nitrogen cooled stage. The fracture exposes particles along the cross-sections. All three regimes predicted by the simulation could be qualitatively shown with this technique. Additionally, PVA-PS films were prepared under similar conditions. The lateral 3D component distribution in the films was measured by imaging cross sections with confocal 3D Raman Spectroscopy. A measured cross section in the evaporation regime is shown in Figure 1.

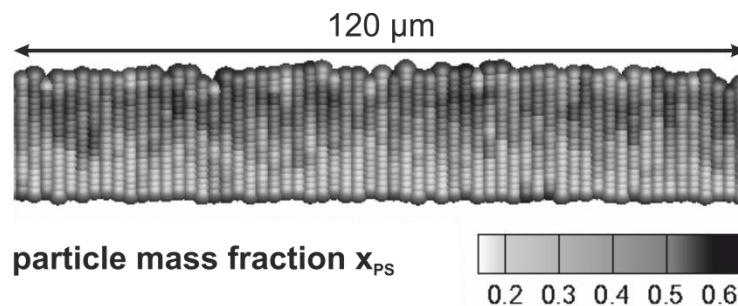


Figure. 1: Cross section image of film in evaporation regime; measured with 3D Confocal Raman Spectroscopy; each point equals one measurement point.

With the use of PS particles in a PVA matrix it was possible to minimize light scattering, which made this disperse system optically available. The results show that the three regimes are also present in the dry films.